



**UNIVERSITATEA "DUNĂREA DE JOS" DIN GALAȚI
FACULTATEA DE METALURGIE, ȘTIINȚA MATERIALELOR ȘI MEDIU**

TEHNOLOGII ȘI MATERIALE AVANSATE

**Lucrările Conferinței Internaționale
UGALMAT 2011
21 - 22 Octombrie 2011**

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SECTION I

**PROCESSES, TECHNOLOGIES
AND EQUIPMENT IN METALLURGY.**



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COOLING RATE DEPENDENCE OF STRUCTURES CHARACTERISTICS IN Ce-INOCULATED LOW-S GREY IRONS

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ABSTRACT

The efficiency of Ce,Ca,Al-FeSi alloy was tested for lower addition rates (0.15-0.25wt.%), as, traditionally, high inoculant addition rates have been used in low sulphur grey cast irons, comparing to the base iron and conventional inoculated irons (Ba,Ca,Al-FeSi commercial alloy). The present work explores chill and associated structures in hypoeutectic grey iron chill wedges, with cooling modulus 0.21 cm and a large variation of the cooling rate, from the apex to the base of W_2 samples [ASTM A 367, furan resin mould]. The chill tendencies of the experimental irons correlate well with the structure characteristics, displayed as the carbides/graphite ratio and presence of undercooled graphite morphologies. Carbide sensitivity is lower with increasing wedge width, but depends on whether the state of the iron is as base iron or inoculated with different alloys. Undercooled graphite was present for both un-inoculated irons and higher cooling rate inoculated irons. As expected, inoculation as well as an increase in wall thickness of the same wedge sample led to improved undercooled graphite control. The difference in effects of the two inoculants addition is seen as the ability to decrease the amount of carbides and undercooled graphite, with Ce-bearing FeSi alloy outperforming the conventional inoculant, especially at the low alloy addition and high cooling rate solidification.

KEYWORDS: Grey iron, Low S, Cooling rate, Inoculation, Ce, Structure, Carbides, Graphite morphology

1. Introduction

Inoculation is a means of controlling the structure and properties of cast iron by minimizing eutectic undercooling and increasing the number of active graphite nucleation sites during solidification. The role of an inoculant, usually as a FeSi-based alloy including one or more inoculating elements (Ca, Ba, Sr, Ce, La etc), is to influence the formation, characteristics and, thereby, the quality of nuclei for flake graphite and the eutectic structure, respectively.

It accomplishes this by improving the micro-inclusions that already exist in the iron melt (such as sulphides), rather than by creating new compounds. However, this is

possible especially as nitrides, in iron melts with very low sulphur content.

Generally, well inoculated grey irons are characterized by graphite nucleation with a low degree of eutectic undercooling, usually as more than 25°C above the metastable (carbide) eutectic equilibrium temperature (T_{mst}), which is the base condition to promote Type A graphite (random graphite flakes form uniformly in the iron matrix).

As the undercooling increases and graphite nucleation start is closer to T_{mst} , the graphite will branch, forming abnormal patterns. This is known as Types B, D and E graphite (**Fig. 1**).

A further increase in undercooling will suppress the formation of graphite and

results in a hard and brittle white iron carbide structure, at very low machinability.

The avoidance of both carbides and undercooled graphite morphologies (B, D,

E) in the advantage of Type A graphite formation is the most important objective of the inoculation in grey cast iron production.

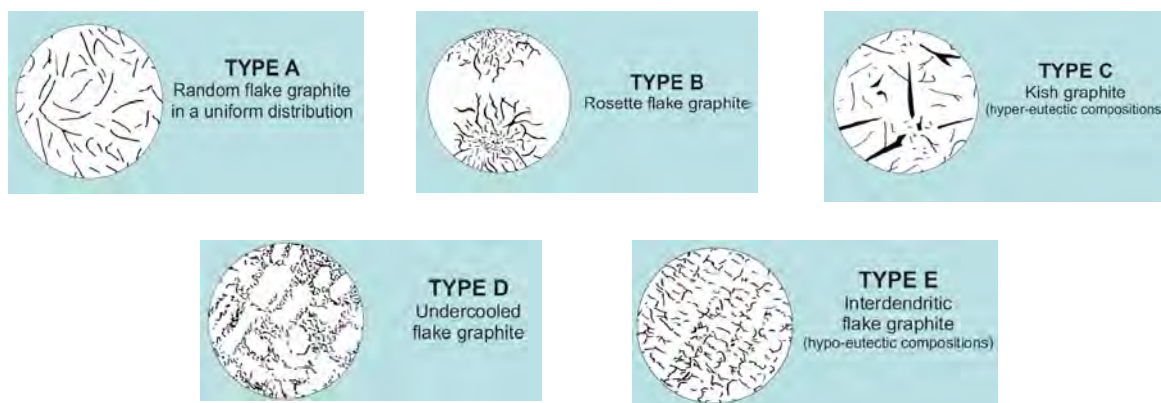


Fig. 1. Typical graphite morphologies in grey cast iron (ASTM)

There are a lot of causes for higher eutectic undercooling and undercooled graphite formation in grey irons, such as lower carbon equivalent level (low carbon and / or silicon), detrimental contents of Mn, S and Al [$< 0.05\%S$, $< 0.03\%Mn$ x ($\%S$) control factor, $< 0.004\%Al$] to sustain complex (Mn,X)S compounds formation as major graphite nucleation sites [1-6], melting practice (high steel scrap amount, high superheating and holding time etc) and pouring practice (low pouring temperature, moulds with high thermal conductivity, thin wall castings etc) [7-9].

The actual world practice in grey iron foundries, involving melting shops including the new generation, acid lined, medium frequency coreless induction furnaces (200-1000Hz, $> 250\text{ kW / t}$ specific power) and thin wall castings production led to critical conditions for iron solidification, as base iron chemistry [$< 0.05\%S$, $< 0.005\%Al$, $< 0.03\%Mn$ x ($\%S$)], more than 1500°C superheating and more than 2°C/sec cooling rate during solidification.

These irons are notoriously difficult to inoculate, in order to avoid carbides and/or undercooled graphite morphologies, especially in economic conditions.

Previous experiments [7,10-12] illustrated the efficiency of some special inoculating variants in low sulphur grey irons, such as Rare Earth (RE) bearing FeSi alloys (Ce, La or Mischmetal variants) or complex inoculants, such as the most representative Ca,Ba,Al-FeSi, Zr,Sr-FeSi, and Ca,Ce,Al-FeSi alloys.

The main objective of the present paper is to examine the effect of Ce,Ca,Al-FeSi alloy on the structure characteristics of low sulphur grey cast irons, comparing to a conventional (commercial) inoculant in Ba,Ca,Al-FeSi alloy system, at lower addition rates procedures ($< 0.3\text{wt}\%$ inoculant) and a large variation of the cooling rate during solidification, as castings geometry.

2. Experimental procedure

The experimental melts were obtained using an induction furnace (acid lining, 100kg, 2400Hz).

The iron melt was heated to 1540°C held for 10 min, then tapped into the pouring ladle (10kg) at 1530°C allowing a final pouring temperature at 1350°C into furan resin sand moulds.

A proprietary Ce-bearing FeSi alloy [1.5-2.0%Ce, 0.75-1.25%Ca, 0.75-1.25%Al, 70-76%Si, Fe bal] [10] was used, comparing to a conventional (commercial) Ba,Ca,Al-FeSi inoculant (typically chemistry: 1.5%Ca, 1.0%Ba, 1.0%Al, 65%Si, Fe bal), both of them at 0.2-0.7mm grain size range.

Addition rates were as 0.15wt.% and 0.25wt.%, point of addition was into the stream when tapping from the furnace into the pouring ladle.

The following final chemical compositions of the inoculated irons were obtained: 3.15-3.3%C, 1.50-1.55%Si, 0.67-0.70%Mn, 0.020-0.025%S, 0.001-0.002%Al, 0.015-0.018%Ti, 0.0060-0.0100%N, 0.05-0.1%Cr, 0.025-0.050%Ni, 0.009-0.015%Mo, 0.004 – 0.006% V, at carbon equivalent 3.6-3.8% CE.

Chill wedges of the type W₂ (10.2mm base width, 31.8mm height, cooling modulus CM=0.21cm) specified in the ASTM A-367 wedge test were considered (resin sand mould), as usually used chill samples in grey iron foundries.

CM is defined as the ratio between volume and the total external casting surface and is an expression of the capacity to transfer a given quantity of heat through an existing surface to the mould.

Higher CM equates to slower cooling rate (CR) and lower undercooling during eutectic solidification. The equivalent cooling modulus, represented by W₂ wedges correspond to round bars with diameter of 8.4 mm.

3. Results and discussion

In a chill wedge, that portion nearest the apex, entirely free of grey areas, is designated as the clear chill zone (W_c).

The portion from the end of the clear chill zone to the location where the last presence of cementite, or white iron is visible, is designated the mottled zone (W_m).

The region from the junction of grey fracture to the first appearance of chilled iron (apex) is designated the total chill (W_t).

The parameters relative clear chill (RCC) and relative total chill (RTC) were also considered:

$$RCC = 100 [W_c / B] (\%) \quad (1)$$

$$RTC = 100 [W_t / B] (\%) \quad (2)$$

Where B is the maximum width of the test wedge.

A medium solidification rate, represented by a W₂ wedge sample, was also used to evaluate the structure formation in un-inoculated and different inoculated irons, with the two considered inoculants (Ce,Ca,Al-FeSi and Ba,Ca,Al-FeSi alloys) at the two addition rates (0.15wt.% and 0.25wt.%) (**Table 1**).

Fractures of W₂-samples (**Fig.2**) were analyzed metallographically, un-etched and etched with Nital (2%), along the geometrical centerline of the chill wedge and at different distances from the apex of the wedge.

Using chill samples, offering different wall thickness simulated different solidification conditions to be explored. At distances farthest from the apex of the chill wedge, the cooling rates are very shallow

The chill tendencies of the experimental irons correlate well with the structure characteristics, displayed as the carbides / graphite ratio and presence of undercooled graphite morphologies. Different structures were obtained at the same area (width) of the wedge sample.

Figures 3a and 3b illustrate that an inverse relationship exists between free carbides level and distance from the apex of the chill wedge, and the wedge width, respectively. Carbide sensitivity is lower with increasing wedge width, but depends on whether the state of the iron is as base iron

or inoculated with different alloys and with different additions, too.

The inoculation was able to totally avoid free carbides formation for more than 6.5mm wall thickness for Ba,Ca-FeSi inoculated irons and 5mm for Ce,Ca-FeSi treatment, with a limited difference for the two inoculant addition rates. Ce-bearing inoculant appears to be more effective

especially for thin wall castings (3-4mm), despite of critical conditions of chemical composition.

It was found that despite the white iron appearance, the samples contained different amounts of free carbides and a small amount of graphite, depending on the inoculant type and addition rate (**Figs. 3c, d**).

Table 1. Structure characteristics [W_2 – wedge sample, ASTM A367]

Wedge width (mm)	Inoc. (%)	Carbides, %			Graphite, %			Undercooled Graphite (B+D+E), %			Ferrite, %		
		U.I	Ba,Ca-FeSi	Ce,Ca-FeSi	U.I	Ba,Ca-FeSi	Ce,Ca-FeSi	U.I	Ba,Ca-FeSi	Ce,Ca-FeSi	U.I	Ba,Ca-FeSi	Ce,Ca-FeSi
1.91	0.15	40	30.0	30.0	1.5	1.5	2.25	100	100	100	0	0	0
	0.25		35.0	30.0		1.75	3.25		100	100		0	0
3.25	0.15	40	29.0	20.0	1.5	2.5	3.5	100	100	100	0	0	4.0
	0.25		22.5	7.5		3.5	4.5		100	100		2.5	4.0
4.89	0.15	39.5	6.5	3.0	1.5	3.25	6.0	100	100	90	0	4.0	5.0
	0.25		4.0	1.5		5.0	6.5		100	80		4.0	2.5
6.62	0.15	35	2.5	2.0	1.75	6.5	8.5	100	90	70	0	5.0	5.0
	0.25		0	0		7.5	9.5		65	40		5.57	2.0
8.18	0.15	39.5	6.5	2.0	1.75	8.5	11.0	100	85	70	0	5.0	5.0
	0.25		0	0		10.0	11.5		50	30		6.5	1.0

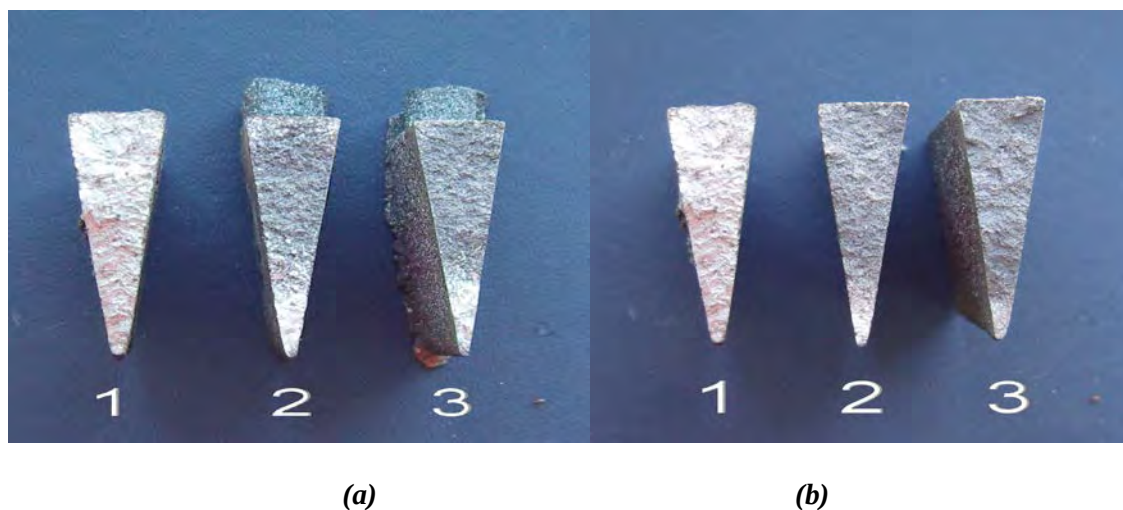


Fig. 2. Influence of Ba,Ca,Al-FeSi (a) and Ce,Ca,Al-FeSi (b) inoculation (1 - un-inoculated, 2 - 0.15% alloy and 3 - 0.25% alloy) on the chill wedge W_2 -ASTM A367 macrostructure

According to higher capacity to prevent free carbides formation, Ce-bearing FeSi alloy led to higher graphite amount for the same cooling rate solidification conditions and for the both addition rate procedures.

Un-inoculated iron is more sensitive not only to free carbides formation (chill tendency) but also to undercooled graphite appearance at the lower solidification rate (at the base of the wedge sample).

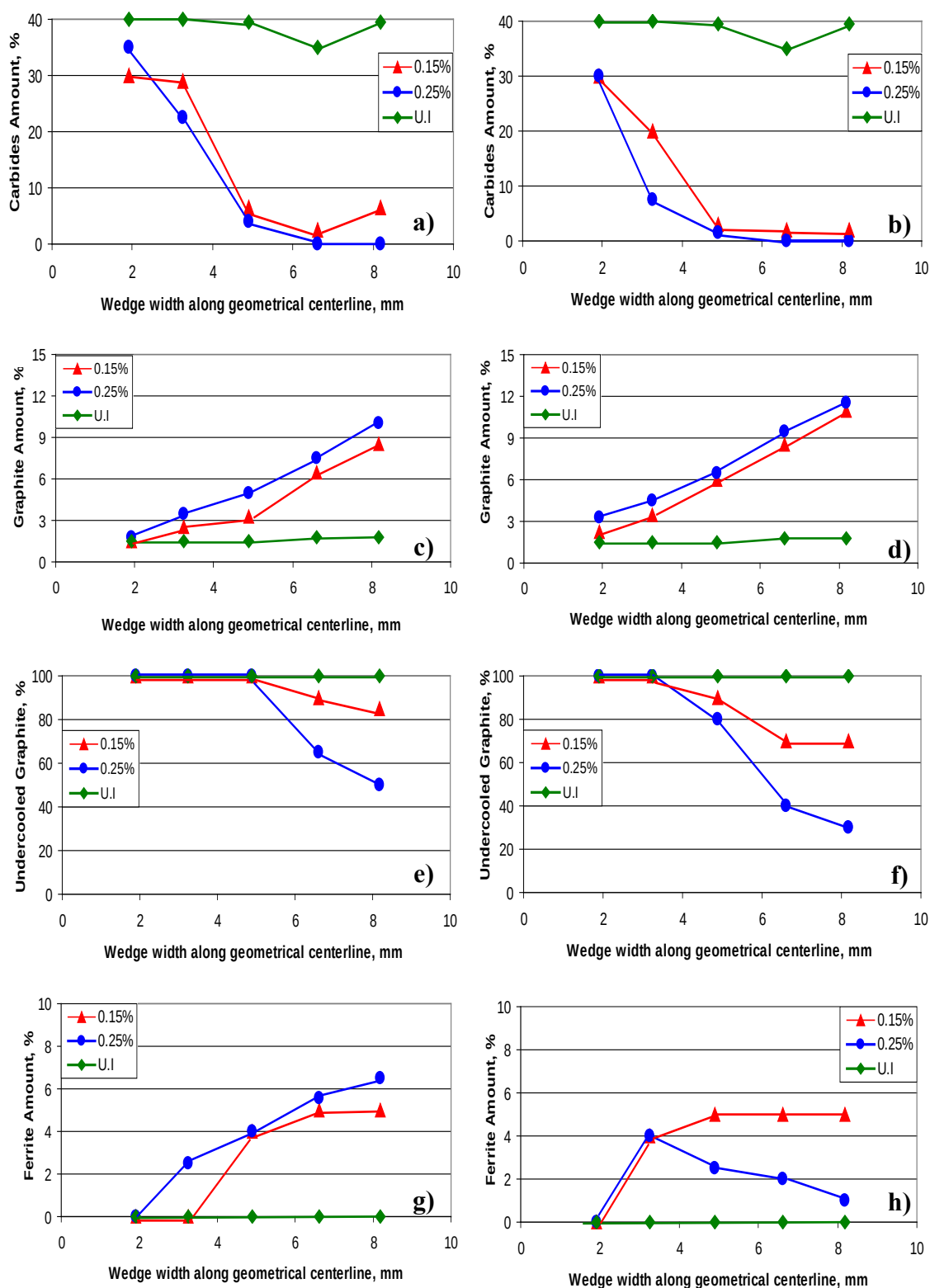


Fig. 3. Influence of inoculant type (a,c,e,g-Ba,Ca,Al-FeSi; b,d,f,h-Ce,Ca,Al-FeSi) and amount (0.15 and 0.25wt.%) on the structure characteristics along the geometrical centerline of W₂-ASTM A367 chill wedge comparing to un-inoculated (UI) irons [a,b-carbides amount; c,d-graphite amount; e,f-undercooled graphite amount; g,h-ferrite amount]

Figures 3e and 3f show an inverse relationship between undercooled graphite levels and distance from the apex of the chill.

Undercooled graphite was present for both un-inoculated irons and higher cooling rate inoculated irons.

As expected, inoculation as well as an increase in wall thickness of the same wedge sample led to improved undercooled graphite control.

The amount of undercooled graphite decreased with increasing distance from the apex of the wedge. The Ce,Ca-bearing inoculant outperformed the Ba-Ca-FeSi alloy, especially at low inoculant additions. The difference in effects of the inoculant addition rates is seen as the ability to decrease the amount of undercooled graphite, especially above a 5.0 mm wedge width.

The amount of ferrite (**Figs. 3g, h**) is strongly dependent on the presence of undercooled graphite: the highest level of

ferrite is typically in the mottled iron area, at the highest undercooled graphite amount.

The association of ferrite and carbides in the same area is an anomaly in the structure (pearlite and carbides normally coexist) is typically linked to the presence of type D undercooled graphite morphologies. Medium eutectic undercooling led to free carbides and type D graphite formation during eutectic solidification (carbides at the beginning and graphite at the end of the eutectic reaction). The presence of type D graphite favors carbon diffusion during the eutectoid reaction due to the shorter distance between graphite particles and consequently ferrite formation (Ferrite + Pearlite = 100%), despite a high cooling rate during the eutectoid reaction (also typical for the center of type B graphite).

There is a difference depending how chill is evaluated for inoculated irons macrostructure (fracture analysis, visual white/mottled iron evaluation) versus microstructure (metallographic analysis, free carbides/graphite presence) (**Fig. 4**).

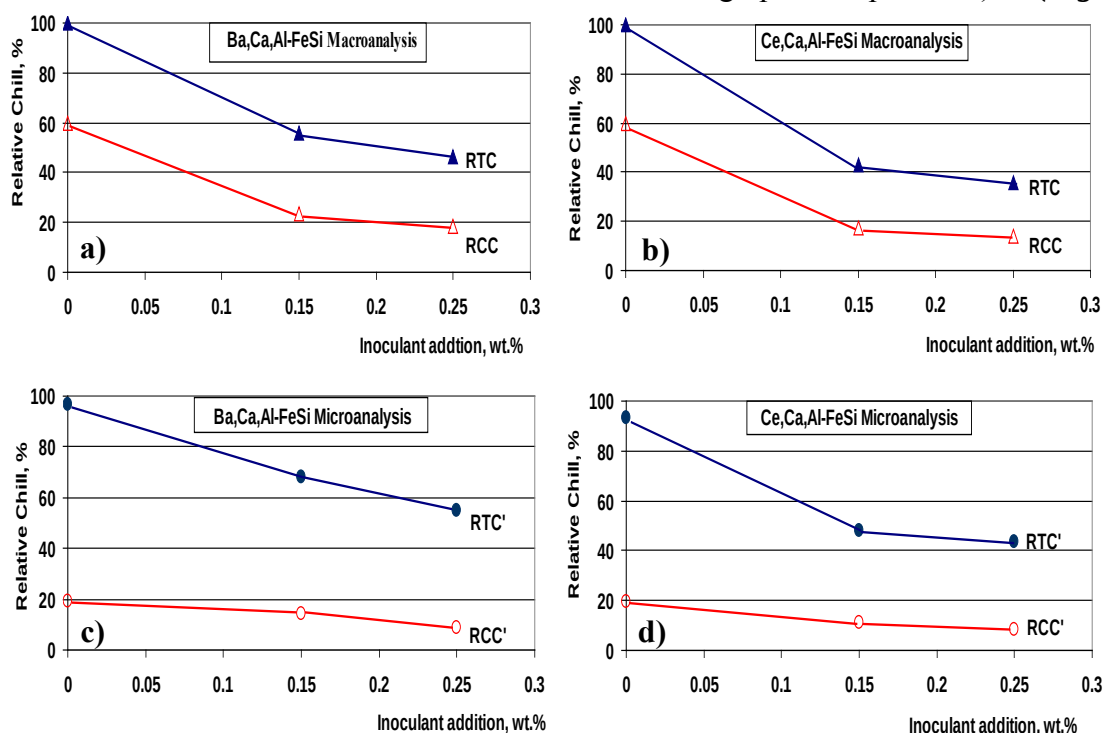


Fig. 4. Relative clear (RCC) and total (RTC) chill evaluated by macro-analysis (a, b) and micro-analysis (c, d) of un-inoculated and Ba,Ca,Al-FeSi (a, c) and Ce,Ca,Al-FeSi (b, d) inoculated irons [W₂-ASTM A367 chill wedge]

This difference is higher in inoculated irons, mainly at lower alloy addition rate, for relative clear chill (RCC) evaluation and bearing inoculant, respectively.

Ba,Ca-FeSi alloy inoculated irons. Specific to the solidification pattern of wedge shaped samples is the end (corner) effect, which is an excessive sensitivity of iron to free carbides and / or undercooled graphite, at the greatest width, corresponding to the B - size parameter.

This phenomenon is more apparent for a lower inoculation potential, such as for 0.15wt.% Ba,Ca-FeSi inoculated cast irons. Ce-bearing FeSi alloy led to the avoidance of this phenomenon, as carbides formation, inclusively at lower addition rate procedure.

High cooling rates, typical for a corner effect [13], led to free carbides and / or undercooled graphite morphologies in all of these cases.

This peculiar solidification pattern of wedge shaped samples could create problems in accurately evaluating chill, especially for thin wall castings and for both relative clear chill and relative total chill criteria.

4. Summary

- The efficiency of a Ce-bearing FeSi inoculant on the structure characteristics (carbide, graphite, metal matrix) of low sulphur [$< 0.025\%S$, $(\%Mn) \times (\%S) < 0.02$], low aluminium [$< 0.002\%Al$], hypoeutectic [3.6-3.8%CE] electric melt [$>1500^{\circ}C$] irons, was tested comparing to a conventional inoculant [Ba,Ca,Al-FeSi alloy], at lower addition rates [$< 0.3wt.\%$] and a large variation of the of the cooling rate during solidification, as casting geometry [1-10mm].
- As expected, an inverse relationship exists between free carbides (in the benefit of graphite) and undercooled graphite level (in the benefit of type-A graphite) and distance from the apex of the chill wedge or wedge width, but depending on the inoculant type and addition rate, too.
- The inoculation was able to totally avoid free carbides formation for more than 6.5 mm wall thickness for Ba,Ca-FeSi inoculated irons and 5 mm for Ce,Ca-FeSi treatment.
- Ce-bearing inoculant appears to be more effective especially for thin wall castings (3-4 mm), despite of critical conditions of chemical composition of the base iron.
- According to higher capacity to prevent free carbides formation, Ce-bearing FeSi alloy led to higher graphite amount for the same cooling rate solidification conditions and for the both addition rate procedures. The Ce-Ca-Al-FeSi inoculant outperformed the Ba-Ca-Al-FeSi alloy, especially at low inoculant additions.
- There appears to be a difference in chill (carbides formation) evaluation, for inoculated irons, between macrostructure (fracture analysis) and micro-structure (metallographic analysis).
- Chill tendency by a microstructure evaluation route appears to be important in thin wall castings after inoculation, for both relative clear chill and relative total chill criteria.
- The end (corner) effect, seen as a higher cooling rate at the highest width, leads to free carbides and / or undercooled graphite morphologies / ferrite, more especially for lower inoculation potential, such as Ba,Ca,Al-FeSi alloy and 0.15wt.% addition rate, respectively.

References

- [1]. **I. Riposan, M. Chisamera, S. Stan, T. Skaland, M.I. Onsoien.** *Analyses of Possible Nucleation Sites in Ca/Sr Overinoculated Grey Irons.* AFS Trans., 2001, Vol. 109, pp. 1151- 1162.
- [2]. **I. Riposan, M. Chisamera, S. Stan, T. Skaland.** *Graphite Nucleants (Microinclusions) Characterization in Ca/Sr Inoculated Grey Irons.* Int. J. Cast Met. Res., 2003, Vol. 16, No. 1-3, pp. 105-111.
- [3]. **I. Riposan, M. Chisamera, S. Stan, C. Hartung, D. White.** *Three-Stage Model for the Nucleation of Graphite in Grey Cast Iron.* Mater. Sci. Techn., 2010, Vol. 26, No. 12, pp. 1439-1447.
- [4]. **I. Riposan, M. Chisamera, S. Stan, C. Ecob, D. Wilkinson.** *Role of Al, Ti, Zr in Grey Iron Preconditioning/Inoculation.* J. Mater. Eng. Perform., 2009, Vol. 18 (1), pp. 83-87.
- [5]. **R. Gundlach.** *Observations on Structure Control to Improve the Properties of Cast Irons.* The 2008 Honorary Cast Iron Lecture, Div. 5, AFS Metalcasting Congress, Atlanta, Georgia, USA, Paper 08-158.
- [6]. **C. Hartung, C. Ecob, D. Wilkinson.** *Improvement of Graphite Morphology in Cast Iron.* Casting Plant and Technology International, 2008, No. 2, pp. 18-21.
- [7]. **CAST IRON INOCULATION, The Technology of Graphite Shape Control Brochure,** Information on www.foundry.elkem.com, May 2009.
- [8]. **I. Riposan, M. Chisamera, S. Stan, G. Grasmø, C. Hartung, D. White.** *Iron Quality Control During Melting in Coreless Induction Furnace.* AFS Trans., 2009, Vol. 117, pp. 423-434.
- [9]. **M. Chisamera, I. Riposan, S. Stan, C. Ecob, G. Grasmø, D. Wilkinson.** *Preconditioning of Electrically Melted Gray Cast Irons.* AFS International Cast Iron Melting Conference, February 21-23, 2009, Orlando, Florida, USA.
- [10]. **Reseed® Inoculant–ELKEM Foundry Products Division Brochure.** Information on <http://www.foundry.elkem.com> (2004).
- [11]. **I. Riposan, M. Chisamera, S. Stan, E. Stefan, C. Hartung.** *Role of Lanthanum in Graphite Nucleation in Grey Cast Iron.* Key Engineering Materials-KEM, Vol.457 [Science and Processing of Cast Iron IX], (2011), pp. 19-24. Trans. Techn. Publications, Switzerland.
- [12]. **I.V. Anton, I. Riposan.** *Structure Characteristics of Ce-Inoculated, Low Sulphur Grey Cast Irons.* Advanced Materials and Structures - AMS '11 International Conference, Timisoara, Romania, Oct. 2011, Paper-045.
- [13]. **S. Stan, M. Chisamera, I. Riposan, E. Stefan, M. Barstow.** *Solidification Pattern of Un- inoculated and Inoculated Gray Cast Irons in Wedge Test Samples.* AFS Trans., 2010, Vol. 118, pp. 295-309.

RELATIVE PERFORMANCE OF Ca, Ba-FeSi INOCULANTS TO CHILL CONTROL IN LOW-S GREY CAST IRONS

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ABSTRACT

Low sulphur irons ($< 0.05\%S$) production is more and more promoted in many parts of the world, as small and less efficient cupolas were replaced by the new generation of induction furnaces, while a single low sulphur base iron is very attractive for grey/ductile/compacted irons production. The problem is that at low S-levels, grey irons usually solidify with high eutectic undercooling, favorable for carbides formation, especially in thin wall castings (automotive industry). Relative performance of different Ca, Ba and Al bearing FeSi alloys was calculated to evaluate their efficiency to control chill tendency, in critical base irons [$< 0.035\%S$, $(\%Mn) \times (\%S) < 0.02$, $0.002\%Al$]. Relative clear/mottled/total chill measurement criteria were applied, for chill wedges with different cooling modulus ($CM = 0.11 - 0.35 \text{ cm}$). The results showed that some inoculants performed better than the other alloys bearing the same base inoculating elements and have different positions for different chill evaluation criteria and wedge size (cooling modulus) parameters reference. An optimum association of Ca, Ba and Al contents at a proper Ba/Ca ratio is more efficient comparing to the increasing of the inoculating elements leveling FeSi-based alloys for inoculation of lower sulphur, electrically melted irons.

KEYWORDS: Grey iron, Low S, Cooling rate, Inoculation, Ca, Ba, Al, Structure, Carbides, Graphite

1. Introduction

Inoculation is a treatment of the molten iron to control the structure and properties of castings by promotion of active nucleation sites available for the growth of graphite flakes in grey irons at lower eutectic undercooling, thereby minimizing the risk of forming chill (hard iron carbides) and/or unfavourable graphite morphologies, such as D-type (undercooled) graphite, particularly in thin sections.

Chilled structures are typically for high eutectic undercooling and are hard and brittle and interfere with machining, necessitate additional heat treatment operations, resulting in non-conformance with specifications and, in general, increase the total cost of production. Lowering the

eutectic undercooling may lead to avoiding of carbides, but, if it is still high, the promoted graphite will branch, forming abnormally patterns, such as Types B, D and E graphite. At enough lower eutectic undercooling level, random graphite flakes form uniformly in the iron matrix, which is known as Type A graphite.

The most effective inoculants are FeSi alloys containing small amounts of one or more of the elements such as Ca, Ba, Sr, generally at concentrations above 0.5wt.% each one. It is considered that inoculating elements contents above 1.5wt.% give improved inoculation under some conditions but may also give a greater tendency to produce slag [1, 2].

Recent research results have identified three groups of elements with important

contributions in formation of graphite nucleation sites as (Mn,X)S - type in commercial grey cast iron: (a) oxide forming elements (Mn, Si, Al, Zr etc) to produce small oxide base sites (usually less than 3µm) in the first stage; (b) Mn and S to sustain MnS-compounds (generally up to 10 µm size) nucleated by stage one particles; (c) inoculating elements, such as Ca, Ba, Sr, Ce, La etc which act in the first stage or/and in the second stage of graphite formation, to improve the capability of (Mn,X)S compounds to nucleate graphite [3-5].

The nucleation of graphite flakes on MnS particles was also confirmed by microstructure simulations [6, 7].

Traditionally, the sulphur level in grey iron was above 0.05%, as the cupola was the typical melting furnace in the cast iron foundries, where the metallurgical coke acts as an efficient re-sulphurizer of the iron melt, but with excessive contribution in many cases.

The new generation of coreless induction furnaces replaced cupolas in the iron melting shops (no metallurgical coke), the expensive pig iron was replaced by steel scrap (lower sulphur), while the high quality carbon riser (lower sulphur) is more and more used, inclusively in grey iron production.

Consequently, less than 0.05%S content is typically now for the base iron in high performance grey iron castings production. The re-sulphurization of the iron melt to attend a control factor at $(\%Mn) \times (\%S) = 0.03-0.05$ level [8] is necessary, but in some cases this is not possible, as ecology limitation or for the necessity to use the same base iron for grey/compacted/ductile irons castings production.

The problem is that at low S-levels, grey irons usually solidify with high eutectic undercooling, favourable for carbides and / or undercooled graphite morphologies, especially in thin wall castings (automotive industry) [9-13]. Lower residual aluminium content in the iron melt (less than

0.004%Al), also typically for the acid lining coreless induction furnaces melting increases the difficulty of (Mn,X)S compounds formation [3-5, 10, 13].

Grey irons with sulphur contents below about 0.05% may only respond to certain specialized inoculants, or necessitate the increasing of the inoculant addition rate, but promoting some detrimental effects, such as the increasing of slag defects. Recently, a strong research activity was recorded, to improve the chemical composition of FeSi-based inoculants, in order to increase their inoculation capability according to low sulphur grey iron characteristics.

New inoculating elements were considered, especially from rare earth (RE) group (Ce, La), or some elements were associated with traditionally inoculating elements, such as Zr + Sr, Zr + Ca or RE + Ca. The review of the conventional inoculants composition was also considered, in order to optimize inoculant's chemistry according to the new conditions of the grey iron melt.

The current experimental investigation in the paper was designed to evaluate the relative performance of the Ca, Ba and Al bearing FeSi alloys at different association of inoculating elements as efficiency in chill control of grey iron; a critical iron chemistry [$< 0.035\%S$, $(\%Mn) \times (\%S) < 0.02$, $0.002\%Al$] for graphite nucleation was also considered, for solidification in different cooling rate conditions.

2. Experimental procedure

Experimental heats at low sulphur level (0.030-0.035%S) and very low residual aluminium content (0.002%Al) were produced in an acid lined coreless induction furnace (100kg, 2400Hz). Un-inoculated and ladle inoculated (0.15wt.% Ca,Ba,Al-FeSi alloys) were considered, at the following final chemical compositions (wt.%): 3.25-3.35C, 1.60-1.65Si, 0.55-0.56Mn, 0.08-0.11P, 0.09-0.10Cu, 0.03-0.04Ni, 0.08-

0.09Cr, 0.01Mo, 0.005V, 0.005-0.006Ti, for carbon equivalent (CE) 3.75-3.85, and $(\%Mn) \times (\%S) = 0.017-0.020$ as control factor.

Different Ca,Ba,Al-FeSi alloys were used, for the 70-75wt.%Si range and appropriate aluminium contents (0.7-0.9wt.%), typically for foundry grade ferrosilicon, but at different inoculating elements (Ca, Ba) levels. The traditionally Ca and Ba inoculating elements were included in the usual range for the commercial inoculants (up to 4wt.% each one), but varied as Ba/Ca ratio (0.8-4) and content associations, for $Ca + Ba = 1.7-6.2wt. \%$ in the inoculants chemistry.

The iron melt was heated up to 1530-1540°C for 10 minutes, and then was tapped into the inoculation ladle (10 kg). Inoculants were added, at 0.2-0.7 mm grain size during tapping into the pouring ladle. Inoculated irons were poured (furan resin moulds) at a strong controlled temperature (1350°C) after a 2.0-2.5 min holding time.

The very narrow chemistries range of the tested irons and very low minor (trace) elements contents, the strong control on the thermal regime and treated iron melt volume, and controlled compositions and grain sizes of the inoculants led to an accurate evaluation of the inoculants effect, inclusively as the Ba/Ca ratio influences.

Wedge W_1 , W_2 and W_3 samples according to ASTM A367, were used (furan resin mould) as “Test Method A-Wedge”. Standard wedges are characterized by size and cooling modulus (CM), which involved different solidification cooling rates, for the same pouring practice and moulding media. For the three considered wedges, representative for thin-medium wall thickness castings, the main characteristics are the follows: W_1 ($B=5.1mm$ base width, 25.4mm height, $CM=0.11cm$ cooling modulus), W_2 (10.2mm base width, 31.8mm height, $CM=0.21cm$) and W_3 (18.6mm base width, 38.1mm height, $CM=0.35cm$).

Cooling modulus (CM) is defined as the ratio between volume and the total external casting surface and is an expression of the capacity to transfer a given quantity of heat through an existing surface to the mould. Higher cooling modulus equates to slower cooling rate and lower undercooling during eutectic solidification.

3. Results and discussion

The measurement of chill was recorded according to a controlled procedure, to avoid hot shaking effect on the solid state transformation. Later the wedges were fractured and their fractures analyzed. That portion nearest the apex, entirely free of grey (graphite) areas, is designated as the clear chill zone (W_c), including only carbides in the structure (**Fig. 1**). The portion from the end of the clear chill zone to the location where the last presence of cementite, or white iron is visible, is designated the mottled zone (W_m), including both carbides and graphite. The region from the junction of grey fracture (no carbides, only graphite) to the first appearance of chilled iron (apex) is designated the total chill (W_t).

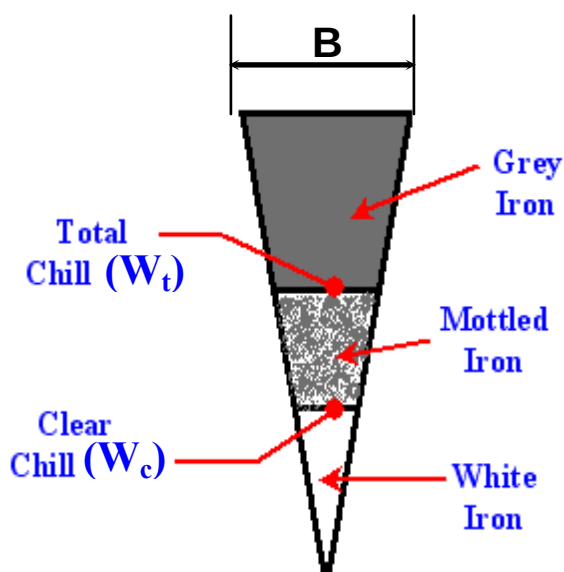


Fig. 1. Typical chill zones on the wedge test samples [B -base width]

The parameters relative clear chill (RCC), relative total chill (RTC) and relative average mottled chill (RMC) were also considered:

$$RCC = 100 [W_c / B] (\%) \quad (1)$$

$$RTC = 100 [W_t / B] (\%) \quad (2)$$

$$RMC = 100 [0.5 (W_c + W_t) / B] (\%) \quad (3)$$

where B is the maximum width of the test wedge.

Table 1 summarized the obtained results for the three chill evaluation criteria (RCC,

RMC, RTC), of un-inoculated and different inoculated irons (A...I inoculants).

The increasing of the cooling modulus (CM) from W_1 (CM=0.11cm) through W_2 (0.21cm) up to the W_3 (0.35cm) led to the decreasing of the cooling rate, and, normally, also of the chill tendency of both un-inoculated and inoculated irons. Un-inoculated irons are characterized by having high chilling tendency. It could be considered as excessive for 3.75-3.85%CE irons.

Table 1. Relative clear (RCC), mottled (RMC) and total (RTC) chill

Alloy	Ca+Ba (%)	Ba/Ca	W ₁ [B=5.3mm; CM=0.11cm]			W ₂ [B=10.2mm; CM=0.21cm]			W ₃ [B=18.6mm; CM=0.35cm]		
			RCC (%)	RMC (%)	RTC (%)	RCC (%)	RMC (%)	RTC (%)	RCC (%)	RMC (%)	RTC (%)
U.I	-	-	100	100	100	100	99.0	98.0	51.5	75.8	100
A	1.70	0.89	55.5	77.8	100	34.0	66.0	98.0	20.0	34.0	48.0
B	2.01	0.62	64.5	82.3	100	36.0	67.0	98.0	24.0	39.3	54.5
C	2.22	1.00	50.5	75.3	100	30.5	64.3	98.0	20.0	35.0	50.0
D	2.40	1.40	52.0	76.0	100	30.5	64.3	98.0	18.5	33.5	48.5
E	2.97	2.06	48.5	74.3	100	33.0	65.5	98.0	20.0	36.0	52.0
F	3.85	3.53	62.5	81.3	100	37.0	50.5	64.0	20.0	33.5	47.0
G	3.85	1.08	55.5	77.8	100	29.0	63.5	98.0	18.7	33.9	49.0
H	4.55	1.76	54.5	77.3	100	34.0	51.8	69.5	17.0	31.5	46.0
I	6.20	1.82	59.5	79.8	100	35.0	52.3	69.5	19.5	33.8	48.0
Average	CL _K		55.9	78.0	100.0	33.2	60.6	87.9	19.7	34.5	49.2
St. Dev.	S _K		5.38	2.70	0.00	2.72	6.88	15.25	1.89	2.17	2.62

High furnace superheating (1540°C), low Al content (0.002%) and less than 0.02 as (%Mn) x (%S) control factor led to difficulties in complex (Mn,X)S compounds formation, as graphite nucleation sites, and, consequently, to excessive chill. Inoculation gave, as expected, overall lower iron chill than with no inoculation, even at lower inoculant (0.15wt.%) in-ladle additions. A 0.15wt.% inoculant addition had a very big influence on chill tendency compared to un-inoculated irons, especially at the higher cooling rate (or lower cooling modulus of wedge samples). At low cooling modulus (CM=0.11cm, W_1 samples), typically for thin wall castings (4.4mm corresponding diameter for a bar sample), an important inoculation effect was obtained for relative

clear chill (RCC) evaluation, as RCC decreased from 100% to 50-65%, much more than for relative mottled chill RMC (from 100% to 75-85%), while the relative total chill RTC was not affected. W_2 type wedges are representative for 8.4 mm diameter bars castings, large used in mechanical engineering.

Inoculation was more effective for these castings as relative clear chill evaluation, comparing to relative mottled chill and especially to relative total chill evaluation, where only some inoculants were efficient. The largest considered wedge sample (W_3), correspondent to 14mm diameter bar castings is visible affected by inoculation for all of chill evaluation criteria and inoculants used.

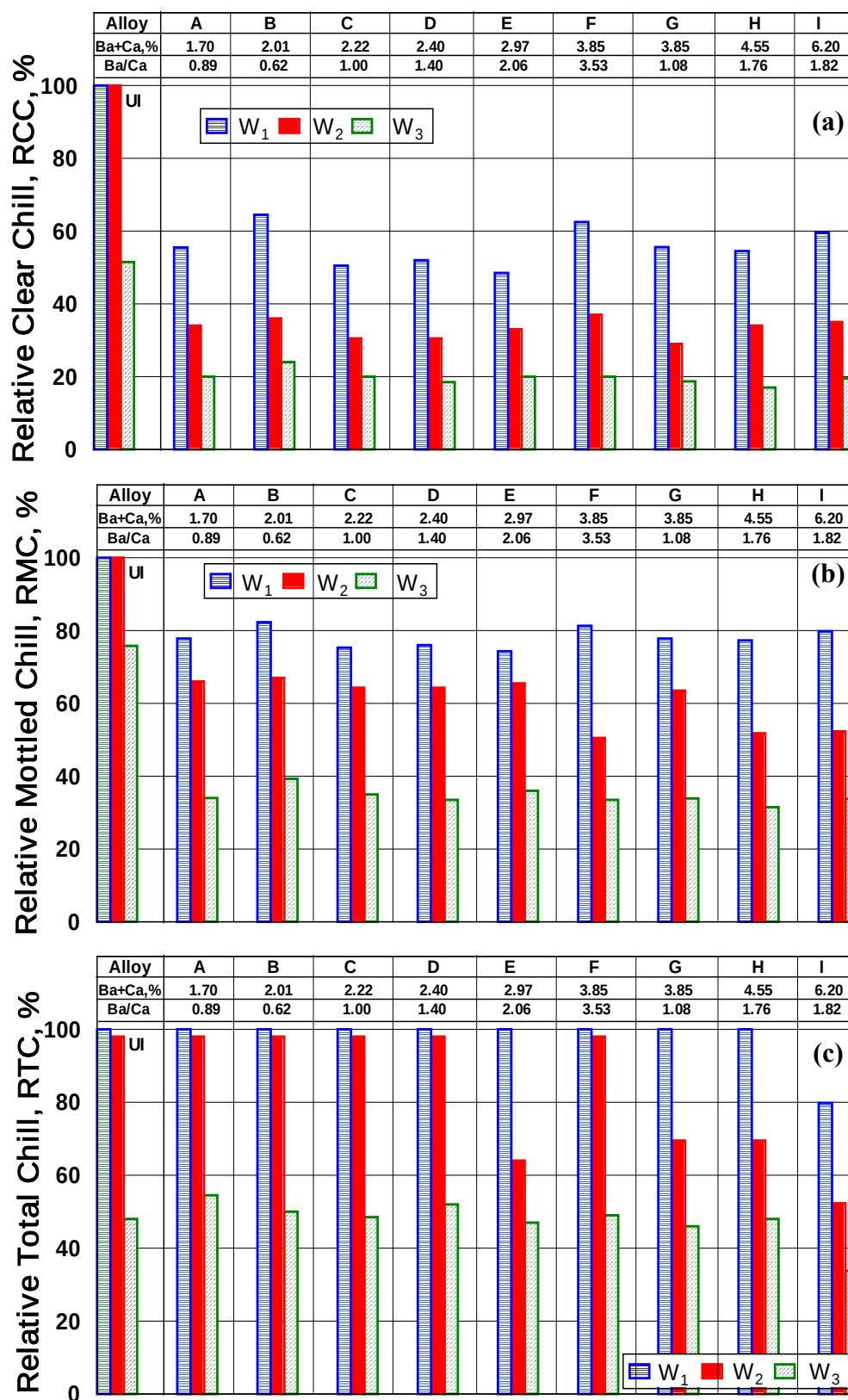


Fig. 2. Relative clear chill (RCC) (a), relative mottled chill (RMC) (b) and relative total chill (RTC) (c) of un-inoculated (UI) and inoculated (A...I) irons, for W_1 , W_2 and W_3 samples.

A number of trends in chill sensitivity could be identified, as the influence of inoculating elements (Ca, Ba) total sum and especially as ratio, specific content of each element and their associations (**Fig. 2**).

Generally, the increasing of the total content of inoculating elements (Ca + Ba sum) in the compositions of Ca,Ba,Al-FeSi alloys does not appear to have an important beneficial influence as chill tendency decreasing of the low sulphur and low aluminium, electrically melted grey irons, with some peculiar exceptions.

It is more visible for intermediary solidification conditions, such as for W_2 (CM=0.21cm) samples and for relative mottled chill (RMC) evaluation criteria, respectively. The relative performance of inoculants to control representative chill tendency parameters was calculated to determine the efficiency of the experimental alloys [14].

The relative performance (R_{Pi}) of inoculants –i- is estimated as:

$$R_{Pi} = \frac{\sum_k (X_{ik} - CL_k)}{S_k} \quad (4)$$

where X_{ik} is measured value of property –k- using inoculants –i-;

CL_k is average value for property set –k-;

S_k is standard deviation from the set.

The reducing of chill tendency performance is averaged and used as one parameter –k-, for each chill evaluation criteria (RCC, RMC, RTC) and each wedge samples (W_1 , W_2 , W_3). Average performance has level 0%.

The performances of inoculants increase as chill tendency decreases, so positive values for relative performance (**Tables 2 and 3, Figures 3 and 4**) means a lower chill comparing to the average level for the group of considered alloys. This tool was used to determine and distinct the close performance of the alloys in all the analyses carried out in this work.

The results showed that some inoculants performed better than the other alloys bearing the same base inoculating element (Ca and Ba), depending on the total Ca + Ba content and the ratio of the two inoculating elements (Ba / Ca), respectively. Inoculants have different positions for different chill evaluation criteria (RCC, RMC, RTC) and wedge size (cooling modulus) parameters.

Thin wall castings (< 5mm wall thickness), represented here by W_1 wedge sample (0.11cm cooling modulus and corresponding to 4.4mm diameter bars), are the most affected by different alloys chemistries.

Table 2. Relative performances of Ca,Ba-FeSi alloys to reduce chill tendency

Alloy	Ca+Ba (%)	Ba/Ca	W ₁ [B=5.3mm; CM=0.11cm]			W ₂ [B=10.2mm; CM=0.21cm]			W ₃ [B=18.6mm; CM=0.35cm]		
			RCC (%)	RMC (%)	RTC (%)	RCC (%)	RMC (%)	RTC (%)	RCC (%)	RMC (%)	RTC (%)
A	1.70	0.89	+7.2	+7.0	0.0	-28.6	-78.9	-66.3	-13.5	+23.1	+46.6
B	2.01	0.62	-159.9	-159.9	0.0	-102.2	-93.4	-66.3	-225.1	-221.3	-201.2
C	2.22	1.00	+100.1	+99.7	0.0	+100.2	-54.1	-66.3	-13.5	-23.1	-29.6
D	2.40	1.40	+72.2	+73.8	0.0	+100.2	-54.1	-66.3	+65.8	+46.1	+27.5
E	2.97	2.06	+137.2	+136.8	0.0	+8.2	-71.6	-66.3	-13.5	-69.2	-105.9
F	3.85	3.53	-122.8	-122.8	0.0	-139.0	+146.6	+156.7	-13.5	+46.1	+84.7
G	3.85	1.08	+7.2	+7.0	0.0	+155.4	-42.5	-66.3	+55.2	+27.7	+8.5
H	4.55	1.76	+25.8	+25.5	0.0	-28.6	+127.7	+120.6	+145.1	+138.3	+122.8
I	6.20	1.82	-67.1	-67.2	0.0	-65.4	+120.4	+120.6	+12.9	+32.3	+46.6

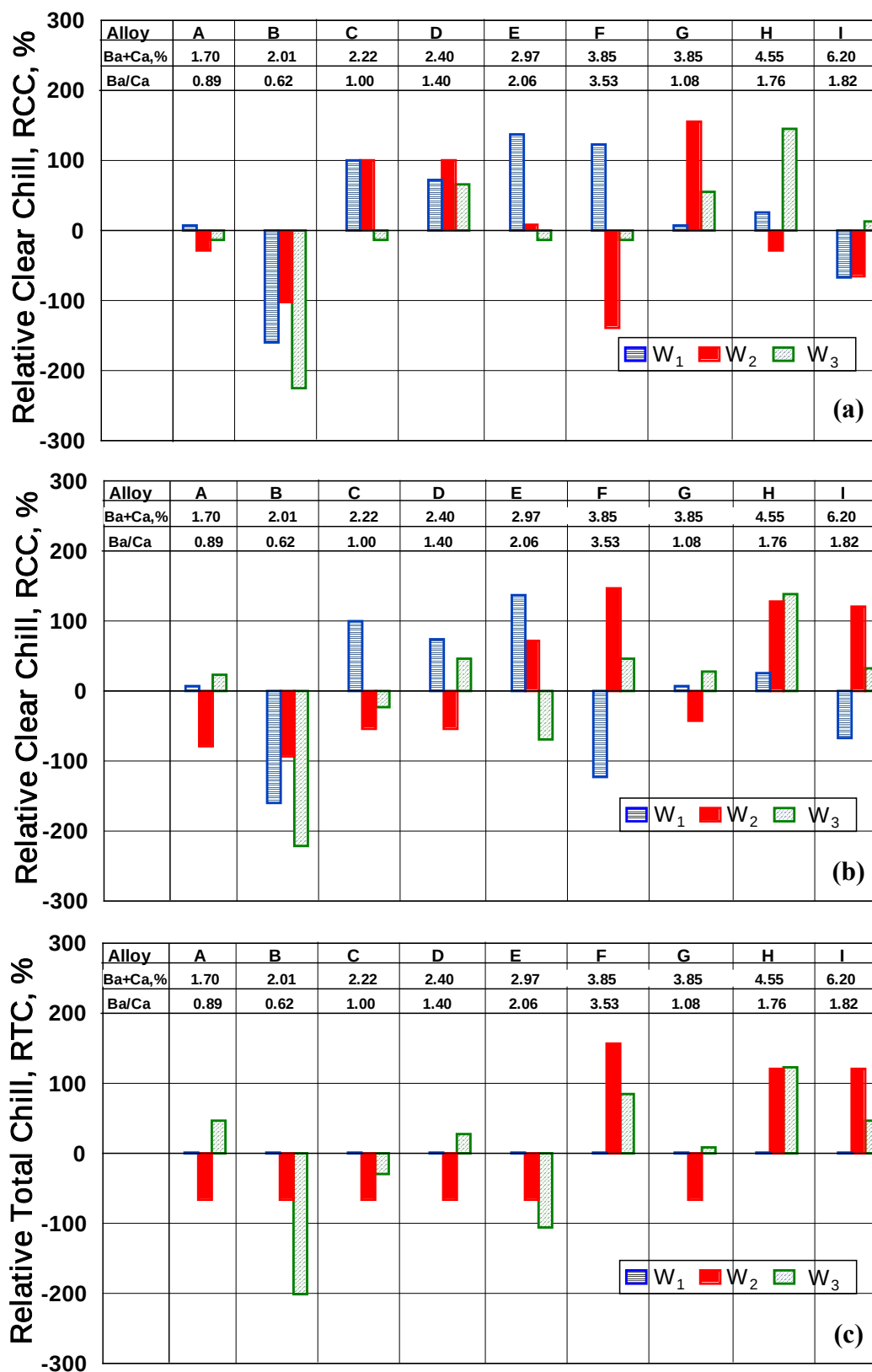


Fig. 3. Relative performance as chill tendency decreasing of Ca,Ba-FeSi alloys for W_1 , W_2 and W_3 wedge samples, as relative clear chill (RCC) (a), relative mottled chill (RMC) (b) and relative total chill (RTC) (c) evaluation criteria.

Table 3. Relative performances of inoculants as chill evaluation criteria and wedge size

Alloy	Ca+Ba (%)	Ba/Ca	Chill evaluation criteria				Wedge samples			
			RCC	RMC	RTC	Total	W ₁	W ₂	W ₃	Total
A	1.70	0.89	-11.6	-16.3	-6.6	-11.5	+4.7	-57.9	+18.7	-11.5
B	2.01	0.62	-162.4	-158.2	-89.2	-136.6	-106.6	-87.3	-215.9	-136.6
C	2.22	1.00	+62.3	+7.5	-32.0	+12.6	+66.6	-6.7	-22.1	+12.6
D	2.40	1.40	+79.4	+21.9	-12.9	+29.5	+48.7	-6.7	+46.5	+29.5
E	2.97	2.06	+44.0	-1.33	-57.4	-4.9	+91.33	-43.2	-62.9	-4.9
F	3.85	3.53	-91.8	+23.3	+80.5	+4.0	-81.9	+54.8	+39.1	+4.0
G	3.85	1.08	+72.6	-2.6	-19.3	+16.9	+4.7	+15.5	+30.5	+16.9
H	4.55	1.76	+47.4	+97.2	+81.1	+75.2	+17.1	+73.2	+135.4	+75.2
I	6.20	1.82	-39.9	+28.5	+55.7	+14.8	-44.8	+58.5	+30.6	+14.8

In clear chill (white iron structure, no graphite presence) control, the highest performance characterized Ca,Ba,Al-FeSi alloys at medium inoculating elements content [2-3% (Ca + Ba)] and Ba/Ca = 1 - 2 ratio. The increasing of the inoculating elements content does not appear to be an economical solution for these irons, independently of their ratio in the chemical composition of these complex alloys. The same behaviour appears in relative mottled chill evaluation (mixture of carbide and graphite zone size), while for total chill control (RTC) these inoculants have not enough power in tested conditions.

Thin to medium size wall thickness castings characterized by W₂ wedge sample (0.21cm cooling modulus, corresponding to 8.4mm diameter bars) present different requirements for Ca,Ba,Al-FeSi alloys as chill control, depending on the chill evaluation criteria. As clear chill approach, the ratio of the two inoculating elements appears to be the most important parameter. The best performance characterized inoculants with Ca and Ba in a relative equilibrium (Ba/Ca = 1.0-1.5), at medium (2.2-2.5%) or high (3.85%) total content of Ca and Ba. In the both chemistry ranges, lower or higher Ba/Ca ratio visible decreased the performance of these inoculants. Mottled and total chill control in these castings required inoculants with higher content of inoculating elements, generally more than 4%.

W₃ wedge sample usually characterizes medium size (more than 10mm wall thickness) castings. Also in this case the ratio of the two inoculating elements is important, as the higher performance inoculants are generally characterized by Ba/Ca = 1.5-2.0 ratio, mainly at more than 4% total content.

Generally, in low sulphur grey cast irons, the higher is the wall thickness (cooling modulus) of castings, the higher is the content of inoculating elements necessary for higher performance of inoculants in Ca-Ba system.

In critical solidification condition, such as thin wall castings, the performance of Ca-Ba bearing FeSi alloys is better for an equilibrium of Ca and Ba contents, the best position is typically for 3% (Ca + Ba) and Ba/Ca = 2 ratio alloy, which performed better than the other alloys, inclusively at higher content of inoculating elements. The high calcium and barium bearing inoculants did not perform well during fast casting of small samples under the conditions in this trial.

Independently of wedge size and chill evaluation criteria, less than 2% (Ca + Ba) and Ba/Ca < 1.0 ratio are not recommended in low sulphur grey cast irons, with critical conditions for graphite nucleation at lower eutectic undercooling.

As iron castings are usually complex parts, at a large range of wall thickness, including from thin (some millimeters) up to

thick (hundreds millimeters) walls, it is very difficult to select a performance inoculant to control the structure in so different solidification conditions.

Figure 4 shows the total relative performance of the tested alloys, for a large range of cooling modulus (0.11-0.35cm) and different chill evaluation criteria.

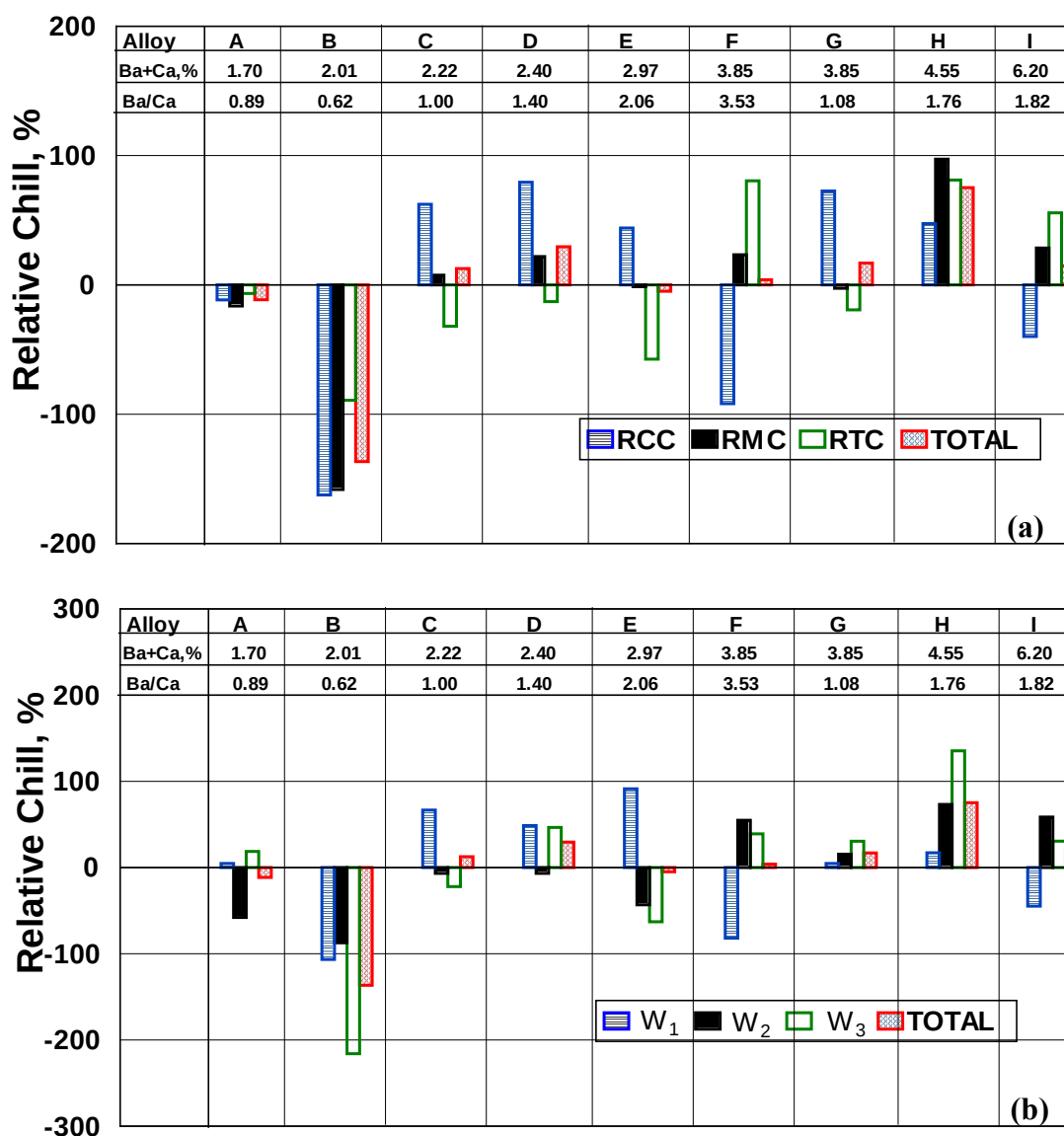


Fig. 4. Relative performance as chill tendency decreasing of Ca,Ba,Al-FeSi alloys for different chill evaluation criteria (a) and different wedge sample size (b).

The best performance inoculant to produce a high quality complex grey iron castings (large wall thickness variation) is characterized by 4.5% (Ca + Ba) total content at 1.75 s specific Ba/Ca ratio, while the second variant refers to an alloy at lower but controlled content of the two

representative inoculating elements: Ca + Ba = 2.4% and Ba/Ca = 1.4.

4. Summary

The relative performance of Ca,Ba,Al-FeSi alloys, at different association of inoculating elements (Ca, Ba), was tested

in chill control in low S grey irons ($< 0.035\%S$) for different solidification cooling rates (W_1 , W_2 and W_3 wedges, ASTM A 367) and chill evaluation criteria (RCC, RMC, RTC). Based on this work the following main conclusions can be drawn.

- Chill tendency of electrically melted base iron having 3.75%CE, 0.03%S, $(\%Mn) \times (\%S) < 0.02$ control factor and 0.002%Al residual is excessively high, demonstrating a relatively high need for inoculation power.
- The results showed that some inoculants performed better than the other alloys bearing the same base inoculating element (Ca and Ba), depending on the total Ca + Ba content and the ratio of the two inoculating elements (Ba/Ca), respectively.
- Un-favourable chemical composition of the inoculated irons as Mn, S and Al contents for $(Mn,X)S$ compounds formation to act as graphite nucleation sites is difficult to be covered by increasing of inoculating elements (Ca, Ba) content, especially for high cooling rate solidification and clear chill parameter control.
- Inoculants have different positions for different chill evaluation criteria (RCC, RMC, RTC) and wedge size (cooling modulus) parameters reference.
- Independently of wedge size and chill evaluation criteria, less than 2% (Ca + Ba) and Ba/Ca < 1.0 ratio are not recommended in low sulphur grey cast irons, with critical conditions for graphite nucleation at lower eutectic undercooling.
- In thin wall castings production, the performance of Ca-Ba bearing FeSi alloys is better for an equilibrium of Ca and Ba contents, the best position is typically for 3% (Ca + Ba) and

Ba/Ca = 2 ratio alloy, which performed better than the other alloys, inclusively at higher content of inoculating elements.

- The best performance inoculant to produce a complex grey iron castings (large wall thickness variation) is characterized by 4.5% (Ca + Ba) total content at 1.75 specific Ba/Ca ratio, while the second variant refers to an alloy at lower but controlled content of the two representative inoculating elements: Ca + Ba = 2.4% and Ba/Ca = 1.4.
- The use of relative performance of inoculants is a tested tool to determine and distinct the close performance of the alloys in all the analyses carried out in this work.

References

- [1]. CAST IRON INOCULATION, The Technology of Graphite Shape Control Brochure, www.foundry.elkem.com, May 2009.
- [2]. ELKEM Technical Information 3, ELKEM ASA, Foundry Products, www.foundry.elkem.com, 2004.
- [3]. I. Riposan, M. Chisamera, S. Stan, T. Skaland, M.I. Onsoien. *Analyses of Possible Nucleation Sites in Ca/Sr Overinoculated Grey Irons*. AFS Trans., 2001, Vol. 109, pp. 1151-1162.
- [4]. I. Riposan, M. Chisamera, S. Stan, T. Skaland. *Graphite Nucleants (Microinclusions) Characterization in Ca/Sr Inoculated Grey Irons*. Int. J. Cast Met. Res., 2003, Vol. 16, No. 1-3, pp.105-111.
- [5]. I. Riposan, M. Chisamera, S. Stan, C. Hartung, D. White. *Three-Stage Model for the Nucleation of Graphite in Grey Cast Iron*. Mater. Sci. Techn., 2010, Vol. 26, No. 12, pp. 1439-1447.
- [6]. A. Sommerfeld, B. Bottger, B. Tonn. *Graphite Nucleation in Cast Iron Melts Based on Solidification Experiments and Microstructure Simulation*. J. Mater. Sci. Techn., 2008, Vol. 24 (3), pp. 321-324.
- [7]. A. Sommerfeld, B. Tonn. *Nucleation of Graphite in Cast Iron Melts Depending on Manganese, Sulphur and Oxygen*. Int. J. Cast Metal Res., 2008, Vol. 21 (1-4), pp. 23-26.
- [8]. R. Gundlach. *Observations on Structure Control to Improve the Properties of Cast Irons*. The 2008 Honorary Cast Iron Lecture, Div. 5, AFS Metalcasting Congress, Atlanta, Georgia, USA, Paper 08-158.



- [9]. **R.L. Naro, J.F. Wallace.** *Trace elements in cast irons.* AFS Trans., 1969, Vol. 77, p. 311; 1970, Vol. 78, p.229 ; AFS Cast Met. Res. J., Sept. 1970, p.131.
- [10]. **M. Chisamera, S. Stan, I. Riposan, G. Costache, M. Barstow.** *Solidification Pattern of In-Mold and Ladle Inoculated Low Sulfur Hypoeutectic Gray Irons.* AFS Trans., 2008, Vol. 116, pp. 641-652.
- [11]. **C.R. Loper Jr.** *Inoculation of Cast Iron-Summary of Current Understanding.* AFS Trans., 1999, Vol. 107, pp. 523-528.
- [12]. **M. Chisamera, I. Riposan, S. Stan, T. Skaland.** *Undercooling, Chill Size, Structure Relationship in Ca/Sr Inoculated Grey Irons under Sulphur/Oxygen Influence.* 64th World Foundry Congress, Paris, France, Sept. 11-14, 2000, Paper RO-62.
- [13]. **M. Chisamera, I. Riposan, S. Stan, D. White, G. Grasmö.** *Graphite Nucleation Control in Grey Cast Iron.* Int. J. Cast Metal Res., 2008, Vol. 21 (1-4), pp. 39-44.
- [14]. **I. Riposan, M. Chisamera, S. Stan, P.Toboc, D. White, C. Ecob, C. Hartung.** *Al Benefits in Ductile Iron Production.* J. Mater. Eng. Perform., 2011, Vol. 20 (1), pp.57 – 64.

QUALITY ASSESSMENT OF COVERED MATERIALS BY INFRARED THERMOGRAPHY

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ABSTRACT

In thermographic interpretation there are two different concepts: one is dealing with imaging for surveillance, localization and recognition of shapes and the second consists in radiometric measurements that result in the assignment of a temperature to a given surface. The aim of thermal imaging is to produce visible images by the transformation of thermal contrasts. The main criteria to obtain quality images are the same quality criteria that are commonly employed for traditional images in photography, television and so on: spatial resolution, image contrast, and dynamic working range, degree of distortion and uniformity of response. In the thermal measurements, the performance of the system must be such that a given cause always produces the same effect, which requires a high measure of temporal stability. The paper deals with the analysis of the quality evaluation possibilities of the covered materials by infrared thermography.

KEYWORDS: covered materials, quality assessment, infrared thermography

1. Introduction

Infrared thermography (IRT) techniques are often used as a tool in quality evaluation of different materials and structures. In the last years, a special attention is oriented to the covered materials [1, 3].

The materials having the external layers which differ from the base layers join usually the mechanical and physical-chemical characteristics of the base material with the properties of the superficial layer. Nowadays, there are at the international level several preoccupations regarding the introduction of non-destructive testing during the manufacturing process of a material both for the process monitoring and for the precocious pointing out of flaws and rapid evaluation of the quality [2, 4, and 5].

In Figure 1 are presented the main specific flaws of the covered materials detectable by IRT [4]. Detection on the specific flaws for covered materials can be made by some non-destructive methods. The

most usual method is the ultrasonic detection by using surface waves.

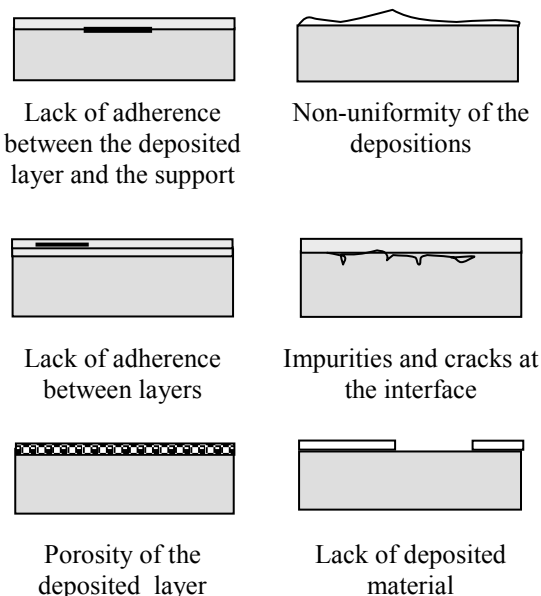


Fig. 1. Specific flaws of covered materials.

But the detection required the scanning of examined product surface with a certain

step, depending on the ultrasonic fascicle dimensions in the interaction area with the product. This scanning step by step is inefficient for large surfaces.

In comparison with other non-destructive inspection methods, applied on the covered materials, infrared thermography has some incontestable advantages such as: high speed of examination, non-contact inspection, large distance, clean and safe examination, clear indications in image format [1, 6, 8]. The main limits of infrared thermography are: the difficult interpretation of images due to the surface reflections, heat loss by convection or absorption of radiation by atmospheric components.

The IRT methods applicable to covered materials examination can be in passive (Fig. 2a) or active variant (Fig. 2b and 2c). The active IRT can be applied on a single surface (Fig. 2b) or by transmission (Fig. 2c). The flaws of covered materials represent a thermal barrier which could be visualized by the aid of an IRT system, by transforming the thermal information in a colors or grey nuances coded image.

The actual tendencies are to use an ensemble of methods, so that to assure an optimum regarding both the examination efficiency and the believable level of results. [2, 6, 7, 9, 10]. Frequently, the examination of large surfaces of covered materials is made on-line by infrared thermography, followed up of other complementary method, such as the local examination with ultrasounds or eddy currents of suspicious areas, thermographic pointed out.

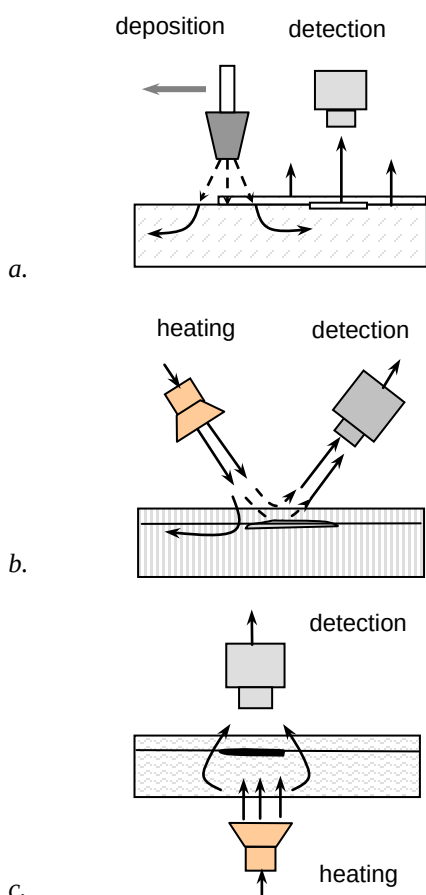


Fig. 2. The principle schemes regarding the thermographic examination applicable to the covered materials: a - passive; b – active on a single surface; c - active by transmission (on two surfaces)

2. Theory and model

The conduction is the form of thermal transfer in solids [1, 4]. According to the Fourier's law, the conductive heating rate is the rate of heat flow: under steady state conditions is directly proportional to the thermal conductivity of the object, cross sectional area of the object, through the heat flows and the temperature difference between the two ends of the object, and inversely proportional to the length or thickness of the object. The three dimensions conductive heat transfer in transitory regime through a material without internal heat sources, considering the body to be homogeneous and isotropic, and the specific heat c as well as the density ρ to be constant, can be characterized by the Fourier' equation:

$$\frac{\partial T}{\partial t} = \frac{\lambda}{\rho \cdot c} \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) \quad \text{or} \quad \frac{1}{a} \frac{\partial T}{\partial t} = \nabla^2 T \quad (1)$$

Where: t is time; λ - thermal conductivity, $\nabla^2 T$ - temperature laplacian; a - thermal diffusivity of material.

In the case of covered materials, with small thickness, heated on one surface, the heat propagation is made, mainly, unidirectional, normal on the heated surface.

To model the thermal transfer in transitory regime it is useful and enough to model the thermal conduction and the heat accumulation into the examined bodies by using filiform electrical circuits with well chosen values for different zones of the material. The modeling can have the purpose to establish the examination regime for control during the fabrication process. Using an adequate program packs it was made the analysis of equivalent electrical circuits for a thermal system to examined the sample presented in figure 3, where b is support thickness and a is cover thickness.

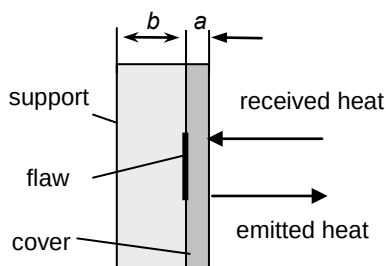


Fig. 3. The sample of covered materials.

The results led to a family of curves (Fig. 4) which describes the thermal contrast as a function of the thickness difference of a deposited layer in terms with a reference thickness a_r for different duration of heating and different moment of recording.

The base material is textolite with the thickness $b = 5$ mm, covered with a copper layer with the thickness $a_r = 0,5$ and $a = 0,1, 0,15, 0,2, 0,25, 0,3, 0,35, 0,45, 0,50, 0,55, 0,6, 0,65, 0,7, 0,75, 0,8, 0,85, \text{ and } 0,9$ mm (heating at constant temperature with 20K bigger than the environment temperature and the time $t_i = 20$ s). The curves 1...17 represent variation of temperature contrast for each layer thickness.

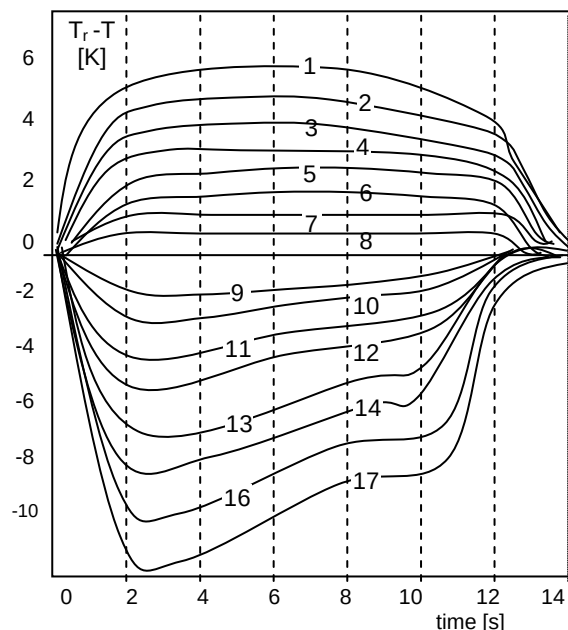


Fig. 4: Variation of thermal contrast, between reference thickness \ different thicknesses of the cover.

3. Experiments

The practical researches were made in the IRT Laboratory of POLITEHNICA University of Bucharest. First of all, experiments required a set of samples with artificial defects of various sizes located at different depths from the examination surface. The main part of the equipment was the infrared camera (IR Camera). It was used the IR Flir Camera SC 640 (Fig. 5) with Focal Plane Array (FPA) detector, uncooled microbolometers, spectral range: 7.5 to 13 μm , spatial resolution (IFOV) 0.65 m rad, thermal sensitivity 60 mK at 30°C.



Fig. 5. IR Camera.

The inspection parameters were the following: ambient temperature, $T_{amb} = 20^{\circ}\text{C}$, emissivity, $\varepsilon = 0.96$, distance, $d = 2\text{ m}$, humidity, $w = 50\%$, surface heating at 40°C , examination on the same surface, recording during the cooling process. In the experimental program the following objectives were taken into account:

- to establish the minimum detectable flaw size by active thermography with impulses for different categories of covered materials;
- to determine the influence of covering layer thickness on the thermal contrast;
- to determine the optimal parameters of the examination regime and to establish the optimal recording moment;
- To evaluate the level of uncertainties of measurements.

In order to achieve these objectives, samples sets with man-made flaws having known sizes and positions were realized. The materials couples used for the samples make-up were very different from thermal characteristics point of view: plastic + metal, glass + aluminum, steel + rubber or teflon, textolite + copper, etc.

The experiments demonstrated the validity of conclusions resulted from the modeling of thermal transfer.

4. Uncertainties

As constitutive part of an infrared IRT system, the detector can be defined as a chain cell that has an *input* and an *output*.

In detector „enters” an infrared radiation flux characterized by the power P of photons. At the „going out” it appears an electric signal U , which can be current, voltage or electric charge.

The first important parameter of the detector is the ratio between the two output and input parameters, U/P .

Taking into account that the parameters of the system can be amplified, if it is necessary, it results that the ratio U/P is not

however the most important parameter, because it does not point out the smallest detectable power.

Therefore, an important parameter of a detector is the ratio between the output signal and its noise, which can be used like criterion to evaluate the quality of the detector. So that, in order to can compare all the detectors, it is necessary to know the main geometrical and physical parameters as well as the specific characteristics which define the detector performance [1, 4, 9, 10].

Geometrical parameters: *the detector surface* and *solid angle* where through the detector sees thermal scene. A detector, which works at the environmental temperature without special protection, receives thermal radiation from all directions that means a solid angle of 4π . If the sensitive surface is cooled on one side, the solid angle is diminishing to 2π .

Physical parameters: *the temperature of the sensitive element*, *polarization*, *the passing band of the amplification device*, and *the equivalent circuit*. The sensitive element is always comprised in an electric circuit. Therefore, it can be defined the impedance $z = dE/dI$, E and I being the tension and current (instantaneous values) to the landmarks of the element. This impedance depends on the incident radiation (power and wavelength), the measurement frequency and polarization parameters, but especially on the continuous current, which pass through the sensitive element.

Specific characteristics, which define the detectors performance:

The sensitivity of the detector, S_U or S_i , represents the transformation ratio between the output electric signal and the thermal flux cached up by the detector:

$$S_U = \frac{dU}{dP} \quad [\text{V/W}] \quad \text{and} \quad S_i = \frac{di}{dP} \quad [\text{A/W}] \quad (2)$$

Where: U , i are the tension and current of the electric signal and P - power of the flux.

The detector sensitivity depends on the spectrum of the incident radiation. When the spectral repartition of the incident flux is

uniform, the detector produces a signal that varies with the wavelength. *The spectral sensitivity*, S_λ , can be defined:

$$S_\lambda = \left(\frac{d i}{d P} \right)_\lambda \quad (3)$$

Another parameter is *the global sensitivity*, S_g , which can be defined such:

$$S_g = \left(\frac{d V}{d P} \right)_g = \frac{\int_0^\infty \left(\frac{d V}{d P} \right) \cdot d \lambda \cdot \frac{d P}{d \lambda} \cdot d \lambda}{\int_0^\infty \frac{d P}{d \lambda} \cdot d \lambda}, \quad (4)$$

Where: $\int_0^\infty \frac{d P}{d \lambda} d \lambda$ is the total flux received by

the detector and $\int_0^\infty \left(\frac{d P}{d \lambda} \right)_\lambda \cdot \frac{d P}{d \lambda} \cdot d \lambda$ is the

answer of the detector or the output signal. Also, a specific characteristic is considered to be *the detector constant*, τ , defined by the relationship: $\tau = 1/(2\pi f_t)$, where f_t is the passing frequency, which corresponds to a reduction with 3 dB of the sensitivity. The time constant characterizes the transducer inertia. *The noise of the detector* is a parameter that results through the combination of several types of noise, such as: the noise of radiation from the environment, the internal noise of the sensitive element, and the noise of the amplifier. The ratio between the output signal and the noise is defined as:

$$\frac{P_s}{P_N} = \frac{(S_f \cdot P_i)^2}{8 \int_0^\infty \frac{A(f)}{A(f_0)} \cdot \frac{d f^2}{d f} \cdot d f} \quad (5)$$

Where: P_s is the power of signal; P_N - the power of noise; A - the amplification.

Other important parameters are *the noise equivalent power* and *the detectivity*.

The noise equivalent power - *N.E.P.* is the smallest incident flux power, which can be detected (that means the power P_0 which gives a signal equal with the noise).

The detectivity, D , is the inversion of the noise equivalent power:

$$D = \frac{1}{P_0} = \frac{S_f}{\sqrt{8 \int_0^\infty \frac{A(f)}{A(f_0)} \cdot \frac{d f^2}{d f} \cdot d f}} [W^{-1}]. \quad (6)$$

The detectivity D depends on several parameters: the modulation spectrum and frequency of thermal radiation, polarization conditions, the working size of spectral band for the detection system, and the detector temperature.

Like any measurements, the IRT presents a degree of uncertainty. The main sources of errors, in IRT measurements, in category, "systematic errors" are: method errors, calibration errors and errors in the electronic system. As results of many experiments, in real terms *errors* occur mainly of the following causes:

- Incorrect assessment of the emissivity of the object and / or incorrect assessment of T_{atm} (atmospheric temperature in K or $^{\circ}C$), or T_{amb} (ambient temperature in K or $^{\circ}C$), or w (moisture, in percent) or d (distance between camera and object);
- The influence of environmental radiation, detected by the IR camera directly and/or by reflections on other objects;
- Incorrect assessment of atmospheric absorption and radiation;
- Failures caused by the inaccuracy of the detector noise assessment.

Examined object emissivity depends on the wavelength, temperature of the object, the nature of the material, quality and surface conditions, the direction of observation, polarization and time of observation. Correct estimation of measurement error component due to incorrect evaluation of the emissivity is important.

Parameter "emissivity" is one of the input quantities, which is used to adjust the camera. When the object has high temperature, emissivity of the object tends to 1. The main *calibration errors* derived from:

- The difference between self-radiation produced by optical components,

electronics, etc. existing at the time of the examination;

- Differences in size and distance calibration of the examination;
- Determination the emissivity uncertainty during calibration, neglecting the influence of environmental radiation;
- Limited precision reference standards and limiting the number of calibration points and interpolation errors.

A third source of error is generated by *optical components and electronic features* of the examination system, the most important being: own variable noise of the detector; cooling system instability (for IR camera with cooling); fluctuations in the electronic signal amplification; limited resolution of the analogue /digital converter.

5. Conclusions

By IRT inspection, defects sizes were estimated with a degree accuracy good enough. *The defects sizes estimation is very close to that obtained by ultrasonic inspection.* The measurement uncertainties are between 50 % for small defects, less than 4 mm and 10-15% for defects with a diameter more than 10 mm located at a depth less than 2 mm, to the examination surface. Among the many sources of error, our experiments have shown that the main sources of uncertainty are: errors in assessing the emissivity of the object examined errors in assessing the atmospheric or background temperature, errors regarding the distance between camera and subject examined errors in assessing the humidity.

Errors in the assessing of emissivity have most significant impact on the measured temperature. It was noted that an over-estimation of emissivity produces an error smaller than its underestimation. If the object examined emissivity is estimate with an error about +10%, for example, temperature measurement error is about -1 ...-3%. If the estimation error of object

emissivity is -20%, for example, temperature measurement error is about +1 ...+3%.

Other errors have a lower influence about the object temperature measurements.

Fortunately, in the quantitative non-destructive examination, the measurement of the temperature often is not required in absolute value. It is useful only to establish the *temperature difference* between two neighboring areas: with defect and without defect. If the entrance parameters are incorrect, for example emissivity, ambient temperature, humidity etc., thermal contrast will be not strong affected by these errors.

The study demonstrated that the use of infrared thermography to characterize the covered materials and, especially for the measurement of deposited layer thickness even during the fabrication process leads to the improvement of the material quality and the reduction of losses volume.

The capacity to detect the flaws or thickness variations of covering layer is a function of the detector sensitivity and thermal resolution of the IR camera. The obtained experimental data pointed out both the advantages and the limits of this examination method. Obviously, often it is necessary to use several methods for a very clear evaluation of the product quality.

The radiation detector is the „heart” of a thermography system, so that the correct choice is essential for a certain examination.

There is no an ideal detector and this is the reason why there are simultaneously several types of detectors.

The main limit regarding the IRT using as NTD method in quantitative inspection is determined by the varied errors that could arise due to the reflections existing in the environment and, on the second hand, due to shallow faults that can be detected.

However, in quality evaluation of covered materials with large surface, IRT inspection is irreplaceable. To diminish the uncertainty of the IRT measurements it is, of course, necessary and useful for an investigation to be repeated and/or to be

ssociated with other complementary methods, like ultrasounds inspection.

References

- [1]. **X. Maldague**, *Nondestructive evaluation of materials by infrared thermography*, London Springer Verlag, 1993, new revised edition, John Willey&Sons Pub. UK, 2001
- [2]. **N. Constantin, A. Mihai**, *Results of Non-destructive Inspection of Layered Composites using IR Thermography and Ultrasonics*, DAMAS 2009, Beijing, China.
- [3]. **H.P. Avdelidis**, *Infrared thermography as a nondestructive tool for materials characterisation and assessment*, Proc. SPIE, 2011, USA
- [4]. **A. Mihai**, *Termografia in infrarosu*, Ed. Tehn., Romania, 2005.
- [5]. **F. Stefanescu**, *Materials of future are made now. Composite materials*, EDP, Buc., 1996.
- [6]. **R. Mitteau**, *Interface Quality Control by Infrared Thermography Measurement*, WCNDT, 2000, Italy
- [7]. **N. Constantin**, *Results of Nondestructive Inspection of Layered Composites using IR Thermography and Ultrasonics*, Key Engineering Materials, Vols 413-414, (p. 343-350) Trans. Tech Publication, Switzerland, 2009.
- [8]. **A. Mihai, F. Stefanescu, G. Neagu**, *Quality Characterization of Composite Material Pipes by Thermographic Inspection*, poster conf., MSE, Darmstadt, Germania, Aug. 24-26, 2010.
- [9]. www.franceinfrarouge.fr 2011.
- [10]. www.infrared-thermography.com 2011.

SYNTHESIS AND SPHEROIDIZATION OF DISPERSE HIGH-MELTING (REFRACTORY) POWDERS IN PLASMA DISCHARGE

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ABSTRACT

One of the areas of using arc and radio-frequency induction (RFI) plasma in metallurgy is to obtain refractory metals and materials with spherical shape of particles. The main advantages of using spherically shaped particles are high purity of particle surface, high bulk density (minimum surface/volume ratio) and ability of gaining control on porous article properties and of separating the particles in fractions. Spherical particles are needed in the formation of powder-metallurgy elements with desired and uniform porosity, which are operated at high temperature, in highly aggressive media and at high velocity fluid flows.

The present work considers the possibilities of using arc and RFI-plasma in metallurgy to obtain high-melting point metals and materials with spherical shape of particles.

KEYWORDS: Arc plasma, RFI plasma, refractory materials, spherically shaped particles

1. Using powder-like materials with spherical particle shape in powder metallurgy and surface welding

One of the areas of using arc and radio-frequency induction (RFI) plasma in metallurgy is to obtain spherical and refractory metals and materials, [1, 6, 9, 12÷17].

It is known that plasma treatment of the initial materials aimed at producing disperse powders with particles of spherical-shape finds still broader application and has become a very perspective method, allowing to produce powders from W, Mo, Cr, Ta, B, Al, oxides, carbides, silicates, etc.

The main advantages of using spherically shaped particles are high purity of particle surface, high bulk density (minimum surface/volume ratio) and ability of gaining control on porous article properties and of separating the particles in fractions. Spherical particles are needed in the formation of powder-metallurgy

elements with desired and uniform porosity, which are operated at high temperature, in highly aggressive media and at high velocity fluid flows.

Powders with spherically shaped particles of high-melting materials make it possible to substantially enhance the performance parameters of the produced articles. For example, porous filters of high-melting-point materials intended for purification of fuels, oils, aggressive liquids and gases contribute to attain higher effectiveness of the processes in chemical, metallurgical, food, pharmaceutical and a number of other industrial areas.

Another branch of high-temperature technique, where powders with spherical particle form find still wider application, is surface welding of complexly shaped elements intended for heavy operation conditions. The quality of the surface-welded layer depends on the regular feeding of the welded material in the gas-flame or plasma devices, [5, 8]. Only powders with

particles of spheroid shape and fixed within a narrow range of granulometric distribution ensure high operation properties of the surface-welded layer, [12, 15], (Fig. 1).

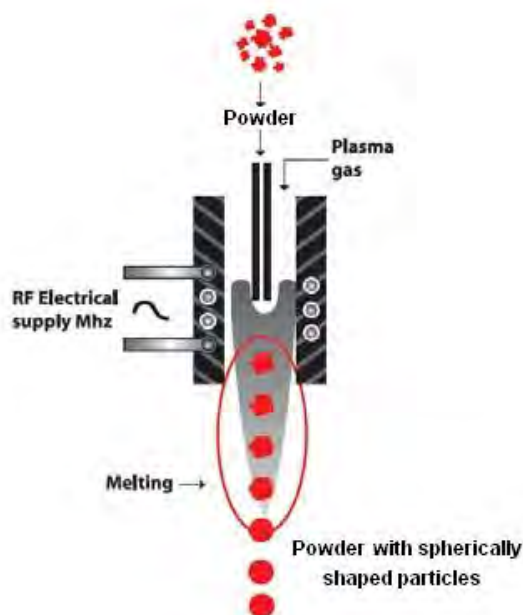


Fig.1. Principle of surface-welding with RFI-plasmotron

The standard fluidity of the material makes it possible to use dosing equipment with simplified construction and high reliability in the process of operation if steady flow of the spheroidized material is achieved, and if constant temperature of the particle is ensured in the moment of its contact with the welded surface.

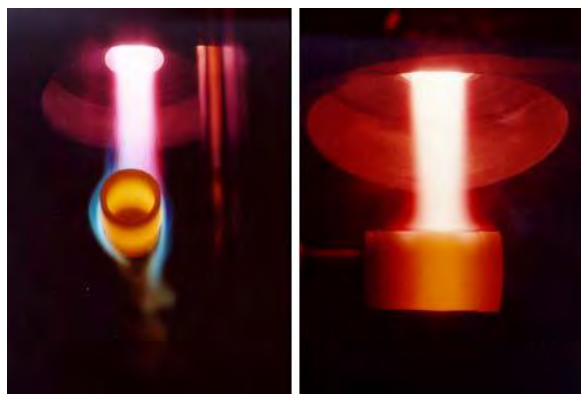


Fig.2. Plasma surface welding of elements with refractory materials

The process of plasma spheroidization is based on the intensive heating of the treated material and rounding of the liquid particles under the effect of surface tension forces, (Fig. 2).

The single stages of the process are:

- Melting and pulverization of the processed material;
- Spheroidization of the molten particles in a hot gas flux;
- Solidification of the particles;
- Cooling and collecting the spheroidized material.

Arc or high-frequency (RF) plasmotron is used for realizing the process.

2. Treatment of powders in an arc plasmotron

The treatment of powders is carried out in ordinary or multi-chamber plasma generators (plasmotrons). This provides the possibility of producing spherical particles with sizes from 1 to 200 μm . The use of protective medium ensures the possibility of preserving the chemical composition of the processed powder-like material. When spheroidizing preliminarily prepared granules, the particles acquire not only a spherical shape, but are also formed with sufficiently uniform grain-size distribution, (Fig.3). At low velocities of the transporting gas, particle kinetic energy is insufficient for their deep penetration in the plasma and the main part of the material passes through the peripheral section of the stream and along the walls of the plasma reactor.

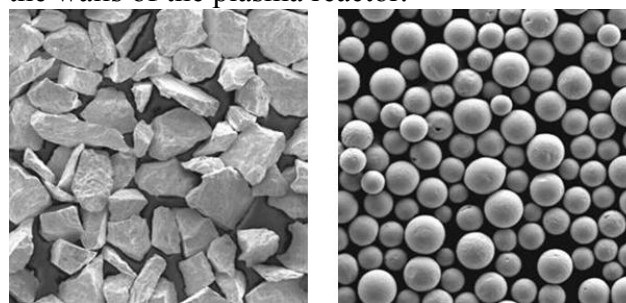
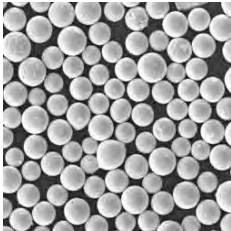


Fig.3. Powdery corundum (Al_2O_3) prior to and after spheroidization, x120

At very high velocities of the transporting gas the particles “break through” the jet, [3, 8, 10].

It has been established that when processing TiC the relative amount of

spherical particles increases with increasing the electric current intensity (as a result of particle intensive heating and increasing jet geometric dimensions).

Physical properties		
Chemical formula	Ti	
Molecular Weight	47.867 g/mol	
Melting point	1668°C	
Boiling point	3287°C	
Density	4.506 g/cm ³	
Heat Capacity	523 J/(kgK)	
Thermal conductivity	22 W/(mK)	

The processing of initial powder with grain sizes of 30µm yields spheroidization of 40% of the particles, the average dimension being reduced to 25µm. It is observed that

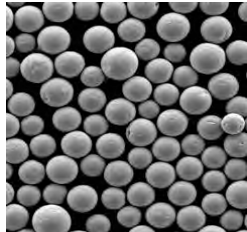
the amount of the spheroidized particles (C, %) depends on the initial sizes of the powder (in the case of TiC pulverization), (Table 1), [1÷3, 14].

Table 1. Quantity of particles on the initial sizes of the powder

Particle size, µm	2	2-5	5-10	10-15	15
C, %	90	90	80	50	30

When processing WC powder with an initial particle size of 5µm, the concentration of spherically shaped particles is 95%, and the average size is 3÷5µm. The studies on TiC and WC behavior during plasma spheroidization in argon show that the impact of high temperature leads to reducing the carbon content in carbides [14, 15]. The

spheroidization is carried out in hermetically sealed columns, where the processing zone is isolated from atmospheric oxygen and nitrogen. The greatest effect is achieved during treatment of carbide powder with 5% of carbon black in a plasma stream. The spherical particles at the outlet amount to 60%.

Physical properties		
Chemical formula	WC	
Molecular Weight	195,9 g/mol	
Melting point	~ 2800°C	
Boiling point	~ 6000°C	
Density	15.7 g/cm ³	

The conclusion is made that the lower the particle heat conductivity and the larger the particle size, the more inefficient is the spheroidization process. By selecting the appropriate regime of powder pulverization

and transportation it is possible to find conditions, under which the processed material passes through the central parts of the jet. When high-melting-point materials are pulverized and spheroidized in plasma

stream, the material often adheres to the internal walls of the die channel and coating is formed [14, 17].

In an arc plasmotron of ordinary construction the powder is introduced in the transporting gas under an angle of 90° with respect to the plasma stream direction. At low values of the kinetic energy the powder particles move under the impact of the plasma stream along a trajectory, which prevents them from sticking to the opposite channel wall. If the particles possess sufficient kinetic energy to break through the plasma jet, they move along a trajectory that leads to the formation of incrustations on the opposite die wall.

Depending on the growth of the external layers of this deposition, it starts melting and is pulverized by the plasma stream in large drops, i.e. the process of powder pulverization is replaced by pulverization of a material in the liquid state. This phenomenon, which is, for example, undesirable when placing coatings (as the evaporation of larger particles exerts adverse impact on surface quality and other characteristics of the coating), could be used for producing coarser powder than the fine-grained one [1÷5, 7, 8, 12, 13].

The experimental results prove that granules with lower density should be applied in the processing in order to ensure conditions for their transportation in the plasma stream without noticeable evaporation. The size of the initial granules should be with 40-50% larger than that of the obtained spherical particles.

Disturbance in chemical composition is often observed during spheroidization of oxide powders in neutral (argon) plasma, and hence partial recovery is needed. In cases when such disproportioning is undesirable, the spheroidization is carried out in oxygen plasma. With this approach it is natural that preference is given to RFI-plasma heating of oxygen or oxygen-containing gas [9].

3. Powder processing in RFI-plasmotrons

The low velocity of the plasma stream and the large volume of plasma in both its transverse and longitudinal cross section allow very effective spheroidization of the particles of different refractory materials. The specificity of Radio-Frequency-Induction (RFI) plasma discharge provides the opportunity of introducing the treated powder immediately along the plasma volume axis and using most effectively the energy of the RFI-discharge.

The current density along the RFI-discharge axis is equal to zero and therefore powder introduction in the central zone does not disturb the stability of discharge burning [4].

Temperature distribution in the plasma discharge volume is not uniform. Its maximum value reaches $\approx 9 \div 10000$ K. There are places along the discharge axis, where temperature is reduced to $500 \div 1000$ K. When the transporting gas is fed, the gas temperature along the RFI-discharge axis is also significantly reduced.

The productivity of the RF-plasma equipment is sufficiently high: when the power of the RFI-discharge is 6.5 kW, about $1 \div 2$ kg/h Al_2O_3 powders with sizes of $63 \div 100 \mu m$ are spheroidized, while the analogous productivity in the arc plasmotron is achieved by power of 100 kW.

The efficiency of spheroidization of plasma heated powder is determined by the duration of particle sojourn in the high-temperature (HT) area of the stream. In the case of RFI-plasma, characterized by low gas velocity, the treated particles move slowly with $2 \div 5$ m/s.

The length of the plasma torch of the RFI-discharge is considerably larger than the length of the arc plasma stream of the same power.

Furthermore, plasma dynamics in RFI-discharge intensifies the heat exchange of the processed powders.

4. Conclusion

All mentioned factors indicate that the duration of particle sojourn in the plasma

RFI-discharge is significantly increased, (Table 2). In its turn, this is the basis for the high efficiency of the RF-plasma processes for powder spheroidization, (Table 3).

Table 2. Technological characteristics

PLASMOTRON	Stream length, mm	Particle velocity, m/s	Duration of particle sojourn in the HT-zone, m/s
One-chamber	50	100	0.5
Multi-chamber	100	25	4
RF-induction	300	3	100

Table 3. Thermal efficiency of heated powders

Spheroidization method	Thermal efficiency of heated powders, %
Arc plasma, neutral wire	1-1.5
Arc plasma, granulated powder	1-5
Arc plasma, conductive wire	8-10
RF-plasma	25-30

RFI-plasma not only enhances the efficiency of the spheroidization process, but also provides the possibility of rounding the larger particles. For example, in arc plasma Al_2O_3 powders with spherical particle shape and sizes of up to $60 \div 70 \mu m$ are obtained, while in RFI-plasma the size of the treated particles may be increased to $600 \div 800 \mu m$. If coarser Al_2O_3 fractions or powders with the same sizes but of higher-melting-point materials are processed, it will be necessary to increase the plasma heat flux towards the particles.

In oxygen plasma it is possible to spheroidize with RFI-discharge MgO and ZrO_2 powders, which cannot be processed in argon plasma and RFI-discharge of the same power.

The analysis of powder spheroidization processes of high-melting-point materials in arc and RFI-plasma proves the undisputable advantage of the latter compared to the shortcomings of the process, realized in arc plasma, namely:

- non-uniform heating of the particles;
- powder feeding devices with complex construction;

- impossibility of ensuring flawless operation of the plasmatron;
- restrictions concerning the type of plasma forming gas;
- possibility for contamination of the processed material with elements from the arc plasmatron electrodes.

The advantages of the RFI-plasma are:

- uniform heating of the particles due to their facilitated introduction in the desired point of the plasma volume;
- possibility of heating particles with relatively large sizes due to the low velocity of the plasma-forming gas and long time of sojourn of the particles in the plasma volume;
- possibility for operation with different technological and plasma forming gases (from neutral to highly aggressive);
- possibility for high purity of the obtained product due to the non-electronic nature of generation of RFI-plasma.

The enumerated facts lead to the still broader application mainly of RFI-plasma for treatment of powders from high-melting point materials, aimed at spheroidization of

their ingredient particles. The calculations and experimental results concerning RFI-plasma generation and the possibilities for its management will be the subject of another publication.

References

- [1]. Danov, C. K., Kurnaev, V. A., Romanovskii, M. K., Tsvetkov, I.V., *Osnovi fizicheskikh protsesov v plazme I plazmenih ustroistvakh*, Moskovskii gosudarstvennii ingenerno-fizicheskii institut, Moskva 2000. (In Russian)
- [2]. Dendy, R., *Plasma Physics: an Introductory Course*. Cambridge Univ. Press, Cambridge, 1995.
- [3]. Boyd T. J. M. & Sanderson J. J., *The Physics of Plasmas* Cambridge University Press Cambridge, U.K.; New York, 2003.
- [4]. Shalom Eliezer, *Introduction to Plasma Physics: The Fourth State of Matter*, Institute of Physics Publishing Bristol and Philadelphia IOP Publishing Ltd 2001.
- [5]. Blinkov I. V., *Fisico-chimia visokih temperatur I davlenii*, Moskva 1988. (In Russian)
- [6]. Shalimov A. G., Gotin V. N., Tulin N. A., *Intensifikatsia protsesov spetsialnoi elektrometalurgii*, Moskva, 1988. (In Russian)
- [7]. Dashkevich I. P., *Visokochestotnie razryadi v Elektrotermii*, vipusk 13, "Mashinostroenie", Leningrad, 1980. (In Russian)
- [8]. *Plasma Technology in metallurgical processing*, Iron and Steel Society, Inc. 1987.
- [9]. Dembovskii V. *Plasmennaya metalurgiya*, "Metalurgiya", M., 1981. (In Russian)
- [10]. Kalinin N. N., *Metalurgicheskie visokochestotnie plazmotroni: Elektro I gazo dinamika*, "Nauka", M., 1987. (In Russian)
- [11]. Tsenov Ts., *Diplomna rabota "Konstruirane I izrobotvane na postoyanno tokova zachranvashta sistema za metalurgichna plazmena instalatsiya"*, UCTM, Sofia 1989. (In Bulgarian)
- [12]. Xu J.L., K.A. Khor, R. Kumar, *Physicochemical differences after densifying radio frequency plasma sprayed hydroxyapatite powders using spark plasma and conventional sintering techniques*, Materials Science and Engineering A 457 (2007), 24–32.
- [13]. Dahl P., I. Kaus, Z. Zhao, M. Johnsson, M. Nygren, K. Wiik, T. Grande, M.-A. Einarsrud, *Densification and properties of zirconia prepared by three different sintering techniques*, Ceramics International 33 (2007), 1603–1610.
- [14]. Anselmi-Tamburini U., J.E. Garay, Z.A. Munir, *Fundamental investigations on the spark plasma sintering/synthesis process III. Current effect on reactivity*, Materials Science and Engineering A 407 (2005), 24–30.
- [15]. Wenbin Liu, Xiaoyan Song, Jiuxing Zhang, Fuxing Yin, Guozhen Zhang, *A novel route to prepare ultrafine-grained WC–Co cemented carbides*, Journal of Alloys and Compounds 458 (2008), 366–371.
- [16]. Zhang Zhao-Hui, Fu-Chi Wang, Lin Wang, Shu-Kui Li, *Ultrafine-grained copper prepared by spark plasma sintering process*, Materials Science and Engineering A 476 (2008), 201–205.
- [17]. Tiwari Devesh, Bikramjit Basu, Koushik Biswas, *Simulation of thermal and electric field evolution during spark plasma sintering*, Ceramics International 35 (2009), 699–708.

METALLIC MATRIX COMPOSITES WITH CERAMIC PARTICLES. WETTING CONDITIONS

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ABSTRACT

The paper presents the principal aspects regarding the mixtures obtaining made up from aluminium melts and different kinds of ceramic particles (silicon carbide and boron carbide). There are synthetically discussed the wetting conditions based on wetting coefficient and the possibilities to improve this one insisting on the alloying metal bath, its overheating and the heat treatment of the particles with the aim to remove the gases from the superficial layer. The critical acceleration necessary for the incorporation of particles into the melt for different temperatures was determined.

KEYWORDS: aluminium, silicon carbide particles, boron carbide particles, wettability, minimum acceleration

1. Introduction

In recent years the production of metallic composites has expanded the use of additional material in the form of particles due to some important advantages: much cheaper compared to fibres; isotropic or controlled heterogeneity materials can be obtained; simple technologies to incorporate the complementary material.

Compared to the organic matrix, metallic materials are used from the need to obtain composites that can be used at relatively high temperatures. For castings destined to be used at smaller temperature than 400°C aluminium and its alloys are used as matrix due to a sum of advantages (low cost, small density, acceptable mechanical properties, electrical and thermal conductivity, corrosion resistance, workability). Titanium used as alloying element improves the behaviour of aluminium at high temperatures [1].

Mechanical, thermal and electric properties of metallic composites depend,

inter alia, on the type, quantity, size, shape, and complementary material distribution.

Generally, particles of graphite, ceramic metallic materials or glass are used to produce metallic composites with low density, high specific properties, dimensional stability and especially wear resistance.

Silicon carbide particles (cubic or hexagonal elementary cell) are frequently used to produce composites due to the low cost, small density, high specific mechanical properties, low thermal expansion coefficient, resistance to thermal shock, hardness etc.

Although less used, boron carbide is also an attractive material to produce metallic composites. In aluminium-based composites boron carbide particles provide a low density, thermal stability, hardness, wear resistance [2]. Due to the close values of densities ($\rho_{B_4C} = 2.52 \text{ g/cm}^3$) the intensity of settling process is diminished in aluminium melts ($(\rho_{Al} = 2.369 \text{ g/cm}^3 \text{ at the melting point})$ [3].

Gravitational casting is still the simplest and inexpensive method of producing metallic composites. Therefore, to produce aluminium – particles mixtures remains a matter of general interest.

2. Wetting conditions

The wettability parameter, $\sigma_{lg} \cos \theta$ where σ_{lg} is the surface tension at the aluminium melt-gas interface and θ - the contact angle, allows analysing the wetting conditions in aluminium – silicon or boron carbide [4]. Positive values of parameter indicate wetting conditions in the system. Evidently, non-wetting occurs when $\sigma_{lg} \cos \theta < 0$.

The values of wettability parameter in different aluminium-based systems are presented in Table 1 and Figure 1. The calculations were made based on the values of surface tension and wetting angle presented by Rohatgi [5]. Wettability parameter values determined confirm non-wetting conditions in the two systems reported, in different conditions [2-3, 6-10]. It should be noted that the layer of alumina formed due to high affinity of aluminium for oxygen prevents correctly estimating of contact angle.

The transfer of a silicon or boron carbide particle from gaseous phase into the aluminium melt is complete when the gas - particle interface is replaced by a particle - liquid interface [11].

In the particular case of a cubic particle (l_p) moving with gravitational acceleration g , the total force that acts during its penetration into the metallic bath is:

$$F_t = G_p + F_\sigma + F_a, \quad (1)$$

where: G_p is gravitational force; F_σ - force determined by the superficial energy; F_a - Archimedes force.

If Y axis of an Oxy coordinate system associated to the particle has the positive

direction towards the melt surface, the particle will be incorporated when $F_t > 0$ [12].

The gravitational force can be determined by the equation:

$$G_p = m_p g, \quad (2)$$

where m_p is the mass of particle.

In order to determine the force caused by the superficial energy ΔE_σ , it is necessary to take into account the following relationship:

$$F_\sigma = 6l_p \sigma_{lg} \cos \theta, \quad (3)$$

Archimedes force is given by the following equation:

$$F_a = -\rho_l V_p g = -m_p g \frac{\rho_l}{\rho_p}, \quad (4)$$

where: ρ_l is the density of the liquid aluminium, V_p - the volume of the particle; ρ_p - the particle density.

Therefore, the necessary force for a particle to penetrate the metal bath is:

$$F_t = m_p g \left(1 - \frac{\rho_l}{\rho_p} \right) + 6l_p \sigma_{lg} \cos \theta. \quad (5)$$

In non-wetting conditions, when $\rho_p < \rho_l$, for the two analysed systems it results that:

$$m_p g \left(1 - \frac{\rho_l}{\rho_p} \right) + 6l_p \sigma_{lg} \cos \theta < 0, \quad (6)$$

and the particle will float.

Therefore, to penetrate the melt, particle needs a minimum acceleration:

$$a_p = -6 \frac{\sigma_{lg}}{l_p^2 (\rho_p - \rho_l)} \cos \theta. \quad (7)$$

Different values of this parameter for aluminium melts are presented in Table 2. The calculations were performed by using Rohatgi's data and the following relations [13]:

$$\rho_{Al} = 2.369 - 3.11 \cdot 10^{-4} (T - T_{top}), \quad (8)$$

$$\rho_{Al-Mg} = 2.376 - 0.009\% Mg. \quad (9)$$

Table 1. Wettability parameter values

System	T, [°C]	Wettability parameter, $\cdot 10^3$, [N·grd/m]	
		SiC	B ₄ C
Al	700	-238.85	- 425.5
	800	-178.95	- 362.95
	900	-161.21	- 275.69
Al-2Cu	700	-242.24	- 378.78
	800	-197.05	-342.38
	900	-145.56	-282.49
Al-4.5 Cu	800	-186.93	- 323.36
Al-2Mg	700	-193.34	- 325.36
	800	-147.04	- 117.12
	900	-120.72	- 66.40
Al-4.5Mg	800	-136.67	- 32.99

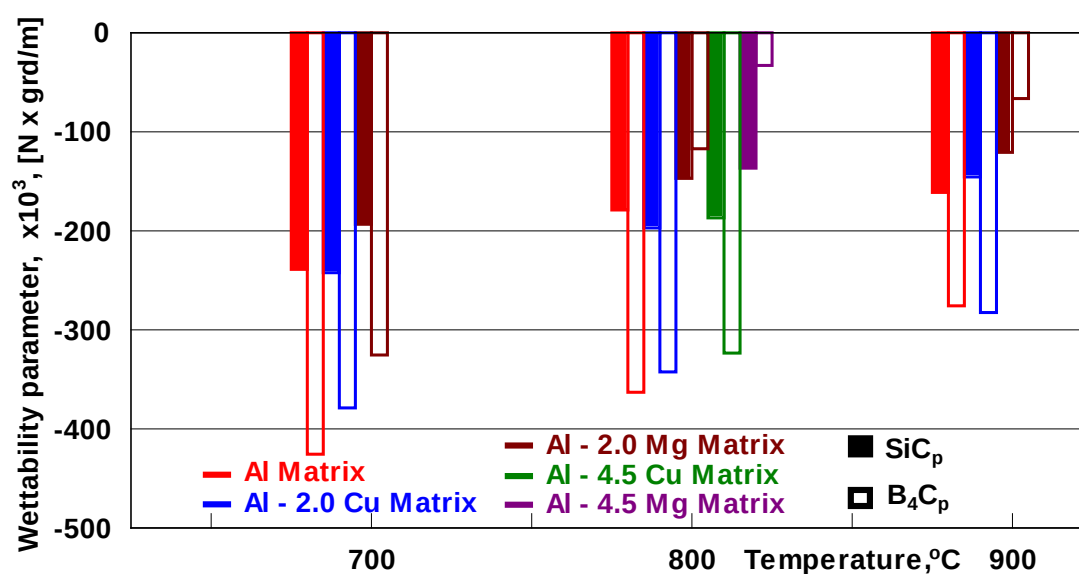


Fig. 1. Wettability parameter

Table 2. The values of minimum acceleration

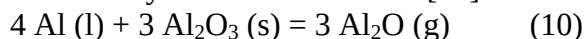
System	T, [°C]	$a_p \cdot 10^4$, [m/s ²]			
		SiC		B ₄ C	
		$l_p=10^{-4}$, [m]	$l_p=2 \cdot 10^{-4}$, [m]	$l_p=10^{-4}$, [m]	$l_p=2 \cdot 10^{-4}$, [m]
Al	700	16.79	4.2	156.2	39.05
	800	12.14	3.03	111.94	27.99
	900	10.56	2.64	73.31	18.33
Al-2Mg	700	13.62	3.4	120.5	30.13

3. Improvement of wetting

The high values calculated for the minimum acceleration impose the necessity to apply some methods to improve the wetting conditions. The simplest methods are:

- *overheating of the melt.* The presence of an oxide film at the aluminium melt surface drastically reduces the wetting angle. For pure aluminium the oxide layer formed at the surface of the melt, due to the small solubility of oxygen, is $\gamma\text{-Al}_2\text{O}_3$ [14].

The wetting becomes possible at higher temperatures when the oxide layer can be removed by a chemical reaction [15]:



For aluminium and its alloys the effect of temperature on the superficial tension is to decrease it. In this way, the wetting angle between the melt and the complementary material reduces.

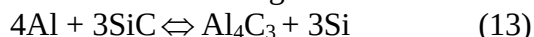
Some empirical relationships such as those proposed by Keene or Shen, can be used to study the effect of temperature on the surface tension [16, 17]:

$$\sigma_{lg} = 985 - 0.19(T - 933) [\text{mJ/m}^2] \quad (11)$$

$$\sigma_{lg} = 890 - 0.182(T - 933) [\text{mJ/m}^2] \quad (12)$$

Generally, a longer time of contact at high temperatures improves the wetting conditions.

In Al-SiC_p system at usual temperatures of the melts the following reaction:



causes the appearance of an undesirable compound [7]. Silicon, used as alloying element, may prevent the formation of this compound.

Boron carbide reacts with both solid and liquid aluminium. In solid state or for overheating degree of the melt up to 110°C it forms Al₃BC or AlB₂ compounds. Over this temperature Al₃BC and Al₃B₄₈C₂ are produced [18]. The appearance of these compounds is also undesirable because it leads to decomposition of complementary material

On the other hand, increasing temperature a reduction of apparent dynamic viscosity of the mixture occurs.

- *heat treatment of dispersed material.*

A gas film exists on the surface of particles and blocks direct contact between the two components. Also this fine film favours ascension movement of the particles although $\rho_{\text{Al}} < \rho_p$ [19, 20].

- *alloying or flux treatment of the melt.*

Some elements introduced in aluminium-based melts assure wetting conditions by:

- reducing of melt surface tension;
- lowering the interfacial energy between the melt and the particle;
- chemical reactions (reactive wetting).

Elements with high affinity to oxygen (lithium or magnesium for example) avoid the appearance of oxide layer on the surface of the complementary material and diminish the interfacial tension.

Introduced in the melt, magnesium creates also advantageous wetting conditions by the diminution of the melt surface tension. Such as, in accordance with Lang's equation, 1 wt% Mg reduces the aluminium surface melt with 5% approximately. Magnesium does not react with silicon carbide. Compared with magnesium tin has a much smaller effect [7, 19].

Titanium improves the wettability of silicon carbide due to the strong affinity for the complementary material constituting TiC, TiSi₂ and Ti₃SiC₂ compounds [7].

Titanium presence in K₂TiF₆ favours improvement of wetting in Al-B₄C system by the appearance of TiB₂ and TiC compounds at the surface of particles [A.R. Kennedy, 2001, Kertli, 2008)..

4. Conclusions

Aluminium-silicon or boron carbide composites have low density, high specific properties, hardness and good wear resistance.

Gravitational casting is a simple and inexpensive method to obtain metallic composites parts.

Non-wetting conditions exist in the two-systems.

The high values calculated for the minimum acceleration impose the necessity to apply some simple methods to improve the wetting conditions: overheating of the metallic bath, alloying or flux treatment of the melt.

Titanium leads to the improvement of wetting conditions as a result of chemical reactions in the melt.

References

- [1]. I.A. Ibrahim, A. Mohamed, E.J. Lavernia, *Particulate reinforced metal matrix composites – a review*, Journal of Materials Science 26 (1991), 1137-1156
- [2]. Q. Lin, P. Shen, F. Qiu, D. Zhang, Q. Jiang, *Wetting of polycrystalline B₄C by molten Al at 1173-1473K*, Scripta Materialia 44 (2009), doi:10.1016/j.scriptamat.2009.02.024
- [3]. B. Previtali, D. Pocci, C. Taccardo, *Application of traditional casting process to aluminium matrix composites*, Composites: Part A (2008), 1606-1617
- [4]. D. Kokaefe, G. Ergin, V. Villeneuve, Y. Kokaefe, *Determination of wetting at elevated temperatures using image analysis*, Archives of Computational Materials Science and Surface Engineering, 1 (2009) 213-224
- [5]. P.K. Rohatgi, *Cast Metal Matrix/Composites*, Metals Handbook, Ninth Edition, Vol. 15, Casting, ASM International (1988) 840-854
- [6]. V. Laurent, D. Chatain, N. Eustathopoulos, *Wettability of SiC by aluminium and Al-Si alloys*, Journal of Materials Science 22 (1987) 244-250
- [7]. N. Sobczak, M. Ksiazek, W. Radziwill, J. Morgiel, W. Baliga, L. Stobierski, *Effect of titanium on wettability and interfaces in the Al/SiC system*, Proceedings of International Conference "High Temperature capillarity", Cracow, Poland (1997) 138-145
- [8]. J. Hashim, L. Looney, M.S.J. Hashmi, *The wettability of SiC particles by molten aluminium alloy*, Journal of Materials Processing Technology 119 (2001) 324-328
- [9]. E. Candan, *Effect of alloying elements to aluminium on the wettability of Al/SiC system*, Turkish Journal of Engineering & Environmental Sciences 26 (2002) 1-5
- [10]. I. Kerti, F. Toptan, *Microstructural variations in cast B₄C-reinforced aluminium matrix composites (AMCs)*, Materials Letters 62 (2008) 1215-1218
- [11]. P.K. Rohatgi, R. Asthana, *Transfer of Particles and Fibres from Gas to Liquid during Solidification Processing of Composites*, International Symposium of Advances in Cast Reinforced Metal Composites, Chicago, Illinois, U.S.A. (1988) 61-66
- [12]. A.S. Kakar, F. Rana, D.M. Ștefănescu, *Kinetics of gas-to-liquid transfer of particles in metal matrix composites*, Materials Science and Engineering, A1 35 (1991) 95-100
- [13]. C. Garcia-Cordovilla, E. Louis, A. Pamies, *The surface tension of liquid pure aluminium and aluminium-magnesium alloy*, Journal of Materials Science 21 (1986) 2787-2792
- [14]. M. Syversten, *Oxide Skin Strength on Molten Aluminium*, Metallurgical and Materials Transactions B 37B (2006) 495-504
- [15]. N. Shinozaki, T. Fujita, K. Mukai, *Wettability of Al₂O₃-MgO substrates by molten aluminium*, Metallurgical and Materials Transactions B 33 (June 2002) 506-509
- [16]. B.J. Keene, *Review of data of surface tension of pure metals*, International Materials Review 38/4 (1993) 157-192
- [17]. P. Shen, H. Fujii, T. Matsumoto, K. Nogi, *Influence of substrate crystallographic orientation on the wettability and adhesion of α -Al₂O₃ single crystals by liquid Al and Cu*, Journal of Materials Science 40 (2005) 2329-2333
- [18]. J.C. Viala, J. Bouix, G. Gonzales, C. Esnouf, *Chemical reactivity of aluminium with boron carbide*, Journal of Materials Science 32 (1997) 4559-4573
- [19]. B.C. Pai, G. Ramani, R.M. Pillai, K.G. Satyanarayana, *Review. Role of magnesium in cast aluminium alloy matrix composites*, Journal of Materials Science 30 (1995) 1903-1911.
- [20]. W. Zhou, M.Z. Xu, *Casting of SiC Reinforced Metal Matrix Composites*, Journal of Materials Processing Technology 63 (1997) 358-363
- [21]. A.R. Kennedy, B. Brampton, *The reactive wetting and incorporation of B₄C particles into molten aluminium*, Scripta Materialia 44(2001) 1077-1082

FEM ANALYSIS OF SPUR GEARS PRESS – ROLLING PROCESS

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ABSTRACT

This paper presents FEM (finite element method) analysis of pressing-rolling process, a new method for obtaining spur gears. Using symmetries, the 3D geometrical model was created for tools and for initial blank. The FEM analysis was carried out using Forge2009, specialized software for study the plastic deformation processes. Objective of this study is to describe the evolution of pressing force and rolling force in press-rolling process.

KEYWORDS: FEM analysis, pressing, rolling, gear

1. Introduction

The main tooth forming techniques are casting, cutting, forming processes (Fig. 1). Rolling techniques are divided into two categories in turn as described in (Fig.2.).

According to this description press-rolling process is part of the forming techniques more exactly is a longitudinal

rolling process. Rolling process is one of the forming processes used in industrial processing has evolved over time from producing necessary prefabricated for other processes, finished products with simple shape to obtain products with complex shape and high dimensional precision complex form [2].

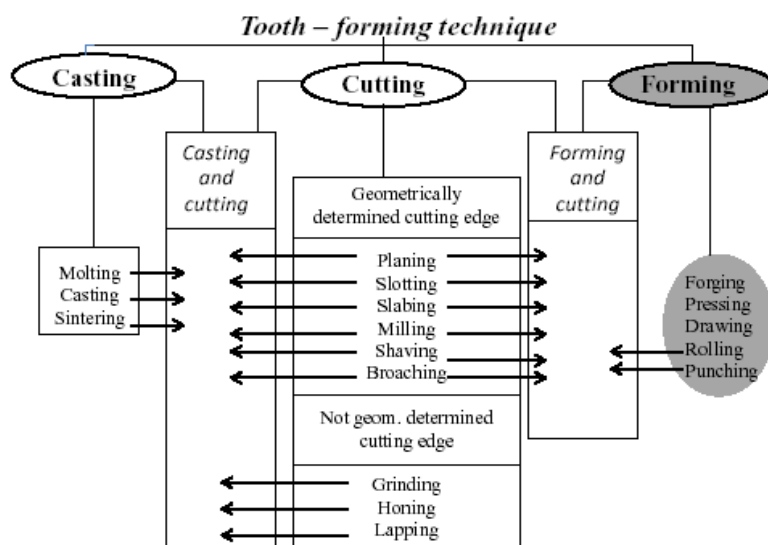


Fig. 1. Tooth-forming techniques [1]

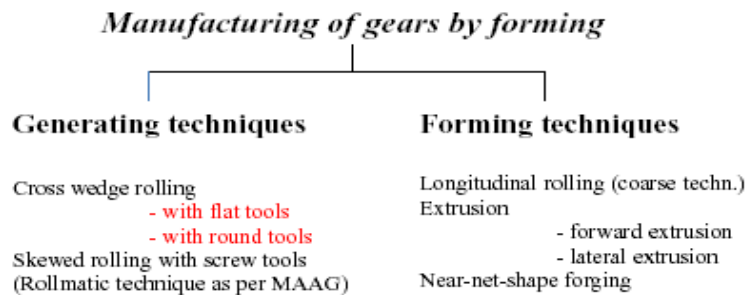


Fig. 2. Various processes for gear manufacturing [1]

By rolling we understand the deforming process supported by the metallic material passing through two or more cylinders in rotating moving [3]. Longitudinal rolling with roll of grooved parts can be classified according to the manner of the deformation:

- superficial pressure (grooves are made successively (Fig. 3 a));
 - deep pressure (grooves are made simultaneously (Fig. 3 b)).
- According to previous classifications press-rolling process (Fig. 4) to obtain spur gears is a longitudinal rolling process with deep pressing. Because in practice acting multiple cylinders (rolls)

with rotation axis in the same plane is difficult, in the press – rolling process advance of work piece in the process and the friction between it and the roll, spinning the roll. So the study of this process is reduced the study of longitudinal profiles rolling process with specification that this process takes place in the vertical direction, which means that the process is directly influenced by the weight of work piece. To achieve simulation of press-rolling process is necessary to describe the analytical model for calculating the rolling force and the pressing force.

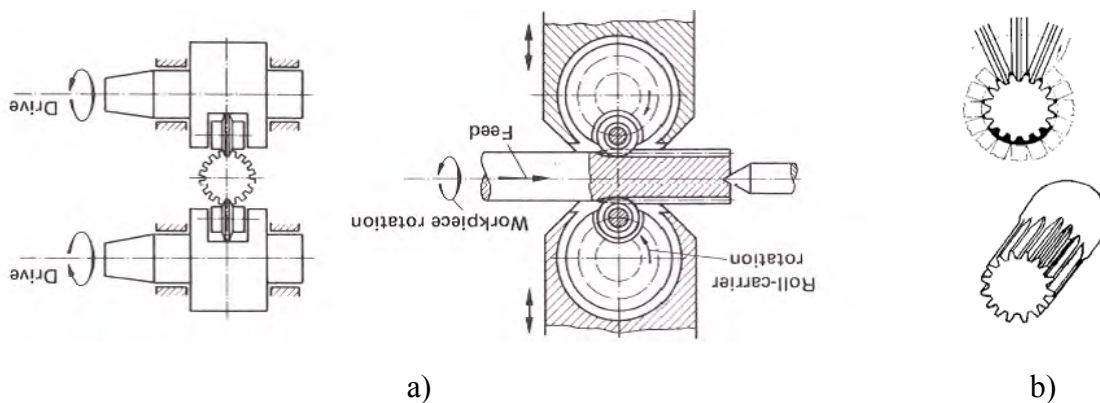


Fig. 3. Longitudinal rolling of grooved parts with: a) superficial pressing [4]
b) deep pressing [5]

Rolling force in flat rolling is determined by the relationship:

$$F = n \cdot b_m \cdot \sigma_m \cdot l_c \quad (1)$$

where:

- n number of rolls;
- b_m average widening;

- l_c contact arc length
- D_R - roll diameter;

$$l_c \cdot b_m = S_c = \sqrt{\frac{D_R}{8} \cdot (D_s + D_i)^2 \cdot (D_s - D_i)} \quad (2)$$

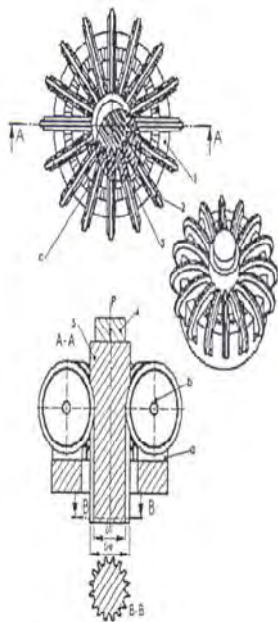
$$\sigma_m = \sigma_d [2 \cdot (D_s/D_i)^\delta - 1] \quad (3)$$

- S_c – contact area;
- σ_m work piece average resistance to deformation,

- D_s initial diameter of work piece;
- D_i - inner diameter of the gear;

$$\delta = 1 + \frac{\mu}{\tan \frac{\alpha}{2}} \quad (4)$$

- μ - friction coefficient and α the contact angle between roll and work piece.



Significance notations 1 - support, 2 - rolls, 3 - roller hub barrel type, 4 - puncher, 5 - cylindrical work piece, a-roll slot, b-circular bearing, c-bearing support for the barrel roll.

Fig. 4. Press- rolling process [2]

Pressing force is calculated using the equation:

$$P = P_d + P_a - G \quad (5)$$

where:

- P_d [2] the force required for material deformation from diameter D_s to diameter D_i ;

$$P_d = \sigma_m \cdot \frac{\pi}{4} (D_s^2 - D_i^2) \quad (6)$$

- P_a [2] force necessary to overcome reactions from support is given by the relation;

$$P_a = n \cdot p_s \cdot S_c \cdot 2 \cdot \frac{\mu_f}{\alpha} \cdot \frac{d_f}{D_R} \quad (7)$$

- p_s - specific pressure;
- μ_f - coefficient of friction in the bearings;
- d_f - spindle diameter roll;
- p -specific pressure exerted on the roller
- G - work piece weight.

According to laboratory work “Experimental Determination of the coefficient of friction in longitudinal rolling”; - Simultaneous measurement method of rolling force and the force of contraction [7], the coefficient of friction is calculated using the relationship and the Fig. 5:

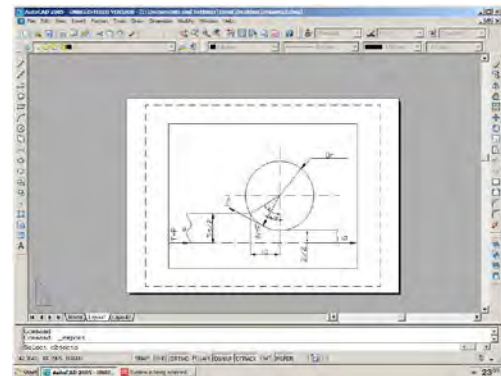


Fig. 5. Graphical representation of forces in press-rolling process, longitudinal section where:

- $F = N$ rolling force;

$$\mu = \frac{T}{2N \cos \frac{\alpha}{2}} + \tan \frac{\alpha}{2} \quad (8)$$

- μ coefficient of friction, force of contraction;

- T for longitudinal rolling

- α grab angle is given by relation .

Considering the force of contraction T of the lamination process equal to pressing force P from the press-rolling process and adding the necessary force to prevail the reactions from bearings and the force of gravity can be written:

$$P = nF \left(\mu - tg \frac{\alpha}{2} \right) \cos \frac{\alpha}{2} + P_a - G \quad (9)$$

From equation 5 and 9 matching the first terms of relations can be write the relation to calculate the rolling force for one roll:

$$F = \frac{\sigma_m \cdot \frac{\pi}{4} (D_s^2 - D_i^2)}{n \cdot \left(\mu - tg \frac{\alpha}{2} \right) \cos \frac{\alpha}{2}} \quad (10)$$

3. Simulation

3.1. Geometries and materials

The geometries of the billet, active roll and stem was generated in “Solid Works” and the meshes within their space domains in “Forge 2009”. Fig. 6 s how the initial meshes of the billet and the tooling in cross section. For saving the computer RAM source and computation time [6] in FEM analyzes was carried out 1/46 section from billet, stem and 1/2 section from one active roll.

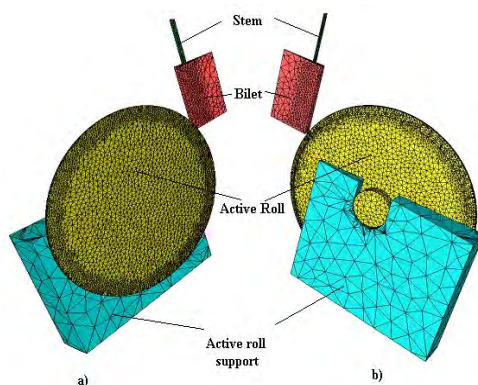


Fig. 6. Sections trough the press rolling process: a) back view b) front view

Puncher (stem) and support were considered as perfectly rigid tools for this tool is not necessary to define the material. Work piece material is Al99% and roll material is steel DIN 1.7350 X210Cr12.

3.2. Simulation parameters

Process parameters are presented in the following Table 1. Initial work piece, tools and environment temperature were

considered 20°C. Stem speed during the process is 10mm / s. The coefficient of friction at the interface active roll-work piece and stem-work piece is 0.7 and friction coefficient at interface active roll-support was chose 0.1 (dry friction).

Table 1. The simulation process parameters

Billet length [mm]	30
Billet diameter [mm]	38...41
Billet temperature [°C]	20
Tooling temperature [°C]	20
Friction factor at interface billet-active roll	0.7
Friction factor at interface active roll - holder	0.1

Also in finite element analysis has been incorporated the heat transfer coefficient between tool-work piece and air.

4. Results and discussions

The graphs shape rolling force is similar to the pressing force (Fig. 7), this are obtained by simulations.

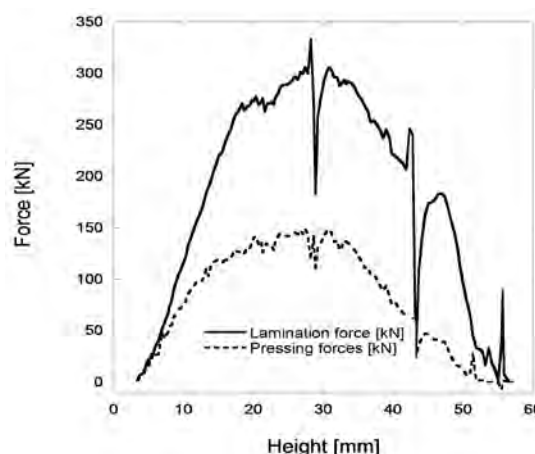


Fig. 7. Graphics of forces obtained by simulation of rolling force and pressing force

In study of press force evolution we can find three main phases (zone) specific to evolution of work piece during the rolling process:

1. Entry zone:
 - Adjustment roll zone (just for open bearing):
 - work piece clamping zone:
2. Pseudo stationary flow zone:
3. Exit zone:
 - Step 1- this zone begin when the material start to flow in reverse direction of rolling;
 - Step 2
 - level a) - the force necessary to deform the material in rolling directions decrease and the force necessary for deform the material how flow in reverse direction is increase;
 - level b) - where the force decrease to zero , the negative value of force jump (point P) corresponding to action of part weight cumulate with the part velocity.

All these zone are described in the Fig. 8.

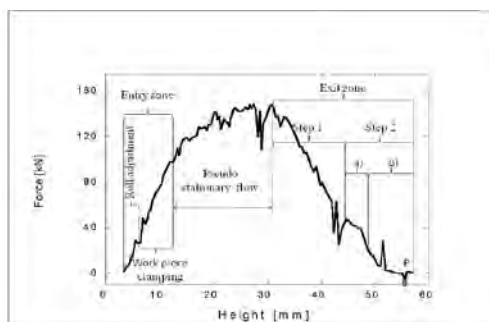


Fig. 8. Phases of pressing force evolution in press-rolling process

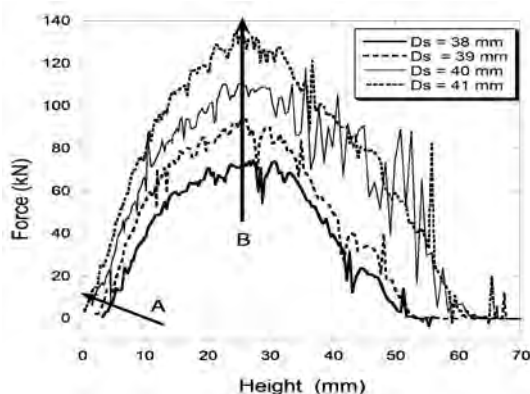


Fig. 9. Pressing force evolution and punching stroke according to the initial work piece diameter

The following comparative study of the evolution of pressing force required for pressing-rolling process and considering the process input variable initial work piece diameter (D_s).

Thus the initial work piece diameter directly influences the press-rolling process as shown in Fig. 9.

- arrow A in Fig. 9 indicates that with increasing work piece diameter the pressing force increases;

- arrow B in Fig. 9 indicates that with increasing diameter, parameters of deformation area changed (increase grip angle, length of contact arc, while achieving a more complete filling of the outbreak strain exactly the gear tooth) while increasing punching required course.

Comparing the pressing force obtained by numerical modeling of the process using FEM with results obtained using the analytical model we can draw the graph represented in Fig. 10.

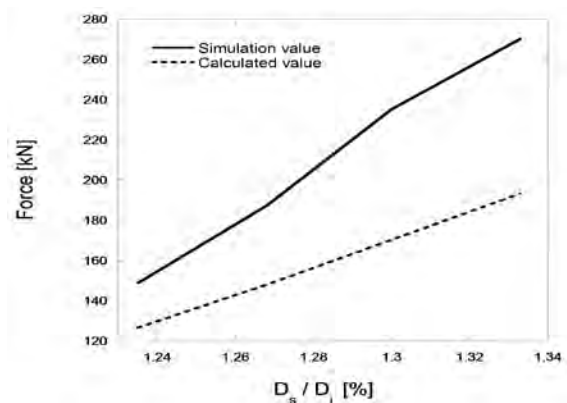


Fig. 10. Pressing force evolution

Thus one can say that the graph of force calculated analytically calculated force closely follows the numerical chart. Calculation errors are largely due to the simplifying assumptions considered in theoretical relationships pressing force.

5. Conclusions

Process necessary force is greater than that calculated using mathematical relations, it is because the work piece sectional area

changes its input in the process (between the punch and focus discharge work piece deformation occurs). Work piece diameter with increasing pressing force initially increases and travel needed punching process. The pressure is directly influenced by the weight of work piece.

Acknowledgment

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References

[1]. **R. Neugebauer, M. Putz, U. Hellfritsch** - *Improved Process Design and Quality for Gear*

Manufacturing with Flat and Round Rolling, CIRP Annals - Manufacturing Technology Volume 56, Issue 1, Pages 307-312, 2007

[2]. **L. Nistor, D. Frunza**, *Evaluare forței în obținerea danturii roților dințate cu dinți drepti prin presare - laminare* (The force evaluation for straight tooth gears manufacturing by pressing – rolling), *Metalurgia*, vol. 58, pg. 14-18, no.5/2006

[3]. **L. Nistor**, *Laminarea metalelor* (Metal rolling) Polytechnic Institute Cluj-Napoca, 1988

[4]. **K. Lange**, *Handbook of metal forming*, Copyright, 1985

[5]. **I. Drăgan**, *Tehnologia deformărilor plastice* (Plastic deformations technology), E.D.P București, 1979

[6]. **H. You-feng, X. Shui-sheng, C. Lei, H. Guo-Jie, F. Yao**, *FEM simulation of aluminum extrusion process in porthole die with pockets*, *Trans. Nonferros Met. Soc. China*, vol. 20, pg. 1067-1071, 2010

[7]. **Adriana Neag, Mariana Pop**, *Deformări plastice - Aplicații* (Plastic deformation - Application) - U.T. Press Cluj Napoca, 2009

A DESIGN OF NEW BRANDS OF MARTENZITE STEELS BY ARTIFICIAL NEURAL NETWORKS

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ABSTRACT

The paper proposes model-based approach for design of martensite structure steels with improved mechanical and plastic characteristics using proper composition and thermal treatment. For that purpose, artificial neural models approximating the dependence of steels strength characteristics on the percentage content of alloying components were trained. These non-linear models are further used within an optimization gradient procedure based on backpropagation of utility function through neural network structure. Optimizing the steel characteristics via its chemical composition several steel brands with high values of tensile strength, yield strength and relative elongation were designed. A steel composition having economical alloying and proper for practical application was determined comparing several obtained decisions. Usage of that steel will lead to lightening of the hardware for automobile industry.

KEYWORDS: metal materials, high strength steels, composition optimization, neural networks

1. Introduction

Development of metallurgy and in particular of steel production for motor industry develops faster during last decades. From one hand, methods and technologies for characteristics optimization of known steel brands are looked for, from the other hand a lot of research efforts are targeted to design of new steel brands with improved physical-chemical and mechanical characteristics.

Especially for the steels used in motor industry, the research aim is to decrease weight of the final product applying high strength steels. Number of high strength steels application increase because they are able to meet at the same time the

contradictive requirements for better deformability, weldability, resistance to stress, fatigue, and corrosion.

Since the motor vehicles are the biggest source of pollutants of the environment (producing harmful emissions of CO₂= 0,2 kg/km), nowadays a lot of efforts are targeted to their weight decreasing. This will lead to improvement of their combustible efficiency and as a result to harmful emissions decrease. In [1] several innovative approaches related to economy of fuel, decrease of harmful emissions and recycling are described. It is demonstrated that application of high strength steels allows decreasing car carriage weight with 25%, and it is expected to achieve even 35 % weight decrease using new generation high

strength steels that are still under development.

While the strength of the most common application steels varies in the range 440–590 MPa, a part of special components steels have tensile strength about 980–1180 MPa. High strength foliate steels still have restricted application because of their restricted plasticity. In Nippon Steel Corporation, three brands of high strength steels (980 MPa) are designed and introduced into vehicle production. [2].

Moreover from functional and economic point of view the high strength steels appear to be the best material for the mentioned application. The iron based materials ensure such a structure and properties that absorb the shock energy. The quick elaboration of the steels applied for motor-car construction leads to definition of steel classes denoted by AHSS (Advanced High Strength Steels). In 2002 a project ULSAB - AVS (Ultra - Light Steel Autobody) started. Fig. 3 shows that the average value of the tensile strength for the developed steels increases from 413 MPa to

758 MPa [3]. Together with the increasing values of the strength there is also a tendency towards improved deformability. The ULSAB - AVS project applies the high strength steels for parts of entirely car. In an investigation of the model Audi A1 one can see that the quota of the high strength steels is approximately two times greater than the conventional low carbon steels-фиг. 4. Farahani [4] gives an investigation published by International Council on Clean Transportation that represent different ways for development.

The short-term plan foresees that in 2014 the mild steel will be changed with the high strength steels. For the analysis a Toyota Venza (model from 2009) has been chosen. The aim is a reduction of the total mass with 20%.

The present study presents a new contemporary method for design of optimized iron-based alloy composition using artificial neural networks (ANN) accounting for economic alloying at the same time.

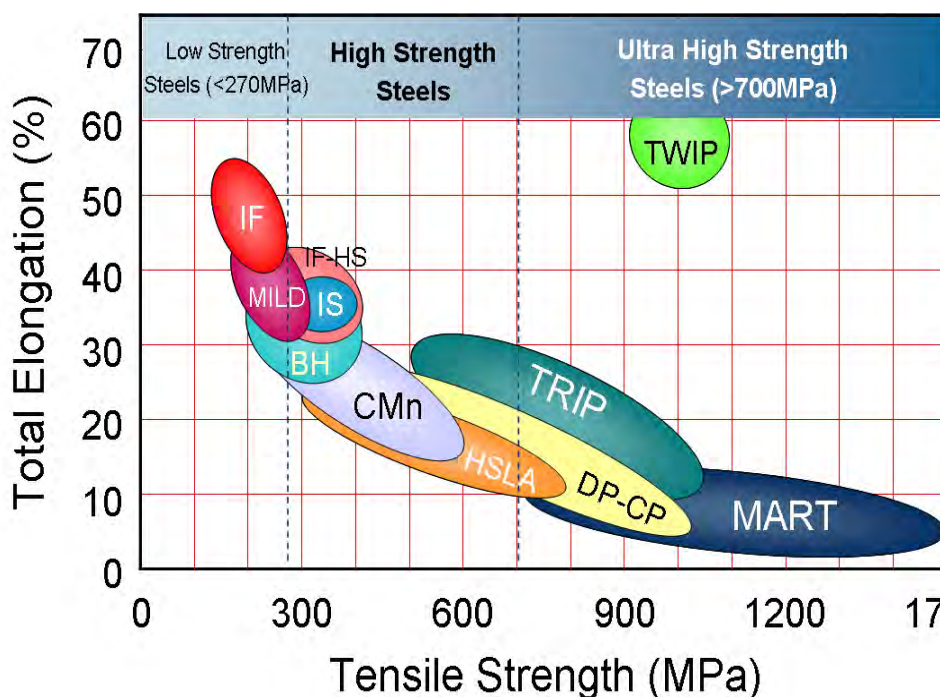


Fig. 1. Areas of variance of steels quality characteristics according to the program ULSAB-AVC

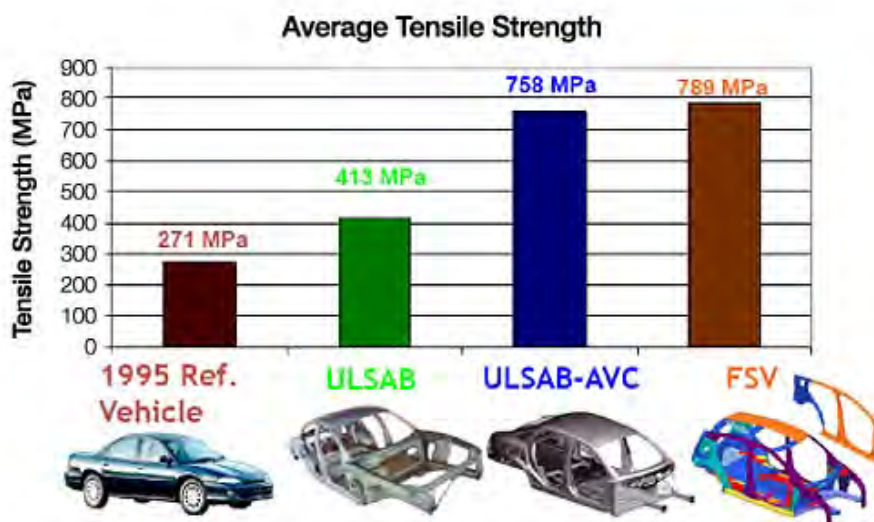


Fig. 2. Change of the average value of the materials tensile strength at different motor-car construction projects.

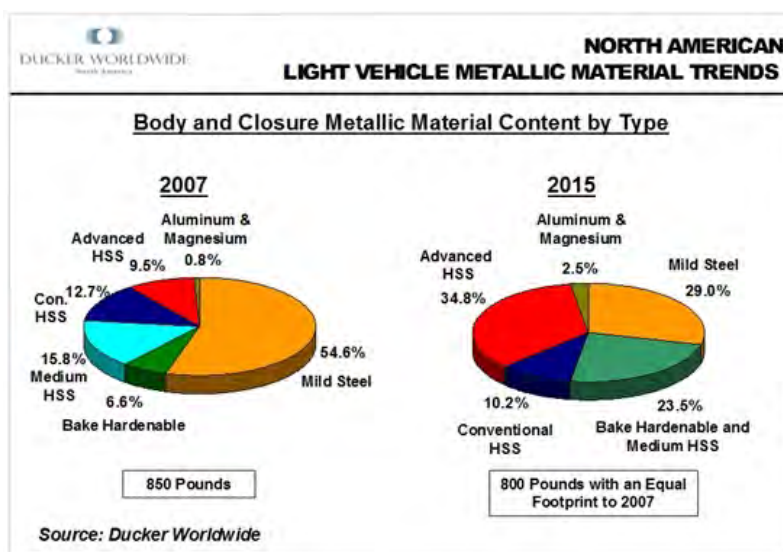


Fig. 3. Distribution of the steel types used by the motor-car construction.

2. Steel types and contemporary trends

During reduction of elements amount in the steels there is need to keep the design balance of the system “composition – treatment regime – characteristics” that will allow to improve its strength and plastic characteristics.

Steels used in vehicle production can be classified based on different indications, as it is shown on Figure 1.

Diphase (DP) steels structure consists of ferrite matrix containing hard martensite part and of soft ferrite phase.

The later insures good conditions for shape changing.

Increase in martensite volume leads to increase of steel strength.

In TRansformation Induced Plasticity (TRIP) steels residual austenite about 5% is included into ferrite matrix together with different amounts of hard phases martensite and bainite. During the deformation, residual austenite is converted into martensite. Complex phase (CP) steels have similar to the TRIP steels microstructure but it doesn't contain residual austenite.

In MART steels, the final structure is obtained from austenite that is converted entirely into martensite matrix containing small amounts of ferrite and/or bainite during hot roll forging. Martensite MART steels possess higher tensile strength, up to 1700 MPa, and at the same time lowest ability to plastic deformation.

As can be seen from the above figure, increase in strength of different types of steel is related with decrease of its total elongation. This unfavorable feature of high strength steels leads to deterioration of their deformability but also improves their stress resistance without increasing of product weight.

Steels chemical composition is of crucial importance for product quality. The quality is determined by the mechanical characteristics of steel obtained after their plastic and thermal treatment. Manganese, chrome, molybdenum, and nickel added as

alloying elements in combination or separately help to increase steels strength. Increasing of carbon amount leads to increase of martensite. Variations in carbon and other alloying elements during optimization must improve not only steels mechanical characteristics but also their technological properties such as weldability, deformability etc.

3. Design of martensite steel with optimal characteristics

The design of steels includes determination of their chemical composition, parameters of thermal treatment regime and obtained mechanical characteristics.

Here we propose design procedure that relates aimed mechanical characteristics with chemical steels composition using multiple criteria optimization. Optimization criteria contain complex of targeted for given application steel characteristics defined as objective functions.

In the present study data base of 92 alloys from [5] was used. It contains alloys chemical compositions and corresponding to them mechanical characteristics. Alteration intervals of considered alloying elements are given on Table 1. Table 2 contains change intervals of mechanical characteristics after thermal treatment (tempering and low temperature lukewarming).

Table 1. Alteration intervals of investigated steels alloying elements.

Element	C	Si	Mn	Ni	S	P	Cr	Mo	V
min, %	0.12	0.27	0.27	0	0.025	0.025	0.15	0	0
max, %	0.5	1.4	1.6	4.22	0.035	0.35	2.5	1.5	0.15

Table 2. Alteration intervals of investigated steels mechanical characteristics.

Mechanical characteristic	R _m , MPa	R _e , MPa	A, %	Z, %	KCU, KJ/m ²	HB*10 ⁻¹ , MPa
min	500	300	7	30	290	179
max	1670	1375	26	70	1830	541

For steel composition optimization purposes, developed in [6] methodology based on ANN was applied.

First step is to train neural network model approximating non-linear dependence between alloying elements amounts and

obtained after thermal treatment mechanical characteristics of the given steel. Our former investigations [6] showed that due to insufficient data it is impossible to train a single accurate NN model for predicting all investigated mechanical characteristics. Here we trained separate NN models for each of the mechanical characteristics from Table 2. Since the amount of sulfur and phosphorus in all investigated steels are equal, they are considered as one variable. The NN structure as in [4] is 8:40:1. The number of inputs is defined by the number of alloying elements, i.e. eight. All NN models have single output neuron for the modeled one of the mechanical characteristics. The number of hidden units was determined by trail and error as in [6].

We also had to account that the database we have is relatively small and it doesn't contain all the possible combinations between alloying elements. Because of that we divide the available data into 18 smaller data sets used for training of 18 NN models excluding each time one of the data sets for testing. Then the best model for each of mechanical characteristics was chosen based on smaller testing error.

Because the investigated input/output space is multidimensional and the modeling dependencies are non-linear, finding of global optima during optimization needs to explore entire input space. However, due to huge number of possible combination, this is time and resource demanding task. That is why here we apply proposed in [6] gradient procedure starting from numerous different initial points. Finally, the obtained optimal compositions are compared and the best one were chosen.

Figure 4 presents main optimization procedure known as "backpropagation of objective function" [7]. The optimization task is the following: find values of input vector X that maximize (minimize) the objective function:

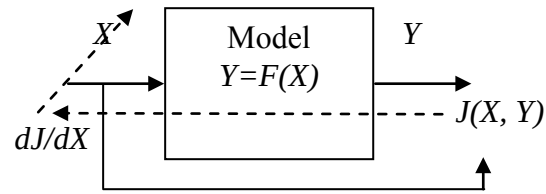


Fig. 4. Optimization procedure. Dashed lines represent gradient calculation direction.

$$J = J(X, Y) \quad (1)$$

Here Y is output variables vector that is related with the input once via a given function (here NN model) F as follows:

$$Y = F(X, p) \quad (2)$$

and p is model parameters vector.

The gradient procedure needs calculation of objective function derivatives with respect to optimized variables as follows:

$$dX = \frac{dJ}{dX} = \frac{\partial J}{\partial X} + \frac{\partial J}{\partial Y} \frac{\partial F}{\partial X} \quad (3)$$

In the cases when J do not depend explicitly on X , the first term in equation (3) is zero, i.e. the derivative depends only on function F .

The layered structure of neural network models offer a convenient way for calculation of derivatives from (3) using backpropagation procedure.

The next step is iterative determination of optimal values of X as follows:

$$X_i = X_{i-1} \pm \alpha \Delta X_i \quad (4)$$

Here α is parameter called learning rate and ΔX_i is step change of X at i -th iteration calculated as follows:

$$\Delta X_i = g(dX_i) \quad (5)$$

Here g is function defining the gradient. Usually it is proportional to dX_i but in some cases it could depend also on previous values of ΔX_i . Here we used simple gradient procedure with $\Delta X_i = dX_i$. The learning rate α is chosen relatively small and stopping criteria was very small change in objective function.

In our case the input vector X consist of concentrations of 8 alloying elements and the output vector – of corresponding steel mechanical characteristics.

The following optimization tasks were solved:

A.Single criteria optimization-maximization of **Re**:

$$J_1 = Re \rightarrow \max \quad (6)$$

Table 3. Chosen optimal compositions, %

Decision Compounds/ characteristics	№1	№2	№3
C	0.27	0.3	0.26
Si	1.10	1.02	1.24
Mn	1.06	1.2	1.18
Ni	2.36	2.35	2.78
S	0.02	0.02	0.02
P	0.02	0.02	0.02
Cr	1.04	0.96	1.26
Mo	0.15	0.18	0.23
V	0.0087	0.0087	0.022
Rm, MPa	1666.9	1678.	1647.5
Re, MPa	1370.3	1355	1370.9
A, %	11.4	12.8	12.2
Z, %	51.1	52.3	54.1
HB	281.6	284.3	287.4

B.Two-criteria optimization: simultaneous maximization of **Re** and of the ratio **Rm/Re**:

$$J_1 = Re \rightarrow \max ,$$

$$J_2 = \frac{Rm}{Re} \rightarrow \max \quad (7)$$

In both cases the restriction $C \leq 0.3$ was imposed aimed at obtaining of low carbon steels.

After applying above optimization procedure three optimal decisions were chosen. They are shown on Table 3 below. The first two of them maximize **Re** while the third one maximizes the ratio **Rm/Re**.

Finally, composition № 2 is chosen because it is the most economical one.

Acknowledgment

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Conclusion

Here we demonstrated an approach to design of optimal steel compositions for transport vehicles industry. The applied methodology is based on artificial neural networks. Via optimization of mechanical characteristics on base of the chemical composition of the steel the values of tensile strength and yield strength are kept high at total elongation of about 12%.

References

- [1]. Krupizer, R. A *Process of Decoupling and Developing Optimized Body Structure for Safety Performance*, 10th European LS-DYNA Conference, March 18, 2004.
- [2]. *Development of High Strength Steels for Automobiles*, Nippon steel technical report No.88, July, 2003.
- [3]. ULSAB-AVC, Advanced Vehicle Concepts Program Results, CD March 2002, www.ulsab-avc.org
- [4]. Farahani A. R. Kolleck, *Hot Forming and Cold Forming—Two Complementary Processes for Lightweight Auto Bodies*, Proceedings from The International Conference „New Development in Sheet



Metal. Forming Technology,” Stuttgart, Germany, 2004, pp. 235-244.

[5]. http://www.splay.kharkov.com/choose_type.php.

[6]. **Koprinkova-Hristova, P., Tontchev, N., Popova, S.** *Neural networks for mechanical characteristics modeling and compositions*

optimization of steel alloys, Int. Conf. Automatic and Informatics’10, Oct. 3-7, 2010, Sofia, Bulgaria, pp.I-49 – I-52

[7]. **Werbos, P.J.**, *Backpropagation through Time: What It Does and How to Do It*. Proceedings of the IEEE vol. 78(10), pp.1550-1560, 1990.

THEORETICAL AND PRACTICAL ASPECTS CONCERNING THE UNIDIRECTIONAL SOLIDIFICATION OF ALUMINIUM ALLOYS

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ABSTRACT

The paper deals with some theoretical and practical aspects regarding the unidirectional solidification, revealing the main factors which have influence on the crystals size and morphology and the advantages of anisotropy obtained by the unidirectional crystallization in the case of classical materials as well as in the case of „in situ” composite materials. From technological point of view the problem is to control the thermal flux so that to assure an approximately unidirectional heat exchange. To reach this aim many thermal systems from the simple to some very complicated were created taking into account the mechanism of crystals grow. In the work is trying to establish the limits to direct the crystals morphology by controlling the cooling regime.

KEYWORDS: *Unidirectional solidification, alluminium alloys, crystallization, heat exchange, theoretical considerations, experimental data*

1. General considerations

As a function of the chemical composition and solidification conditions it can be obtained a macrostructure which to contain only two structural zones or even a single one. Thus, in the case of stainless steel the macrostructure is predominant columnar, without the large equiaxed crystals zone and with a small crystals zone or without this zone at the contact with the mould. In the modified aluminium alloys the macrostructure is formed only from equiaxed crystals. Generally, it is desirable to obtain fine equiaxed crystals on the whole section of castings except the few cases when a columnar macrostructure is desired, in order to realize a special anisotropy [1,2]. The growth in perpendicular direction on the wall takes place more difficult because it occurs at a smaller undercooling degree and on more growth directions. However, the columnar zone appears due to the following reasons: the existence of a permanent

contact between the tips of crystals and the metallic melt; the lateral regions come in contact with a phase enriched in alloying elements with low melting temperature; that means a low undercooling degree and a hindered growth; the appearance of a large thermal gradient in the heat flow direction (perpendicular on the mould wall); in the perpendicular direction on the main axes of crystals the thermal gradient is much smaller.

Columnar structure is specific to pure metals, because in the case of alloys the segregation phenomena limit the zone of this kind of crystals. Also, the columnar zone is bigger for a higher superheating degree as well as in the case of a diminished solid-liquid zone. The strong anisotropy can have importance in some industrial applications such as in the production of turbine blades or permanent magnets.

Unidirectional solidification is useful too in composite materials production. So, for some alloys of eutectic composition, it

can be realized an orientation of phases by unidirectional solidification, the crystallization front being plane and perpendicular on the heat exchange direction. In this way, the reinforcement material is formed directly ("in situ") from the alloy. If the eutectic has a regular microstructure the phase found in minority will grow like fibres while the phase found in majority will constitute the matrix [3].

From the thermal point of view, it is necessary to realize a unidirectional heat flux parallel with the growth direction of crystals, assuring a maximum diminution of the lateral fluxes. The unidirectional solidification is realized at high values of the thermal gradient and at low solidification rates.

The increase of the tensile strength by unidirectional solidification of Al-Al₃Ni eutectic (where Al₃Ni grows as fibres) is important. The tensile strength becomes much larger as that obtained in the case of multidirectional solidification.

Fibres production by unidirectional solidification includes usually two stages:

- the production of usual cast bars;
- the remelting and directional solidification of bars.

The use of this method for composite materials production is very advantageous, but it is limited to a reduced number of materials because the phase grown in shape of fibres has not always satisfactory mechanical properties or does not represent the required volume fraction. In addition, some phases have a lamellar growth with multiple branches and flaws.

For the extension of the application field of this proceeding, it must use eutectic or almost eutectic alloys from ternary or complex systems. In this way, composites such as Co-Ta-C/TaC, Ni-Al/Cr, or Fe-Cr-Nb/Nb₅Fe₇Cr₂ can be obtained.

An important part of superalloys can be replaced with the following unidirectional solidified alloys Ni-Cr/TaC, Co-Cr/TaC, Ni-

Co-Cr-Al/TaC, Co-Cr-Ni/TaC, Co-Cr-Ni/NbC, and so on.

To realize a supplementary mechanical resistance, it is necessary to obtain secondary fibres by precipitation from solid state.

By controlling the eutectic reaction in Fe - 2.8% C, 35% Cr alloy found in unidirectional solidification it was possible to obtain the most favourable microstructure. Such structure contains a large number of oriented and continuous single-phase fibres (Cr-carbides) with constant cross-section and high tensile strength, bound tightly to the metallic matrix. The solidification rate has a small effect on the volume fraction change of the carbide phase in the eutectic. When the solidification rate is increased, the diameter of the carbides and the inter-fibres length decrease.

The properties of a metallic material depend on the morphology, which means the shape and orientation of crystals. The unidirectional solidification contributes to obtain materials with superior mechanical properties on one direction. Perhaps it could be a correlation between the mechanical properties of unidirectional solidified castings and the dendritic parameters of arm spacing. Columnar crystals have a strong crystalline orientation, which correspond to the preferential growth directions of dendrites. The crystals selection and the mechanism of growth were studied in detail by D. Walton and B. Chalmers. Thus, at the beginning of the growth period the dendrites that are developed parallel with the mould wall are encouraged

When the first crystals will be molten partially due to the convection currents, the new crystals will be formed when the liquid reaches again the nucleation temperature, but, because of the little undercooling degree they will be in small number and their growth will occur more free.

The mechanical properties are better along the main axis of columnar crystals,

because of the reduced grain boundaries, which are weak zones from the mechanical resistance point of view.

In the work [4], H. Kahn shows that the first research concerning the properties of columnar crystals was made by H.L. Northcott, who studied this structure in the case of some copper alloys cast in a mould made up from refractory material, seated on a plate from copper.

Unidirectional structure can be obtained easier in the case of pure metals, because in the case of alloys the segregation phenomena limit the zone of this kind of crystals. Also, the columnar zone is bigger for a higher superheating degree as well as in the case of a diminished solid-liquid zone. Generally, for an alloy with a given composition, it is expected that the size of the columnar zone to increase with the increase of pouring temperature, and for a given pouring temperature this zone is diminished while the alloying elements concentration increases.

Unidirectional crystallization and solidification could be easily obtained by using a multizone furnace operating under the control realized by means of a special algorithm. These types of furnaces are named Bridgman furnaces and are designed for crystal growth applications and can produce thermal gradients within the range of 0.2-4.5°C/mm and can melt different types of alloys and materials. The control system maintains the desired thermal profile during the crystal growth [5]. The final quality of a crystal depends on more physical phenomena such as: thermal transfer, hydrodynamic and chemical processes or thermo-mechanics stresses [6].

2. Experimental conditions and results

Experimental data were obtained by the casting and directional crystallization of Φ 30 x 150 mm samples from technical pure aluminium. Three different pouring temperatures were used: $T_p = 705^\circ\text{C}$; $T_p =$

756°C ; $T_p = 804^\circ\text{C}$. The mould was realized from quartz sand and resin (used as binder). The thermal regime was varied in order to obtain a slower and faster heat extraction on the sample bottom [7,8], the cooling medium being characterized by the complex coefficient b_m (the heat accumulation coefficient), which took three distinct values: I – $b_m = 12\,500\text{ Ws}^{1/2}/(\text{m}^2\cdot\text{K})$; II – $b_m = 24\,000\text{ Ws}^{1/2}/(\text{m}^2\cdot\text{K})$, and III – $b_m = 40\,000\text{ Ws}^{1/2}/(\text{m}^2\cdot\text{K})$. Temperature variations were registered by using four thermocouples: on the bottom of sample; at 20 mm from the bottom side, in central zone, axial; on the separation surface metal-mould at 20 mm from the bottom of sample; at 10 mm from the surface, in the casting mould, at 20 mm from the bottom of sample. Some results are shown in figures 1 and 2.

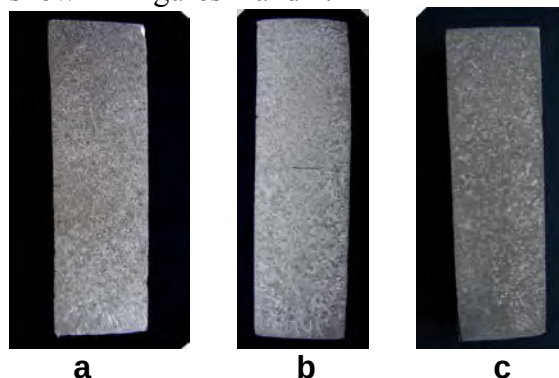


Fig. 1. Macrostructure of cast samples:
 a – thermal regime I, b – thermal regime II,
 c – thermal regime III
 (pouring temperature 705 °C).

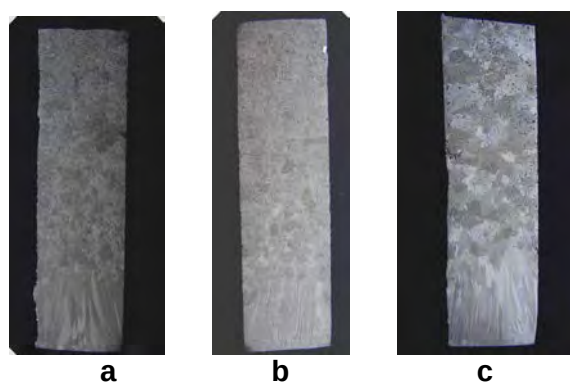


Fig. 2. Macrostructure of cast samples:
 a – thermal regime I, b – thermal regime II,
 c – thermal regime III
 (pouring temperature 804 °C).

The transcrystallization zone increases when the pouring temperature becomes higher, because the duration of heat exchange is longer and crystals have the necessary exchange process during the unidirectional crystallization). time to grow;

The unidirectional crystals zone is increasing when the heat extraction rate is larger (the b_m coefficient is a syntetical parameter which can characterize the heat

3. Conclusions

- Experimental data revealed the main factors which have influence on the crystals morphology obtained in directional crystallization conditions.
- The thermal regime was defined by the heat accumulation coefficient, wich expresses the capacity of heat extraction from the cast metallic specimen.
- A very important factor seems to be the initial melting temperature, which has a strong influence on the transcrystallization process and, therefore, on the formation of a columnar crystals structure, in the heat extraction direction.
- The crystalline structure of metals and alloys is determined by three important factors:
 - *the chemical composition*, which has influence on the primary structure formation by the repartition coefficient and diffusion coefficients of alloying elements in solid and liquid phases – which influence the compositional undercooling tendency. The chemical composition determines the primary structure in the case of mono-phasic alloys or with eutectic grains or combinations of both of them;
 - *thermal conditions*, which are expressed by the temperature distribution and the cooling rate of castings, depended on t he initial temperature of liquid alloy and mould, as well as their thermal properties;

- *nucleation and growth from liquid conditions*, expressed by the homogeneous and heterogeneous conditions, which depend on the presence of solid particles existent or especially introduced into the liquid alloy.

- Experimental data demonstrated the major influence of the thermal regime on the crystallization-solidification process and they releaved the limits to direct the crystals formation by changing the cooling regime.

References

- [1]. **Fl. Ștefănescu**, *Cercetări privind dirijarea procesului de solidificare a aliajelor turnate in piese*, Teză de doctorat, IPB, 1989.
- [2]. **Fl. Ștefănescu, G. Neagu, Alexandrina Mihai**, *Solidification of Metallic Materials (Theory of solidification, Directional solidification, Non-destructive testing)*, Editura Printech, 2001.
- [3]. **Ghosh, P.K., Ray. S.** *Solidification Structure in Compocast Al(Mg)-Al₂O₃ Particulate Composite. Solidification of Metal Matrix Composites*. The Minerals, Metals & Materials Society, 1990.
- [4]. **H. Khan**, *La solidification dirigee. Technique et effets de la solidification dirigee sur la structure, la sante et les caracteristicques mecaniques des pieces moulees*, Fonderie-Fondeur d'aujourd'hui, nr. 12, 1982, p. 17-23.
- [5]. **C. Batur, W. M. B. Duval, R. J. Bennett**, *Performance of Bridgman furnace operating under projective control*, American Control Conference, 1999, Volume 6, p. 4101-4105.
- [6]. **M. Margulies, P. Witomski, T. Duffar**, *Optimization of the Bridgman crystal growth process*. Journal of Crystal Growth 266 (2004), p. 175-181.
- [7]. **Fl. Ștefănescu, G. Neagu, A. Mihai, F. Hăntilă, C.P. Mihai**, *Some Aspects Concerning the Production of Anisotropic Metallic Materials by Unidirectional Crystallization*. Proceedings of the 8th International Conference of Technology and Quality for Sustained Development, 30-31 October 2008, Bucuresti, Romania, p. 379-382.
- [8]. **Fl. Ștefănescu, F. Hăntilă, G. Neagu, A. Mihai, C.P. Mihai**, *Unidirectional Solidification of Aluminium Alloys by Using Eddy-Currents for a Controlled Temperature Distribution*. 6th Japanese – Mediterranean Workshop on Applied Electromagnetic Engineering for Magnetic Superconducting and Nano Materials, July 27-29, 2009, p. 79-80.

PROPERTIES OF SLAGS IN THE SYSTEM $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ IMPORTANT IN DEOXIDIZATION AND DESULPHURIZATION OF LOW CARBON ALUMINIUM KILLED STEELS

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ABSTRACT

Properties of refining slags belonging to the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ are important in simultaneous or successive refining treatment processes in the ladle and other refining metallurgical reactors. The efficiency of treatments depends upon values of physicochemical properties of treatment slags which become important technological parameters. Surface tension of slags and interfacial tension in the system slag steel also, viscosity and density are important in managing refining processes which must be correctly evaluated as values and influence exerted by modification of slag composition, mainly by sulphur content

KEYWORDS: $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ system, surface tension, interfacial tension, viscosity, density, sulphur solubility.

Introduction

In the analysis of the dynamical effects at steel-slag interface during the desulphurization process, usually only the surface tension of steel, the interfacial tension steel-slag effects and the steel side of the interface are taken into account. It is a reality that the influences due to the contribution of solutal effects in slag, seems to be un-approached and sometimes even neglected. Many special particularities appear from the particularities of the slags used in deoxidization and desulphurization of the low carbon and/or low alloyed steels. Possible contributions of slags to the dynamic effects are due to special nature and properties of refining desulphurizing slags and sometimes of the steel, which form the interface. For sustaining, besides the criteria, classically used to appreciate the possibility that certain dynamic effects as the Marangoni convection occur, it must be supplementary considered the lower solubility of sulphur in slags, taken into

account as thermodynamically homogeneous liquid solutions, coupled with the fact that, at industrial scale, the amounts of desulphurizing slags are usually between 8-14kg/tonne of steel [1]. While in steel the desulphurization under slags leads to a sulphur content decreasing about 0.01-0.02% mass, in the same time, in the desulphurization slag, the sulphur content increases about one hundred times faster up to contents of 1-2%mass[1]. When desulphurization reaction takes place in a non uniform manner on the whole interface, due to different conditions, higher concentrations of sulphur in slag locally appear, overcoming the limits corresponding to the existence of the thermodynamically and physically homogeneous liquid solutions and the whole panel of conditions are changed. Therefore an extended analysis of such properties as surface and interfacial tension, viscosity and density of slags in the mentioned system could contribute to obtain an improved image and perception of the conditions leading to performances.

Influence of the sulphur content on the surface and interfacial tension in CaO-Al₂O₃-CaS slags at 1873K

The only available experimental reported data, covering a wider range of compositions, are those reported in the ref.[2][3] for surface tension in the system CaO-Al₂O₃-CaS and interface tension between the same slags and a liquid steel of a specified grade. It must be mentioned that the paper[2] is focused on the influence of sulphur in the system CaO-Al₂O₃-CaF₂, but this research includes points without CaF₂. From them, two sets of data have been extracted as selected points from the graphical representation given in ref.[3], mainly taking into consideration their coincidence with the chemical compositions of slags used in practical activities of steel desulphurization and refining. They have been used to generate different statistical dependence relations, finally being selected those having the highest value of the determination coefficient R^2 . The regression equations serve to study the comparative behavioral trends of the respective quantities using computed values, not only the impression due to visual aspects, but especially as their values. This procedure will be very useful for the purpose of the present paper. In the legend of figures presented in the present paper, both the regression relations and determination coefficients are given. As it is shown, in each case $R^2=1$ or it is closed to this value. According to the initial composition of the slags, in % mass, they will be nominated as slag A (or C/A=1.5) at initial composition 60% CaO-40% Al₂O₃ and slag B (or C/A=1) at initial composition 50% CaO-50% Al₂O₃. They are presented in the form of dependences upon the concentration of sulphur, and the sulphur content is calculated in the sense of the procedure used during the reported experiments, consisting in additions of different percentages of CaS to such slags. In fig.1 are presented the dependences

of the surface tension of both mentioned slags upon the sulphur content (in % mass) at 1873K. In fig.2 are presented the dependences of the interfacial tension between the two mentioned slags and a steel grade H52-3 at a fixed composition of this (0.11%C; 0.44%Si; 1.32%Mn; 0.022%P; 0.035%S; 0.0045%O; 0.0115%N) [2]. It is evident a similar influence exerted by sulphur content up to 2.5% mass, on surface tension dependences (fig.1) and the ratio K (fig.3) in the case of both slags, A and B. In the fig.4 are represented dependences of the surface tension variations of the slags A and B obtained based on the partial molar surface tension of each slag upon the mole fraction of sulphur in slags, compared with the predictions made using the general statistic relation deduced and presented in ref.[4] based on relation given in ref.[5]. In the fig.4, besides the similarity of the trends, consisting in a parabolic type dependence and therefore in the existence of a minimal value at a specific sulphur concentration, on each curve, it is obvious the difference between predicted values in the cases of the slags A and B, belonging to CaO-Al₂O₃-CaS, and the predicted values using the general statistic relation. This means that all effects connected to this quantity are less intensive influenced in the particular cases of slags A and B than those obtained with the general statistical averaged relation. It can be remarked also that the dependences of the products $X_S \partial \sigma / \partial X_S$ for slags A and B are practically superposed in the range of sulphur concentration lower than $X_S \leq 0.015$. The value of the interfacial tension at 1873K, between CaO-Al₂O₃ slag and iron iron decreases from 1238mN/m for a ratio C/A=1 decreases to 1200mN/m at C/A=1.5 [6]. A slight increasing to the value 1250mN/m results from the ref.[7] at C/A=1.5 and iron containing 0.1%C. At 1843K from the ref.[8] it results, at 0.1% mass carbon content in iron, an interfacial tension about 1300mN/m,

between this alloy and a slag 50% CaO-50%Al₂O₃.

Many difficulties are due to the atypical behaviour of the system CaO-Al₂O₃, which is proven to be in a way "out of rules" in

many respects, making difficult the including of the system in a general model of establishing the quantities contributing to viscosity, density, and even to the surface tension.

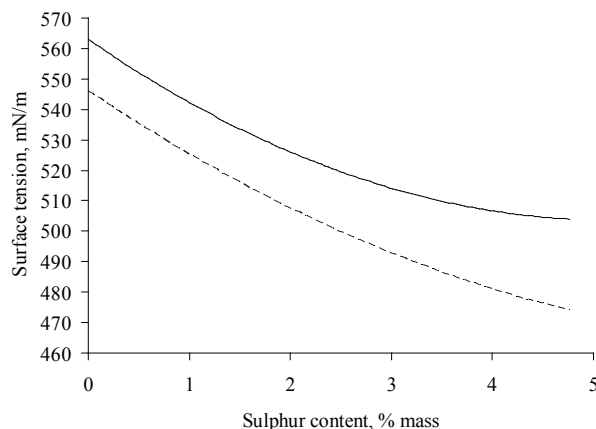


Fig.1 Dependence of the surface tension upon the sulphur content in CaO-Al₂O₃- CaS slags at 1873K.

— $C/A=1.5 \sigma_A=2.1217(\%S)^2-22.922(\%S)+563$
($R^2=1$);
--- $C/A=1 \sigma_B=1.4781(\%S)^2-22.159(\%S)+546$
($R^2=1$).

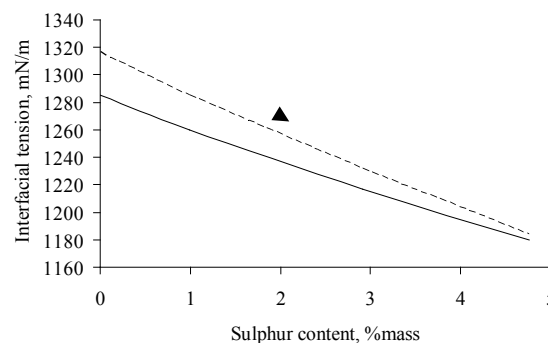


Fig.2. Influence of the sulphur content in slag on the interfacial tension between CaO-Al₂O₃-CaS slags and a low carbon steel (H52-3 grade) at temperature 1873K;

— $C/A=1.5, (\sigma_{\text{interf.A}}=0.7353(\%S)^2-25.504(\%S)+1284.8)$;
--- $C/A=1, (\sigma_{\text{interf.B}}=0.7928(\%S)^2-31.548(\%S)+1316.5)$.

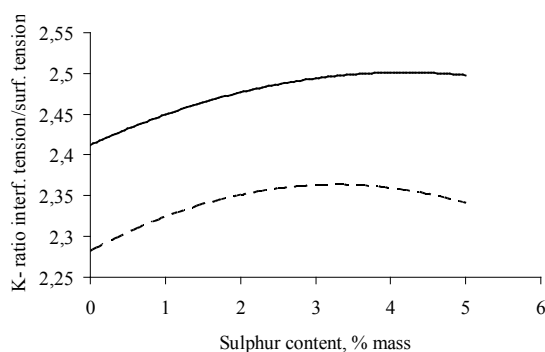


Fig. 3. Ratio(K) between the interfacial tension and the surface tension in the system CaO-Al₂O₃- CaS at 1873K, upon the sulphur content in slags;

— $C/A=1.5(K_{1.5}= -0.0051(\%S)^2+0.0425(\%S)+2.412)$;
--- $C/A=1(K_1= -0.0076(\%S)^2+0.0489(\%S)+2.282)$.

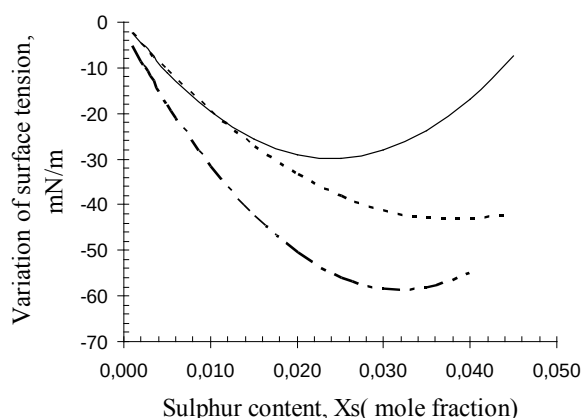


Fig.4. Dependence of the surface tension decreasing ($X_s \partial \sigma / \partial X_s$) upon the sulphur content (X_s) in CaO-Al₂O₃- CaS at temperature 1873K.

— $C/A=1.5(X_s \partial \sigma / \partial X_s = 55778X_s^2 - 2498X_s + 0.2919)$;
..... $C/A=1(X_s \partial \sigma / \partial X_s = 28894X_s^2 - 2226.3X_s + 0.3045)$;
— · — · according to ref. [3].

Viscosities in CaO-Al₂O₃-CaS slags, at 1873K

Despite the presumed simplicity due to the number of components, the viscosity values in the system CaO-Al₂O₃ are not enough accurate as experimental or predicted values using models. Some trials to establish the general trend of the viscosities in the CaO-Al₂O₃ system, have led by finding a decreasing one and another one, of increasing with the increasing of the CaO content.

In the ref[9], in a systematic experimental research, at a slag composition 50% CaO-50%Al₂O₃ it was obtained the value 0.23Pa.s. From the relations established in the ref [10], it results the value $\eta=0.1956\text{Pa.s}$ at a close composition (51.5%CaO+ 48.5%Al₂O₃) and the value $\eta=0.199\text{Pa.s}$ at a composition (49.5% CaO +50.5% Al₂O₃). Using Urbain model a value 0.4396Pa.s is obtained.

In slag 60%CaO-40%Al₂O₃ a value $\eta=0.1184\text{Pa.s}$ is obtained by extrapolating at 1873K a statistic relation ($\lg\eta=23.10^{-7}T^2-0.010556T+10.776$, $R^2=1$), established in the present study, based on data obtained in ref.[1], on the interval 1973-2073K. From ref.[10], at the a relative closed composition (55.5% CaO-43.5%Al₂O₃-1% SiO₂) a value $\eta=0.162\text{Pa.s}$ is obtained. Using Urbain model a value $\eta=0.2735\text{Pa.s}$ is obtained. The values obtained using the Riboud model are much lower than the lower experimental value, in case of both composition of slags.

There are not data concerning the influence of the sulphur content on the viscosity in slags based on the simple CaO-Al₂O₃ system. Some trends of influence result from data in other systems. In the system CaO-CaS-SiO₂, at 1873K and ratios of mole fractions representing $(X_{\text{CaO}}+X_{\text{CaS}})/X_{\text{SiO}_2}=1.5-2$, at contents of $X_{\text{CaS}}=0.02-0.1$, there are not sensible influences of the sulphur content [11][12]. At 1773K, in a complex system CaO-SiO₂-Al₂O₃-MgO-MnO-CaS, at basicity index $b=\% \text{massCaO}/\% \text{massSiO}_2=1.3$ the replacing

of about 3%CaO by CaS leads to increasing of the viscosity with about 10%(from 0.3 to 0.33Pa.s) and at $b=1.43$, the replacing of about 6%CaO by CaS leads to decreasing of the viscosity with about 16% (from 0.38 to 0.32Pa.s)[13]. The presented data lead, by a certain similitude, to the acceptance of a low influence of the sulphur content on the viscosity, in the system CaO-Al₂O₃-CaS at 1873K, up to 6% CaS.

Densities in CaO-Al₂O₃ system, at 1873K

In slags 50% CaO-50%Al₂O₃, values 2710kg.m⁻³[14], 2750kg.m⁻³ [15][16] and 2870kg.m⁻³ [17] have been found as points in diagrams[12]; in the ref.[18], a value of 2710kg.m⁻³ is given also. For slag 60% CaO-40%Al₂O₃, a value 2685kg.m⁻³ is given [11][19].

Sulphur solubility in slags and its influence

From data presented before it results that the major effect, during the desulphurization of the steels using slags based on the oxydic system CaO-Al₂O₃, is the decreasing of the surface tension of the slag and of the interfacial tension between slag and the mentioned low carbon steel, due to the increasing of the sulphur content of the slag. In the industrial practice only rarely the final sulphur content is higher than 2%mass. At each temperature in the range of interest, for every chemical composition of the slag a certain value of the sulphur capacity C_S' corresponds, at equilibrium with metallic bath and therefore, there is a limit of solubility of sulphur; up to this limit the sulphur forms with the other components of slag a fully liquid slags. The content of sulphur overcoming the solubility limit will precipitate in slag as CaS, which will float in the slag as crystals, as it was observed experimentally[20]. The limits of CaS solubility in CaO-Al₂O₃ slags are given by the relation in the fig.5 and can be transformed in the corresponding limits of sulphur solubility. For the considered CaO-

Al_2O_3 slags, the limit of sulphur solubility is 2.092 %mass at $C/A=1.5$ and 1.46% mass at $C/A=1$. It follows that all effects taking into consideration the chemical composition of the slag, must be analyzed under the consideration of the effects due to CaS precipitation as crystals in the slag. In ref.[20] it is mentioned that the CaS precipitation inhibits the generation of interfacial convection. Using the effects of the chemical composition shown in the fig.3 and fig.5 this could be explained by the

strong lowering of the sulphur content in the liquid surrounding the CaS precipitated crystals and the corresponding lowering of the product $X_S \partial \sigma / \partial X_S$ which give a measure of the maximal surface tension decreasing which could contribute to the interfacial convection evaluated as Marangoni effect. This can be seen also on the fig 4. where at lower sulphur contents the decrease of the surface tension is more important than at higher sulphur contents.

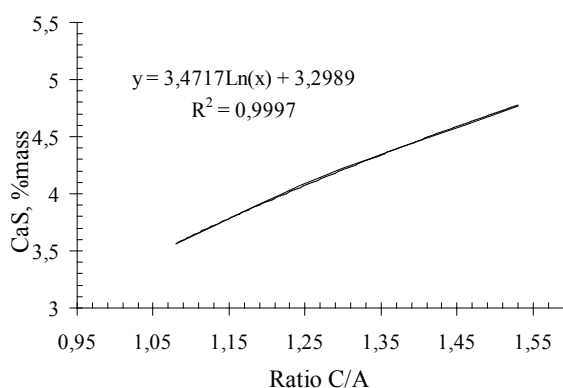


Fig.5. Solubility limit of CaS in slags $\text{CaO}-\text{Al}_2\text{O}_3$ at 1873K, as function of the ratio $C/A = (\% \text{mass CaO})/(\% \text{mass Al}_2\text{O}_3)$, according to experimental values of sulphur solubility from ref.[2]. The equivalent relation of the solubility of sulphur in slag is $(\%S) = 1,5428 \ln(C/A) + 1,466$

Conclusions

The present values of physico-chemical properties of slags in the system $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ are important by their values and influence exerted by sulphur content in refining processes of deoxidization and desulphurization which occur simultaneously and subsequent during steel treatment in ladle reactors and other refining reactors. Based on several values of important quantities and parameters influenced by these properties the processing route and parameters of treatment could be better established to obtain an optimized maximal efficiency in steel refining processes at industrial scale. All these are possible only based on a correct evaluations of the properties presented. Because of some important differences of values found in the literature it is necessary to improve and to

establish standard procedure for measurements of slag properties and not only.

References

- [1]. P.S. Nita, I. Butnariu, N.Constantin, Revista de metalurgia(Madrid), ISSN 0034-8570, vol.46. No 1, 2010, pp.5-14.
- [2]. B,van Muu, H.W.,Fenzke , Freib. Forschungsh. B, Metall. Werkstofftech. Vol. B252, pp. 40-50. 1985.
- [3]. Slag Atlas, 2nd Edition, Verlag Stahleisen GmbH, D-Düsseldorf, 1995
- [4]. P.S.Nita, Materials Science and Engineering A 495(2008), 320-325
- [5]. Mills,K.C., Keene, B.J. International Materials Research vol32,no1-2,(1987),107.
- [6]. J.L. Bretonnet, L.D.Lucas, M.Olette , Circ. Inf. Techn., Cent. Doc. Sider. 33 (1976), 105-108.
- [7]. J.L. Bretonnet, L.D.Lucas, M.Olette C.R. Hebd. Seances Acad. Sci. Vol. 285C, no. 2., 11 July, (1977), 45-47

- [8]. Mukai, K., Kato, Sakao, H., Tetsu-to-Hagane, 59(1)(1973), 55.
- [9]. Elyutin, V.P., Kostikov, V.I., Mitin, B.S., Nagibin, Yu.A. Russian Journal of Physical Chemistry, 43(3)(1969), p.316-319.
- [10]. Shalimov, A.G. *The establishing of optimal parameters of the steel refining process with liquid sinthetical slags in the pouring ladle*. Thesis for Ph. Dr. in Technical Science, Moskow, 1957, cited in: Bornatskii, I.I. D esul'furatsiia metalla, 1970, Moskva, Metallurgiiia, romanian translation-Desulfurarea fontelor si otelurilor, ed.tehnica, Bucuresti, 1972, tab.117, p334.
- [11]. Panov, A.S., Kulikov, I.S., Selev, L.M., Isv.Akad.Nauk SSSR, ot del Teckn.nauk, Metallurgiiia I toplivo (1961)(3), 25-30.
- [12]. Slag Atlas, 2nd Edition, Verlag Stahleisen GmbH, D-Düsseldorf, 1995, fig.9.61.b., tab.9.15, 8.13, 8.14, 8.17.
- [13]. Kozakevich, P. Rev. Metall 51(1954), 571-573.
- [14]. Zhmoidin G.I., Sokolov L.N., Podgornov G.V., Smirnov G.S. Teoriia Metallurgicheskikh Protsesov, (3)(1975), p150.
- [15]. Zelinski M., Sikora B., Pr.Inst.Metall, Zelaza im St.Stasgira, 29(3-4), (1977), p157.
- [16]. El Gammal T., Müllenberg R.-D. Arch. Eisenhüttenw. 51(6), (1980), p221
- [17]. Sikora, B., Zelinski, M, Hutnik 41(9)(1974), p433
- [18]. Hara, S., Ogino, K. Can.Met.Quaterly, 20(1981), 113
- [19]. Dymov, V.V., Baidov, V.V. Sb.Tr.Tsent.Nauch-Issled Inst.Chem.Met. 619(1968), 78
- [20]. Deng, J., Oeters, F. Steel Research 61(1990) 443-448.
- [21]. Öztürk, B., Turkdogan, E.T. Metal Science, vol.15. june 1884, 299-305.

REDUCTION OF ENERGY CONSUMPTION FURNACES HEAT TREATMENT

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ABSTRACT

This paper presents solutions to reduce energy consumption of the furnace heat treatment of metallic materials used in industry. To analyze the various solutions use a mathematical model for the development of these furnaces energy audit. Energy audit contains a description of heat treatment furnace, energy balance measurements for actual preparation for various operating modes, the analysis in terms of furnace operation technology, energy and environmental optimization measures and developing optimized energy balance in accordance with the measures considered.

The mathematical model for the development of energy audit of the heat treatment furnace was transcribed into a Microsoft Excel program, using various measures that can quantify optimization.

An application of this software in a tunnel furnace for heat treatment is presented for operation in real conditions and the conditions under which various measures are taken to optimize: introduction of an air preheater; introduction of a preheater for billets; introduction of a gas-dynamic sealing facilities.

KEYWORDS: energy consumption, furnace, heat treatment

1. Introduction

The metallic materials industry is one of the high energy consuming branches, and the highest part of the energy is required as thermal energy. Efficient energy use in metallurgy is not a simple issue because of high production capacities of industrial installations, as well as because of the complexity of the technological processes that take place. As natural energetic resources are not renewable and more and more expensive, their use needs reconsideration by saving methods, methods to reduce loss and to update energy consuming installations and technologies.

An analysis study of energy consumptions can be conducted based on energy balances, developed for installations, aggregates, technological processes. This analysis, named *energetic audit* as well, aims to set the necessary directions and

measures, technical and organizational, to eliminate and reduce loss and to value secondary energetic resources as efficiently as possible [Gaba A...,2003].

The sector of heat treatment furnaces is included among those with high energy consumptions in the metallic materials industry. In order to reduce the energetic consumptions of heat treatment furnaces, the following measures are considered, falling into two categories in terms of investments:

A. Measures that do not require investments:

- operation with optimal productivities, for which energy consumptions are minimum;
- conducting thermal treatments diagrams according to those set by technology;
- operation with minimum excess air coefficients;

- follow up of furnace operation so as the working openings should be closed as long as possible.

B. Measures that require investments:

- introduction of an air pre-heater or its updating, so as to obtain increased temperatures for pre-heating the combustion air and respectively the fuel, if appropriate;
- introduction of a material pre-heater;
- introduction of a gas-dynamic sealing system for the working openings of the oven;
- replacement of the burner installation with high performance burners (e.g. recuperative), to allow operation with lower excess air coefficients, reducing pollutant emissions at the same time;
- update of the burning process management system and of the furnace automation system;
- replacement of thermal insulation systems based on massive masonry made of refractory bricks by using ceramic fibre-based materials

As thermal treatment furnaces are high energy consuming installations, with high fuel consumption and low efficiency, it is necessary to develop a more detailed analysis for the possibilities to improve operation systems using modern technologies.

The most used analysis method for the processes taking place in a thermal-energetic system is based on energy balance. The purpose of the energy balance is to know the energy flows within the boundaries of the analysed process, in order to find out energy consumptions, useful energy flows and energy losses. By finding out these energy flows, it is possible to set measures to rationalise consumptions or losses, by saving energy for components that allow for proper technical and organizational measures to be applied [Berinde T., 1976].

Optimization of each technological process is based on a mathematical model that must reproduce the respective process as

truthful as possible, the mathematical model is the main element in conducting the process, characterized by two variable values: energy input and output flows [Feldmann V., 1976].

2. Mathematical model description

As the energy balance sets the heat quantities and the technical and economical indexes in detail, it represents the most efficient method to identify ways to save and rationalize the fuel consumption.

The mathematical model of the energy balance for heat treatment furnaces expresses the conservation of energy principle, according to the relation:

$$\sum_{i=1}^a Q_{i_i} = \sum_{j=1}^b Q_{e_j} \quad (1)$$

where Q_{i_i} and Q_{e_j} are input, respectively output heat quantities, as related to the framework set for the balance. The heat quantities Q_{i_i} and Q_{e_j} are calculated with relations found in the specialised literature [1, 2, 3, 4, 5], depending on certain parameters.

By applying the mathematical model, using the parameters measured directly on the operational heat treatment furnace, the actual energy balance is obtained.

The technical and organizational measures resulted following the analysis of the actual energy balance lead to energy saving which, deducted from the energy loss components set in the actual balance, set part of the heat quantities of the optimal energy balance. The other components are obtained from the relation (2):

$$\sum_{k=1}^c Q_{i_k} (C_0) + \sum_{l=1}^{a-c} Q_{i_l} = \sum_{m=1}^d Q_{em} (C_0) + \sum_{n=1}^{b-d} Q_{e_n} \quad (2)$$

where C_0 is the optimal fuel flow.

The quantification of these measures within the energy balance requires laborious calculations, as not only the characteristics

of the furnace, but also the characteristics of thermally treated materials should be considered.

An optimal balance mathematical model for all heat treatment furnaces can be used only if the particularities of each separate furnace are taken into account. This condition is met by the model shown below by using generally valid relations, where certain parameters are found out directly by the model, and the others are found out by each separate furnace by the energetic and technology specialists supervising the respective furnace.

The mathematical model has been designed so as to be used for both continuous and discontinuous running furnaces. Also, the mathematical model takes into account the situations where heat treatment furnaces are provided or not with air-preheating devices, developing both separate balances for the furnace and the recovery device, as well as on the boundary including the furnace and the recovery device together. Based on the data from the measurements performed for the operational furnace and recovery device (if available) and of the other parameters in the calculations, using relation (1), the actual energy balances are developed for the furnace, recovery device and the general balance, setting in detail the input and output heat quantities, the amount of input heat, the amount of output heat and technical and economical indexes, for each separate boundary..

Following the analysis of the actual energy balance, the energetic and technology specialists supervising the respective installation develop an action plan. The measures and actions to save energy are usually proposed in stages, because of financial limits. Following these measures, there are new values resulted for certain characteristic parameters for each installation, which will serve as calculation

data for the optimal energy balance, namely:

- excess air coefficients in the burning installation, at furnace exit, at pre-heater entry, at pre-heater exit;
- preheated air temperature;
- preheated material temperature;
- maximum admitted temperature of the burning gases at pre-heater entry;
- number of open holes;
- opening duration for each hole.

On the other hand, in order to develop the optimal energy balance, the mathematic model contains certain generally valid relations; some of them resulted from the following assumptions:

- burning is complete;
- the air flow introduced in the burning installation is equal to the one exited from the air pre-heater and is found out from the equations of complete burning at the imposed excess air coefficient when entering the burning installation.

Based on these assumptions and on the values of the parameters modified following the analysis of the actual energy balance, the optimal fuel flow is found out from a relation type (2), where the temperature of the burned gas at furnace exit is assumed to be equal to the one in the actual energy balance.

The mathematical model has been transposed into an electronic calculation sheet in Microsoft EXCEL and tested for various types of heat treatment furnaces. The development of this model took into account the possibility to be used for a number of types of heat treatment furnaces as large as possible, as well as the adaptation possibility, by small changes, so as their use for other heating furnaces should be possible. The mathematical model presented allows reduction of the necessary time to develop and analyse the energy balances in order to save energy.

An example of using the energy balance calculation program is presented for a heat treatment furnace.

3. Results of the program for developing energy balances for heat treatment furnace. SCHMIDT

The furnace is especially designed for heat treatment furnace annealing after forging, roller hearth type.

Maximum productivity of the furnace is 2.5 tons / hour.

The fuel used is methane gas.

Maximum working temperature in the furnace is 900 ° C.

Refractory lining is composed of prefabricated molding bricks, bricks of normal standard of sorts stamping materials with sillimanite, hard firebrick, firebrick and refractory easy choice. Insulation around - round insulation is made of bricks: Moller and sealants for stamping. Gas pressure is adjusted with a pressure regulator.

- Combustion gas recirculation is as follows: vacuum heating gas recirculation blower 18 in the ceiling of the oven and return to burner gas channels of the side walls.

As a result of combustion gas analysis taken from different areas such as flue and showed that:

- Combustion gases are removed through the two doors of the oven kept open for passage of material in the flue gas channel found only trace amounts of gas. To determine the average temperature and average analysis of combustion gases

discharged from the oven temperatures were measured and tests were carried out combustion gases discharged through the two ends of the oven, while measuring fuel flow and air introduced into each area and considering the movement of middle oven flue gas to the two extremes.

To achieve optimum performance of the furnace was considered:

- evacuation of combustion gases from the furnace will be made through the flue is fitted air preheater will preheat the combustion air flow required at a temperature of 150 ° C and the increase of excess air coefficient is 0.2;

- flue gas temperature at the entrance to recovery will be 638.5 ° C and air ratio equal to 2.4;

Based on measurements obtained during operation of the furnace, in comparison with the real optimal thermal balance, it appears that the optimal variant, fuel flow drops from 114 m³N / h to 85.971 m³N / h and specific fuel consumption decreases from 85.45 m³N / t to 64 305 MCN / t. In terms of process technology increases the thermal efficiency of 17.08% to 20.6%.

In Fig. 1 presents a comparison between the values obtained for heat between optimal balance, that is real, and in Fig. 2 presents the comparison between the values obtained for Heat output for optimal balance, respectively real.20, 6%

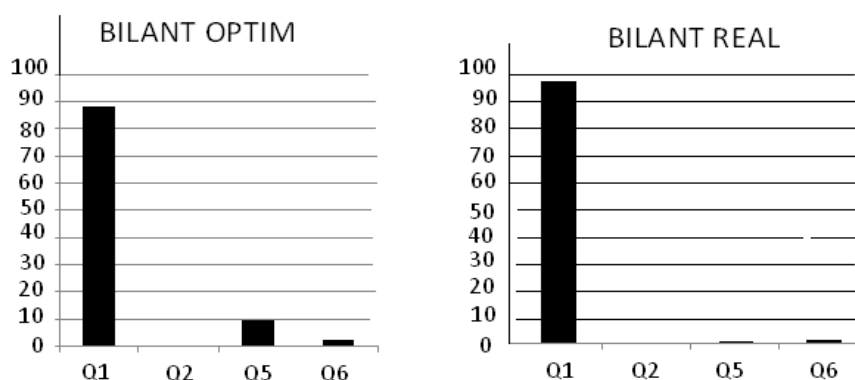


Fig.1. Heat Q values entered into optimal thermal balance, actual respectively

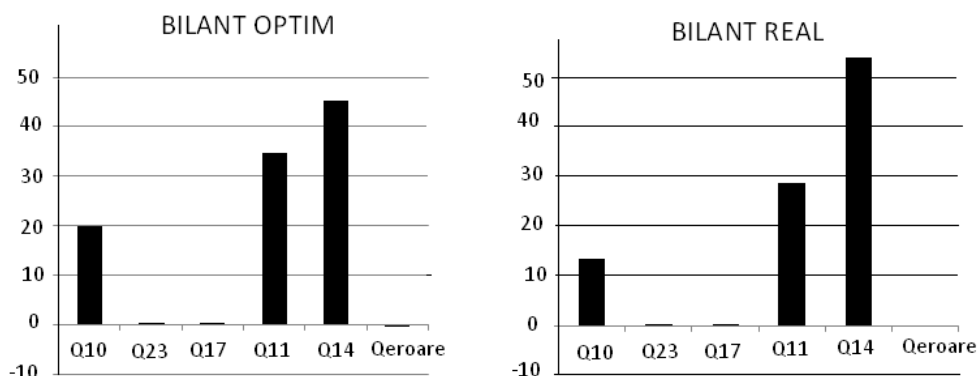


Fig.2. Heat values Q projecting optimal thermal balance, actual respectively
Q1- fuel chemical heat; Q2- fuel sensitive heat; Q3- load physical heat; Q5- total heat introduced by the combustion air; Q7- sensitive heat of the protection gas at the entry; Q10- sensitive heat of the main product at the exit of the actual furnace; Q11- heat lost through walls and hearth; Q13- radiant heat through non-tightened parts; Q14- heat lost at the chimney; Q17- the sensitive heat of the secondary products and auxiliary devices; Q24- sensitive heat of the protection gas at the furnace exit; Qeroare- error when closing the energy balance.

Actual energy balance calculation were made using the mathematical model, based on measurements made on the heat treatment furnace operation Schmidt type. In Fig.3 is presented in the form of seizures in Excel, actual structure of the energy balance for

maximum operating regime of heat treatment furnace itself (without cooling zone, as we intend to highlight effective use of the mathematical model in the analysis of energy saving measures).

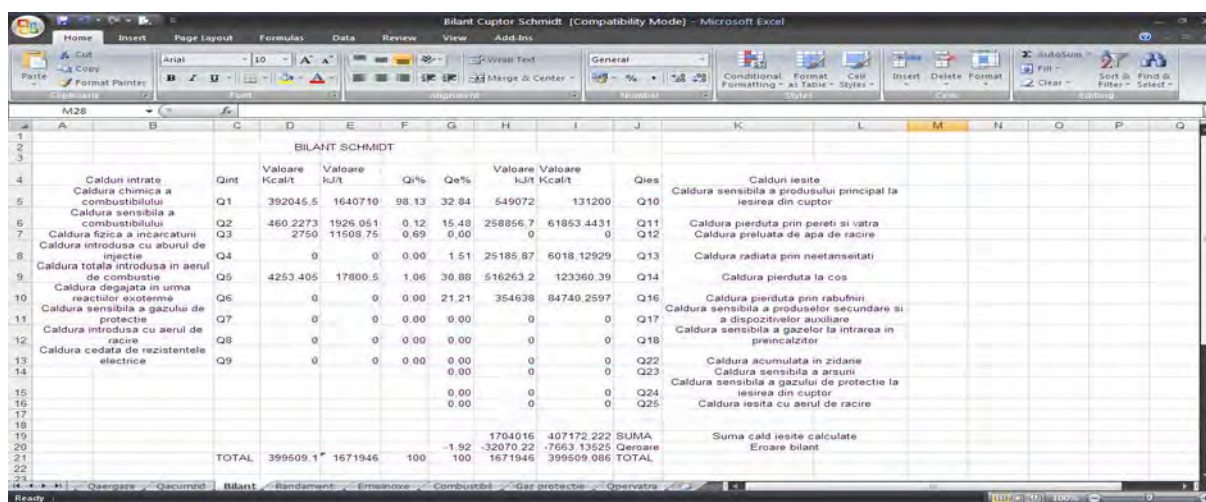


Fig.3. Structure in the form of seizures in Excel, the actual energy balance for maximum operating regime of heat treatment furnace

The analysis of the operation of heat treatment furnace leads to the application of certain measures to reduce fuel consumption that we can quantify by mathematical model application.

Therefore, by applying the mathematical model, under various

operating with excess air ratios, based on the real situation to a minimum excess air coefficient obtained from the best radiant tube burners, energy balances are developed optimal of specific fuel consumption resulting in Fig. 4. Similarly, by introducing a material pre-heater, optimal energy

balances are developed for various material pre-heating temperatures, from where

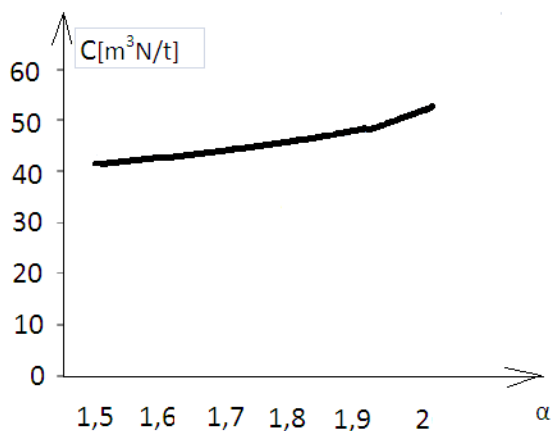


Fig.4. Specific fuel consumption , C , depending on the material pre-heating temperature T

specific fuel consumptions shown in Fig. 5.

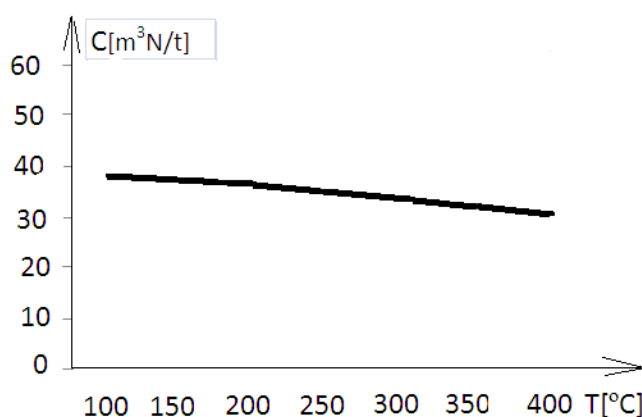


Fig.5. Specific fuel consumption , C , depending on the excess air coefficient α

4. Conclusions

The methods to achieve fuel economy were highlighted based on the mathematical model for calculating the actual energy balance and optimum heat treatment furnaces used in steel construction materials. An application for a continuous annealing furnace, roller hearth, presents actual and optimal energy balance, based on data measured in operation.

Also, by applying the mathematical model, under various operating with excess air ratios, based on the real situation to a minimum excess air coefficient, obtained from the best radiant tube burners, balances are developed resulting energy specific fuel consumption.

Similarly, by introducing a preheater materials, energy balances are developed for

various preheat temperatures of materials, resulting in specific fuel consumption.

References

- [1]. Gaba A., Vâlceanu S., Catangiu A., Paunescu L., 2003, *Auditul energetic în metalurgie*, Ed.Bibliotheca,Târgoviste
- [2]. Răducanu C., Pătrașcu R., Paraschiv D., Gaba A.,2000, *Auditul energetic*, Ed. AGIR, Bucuresti,
- [3]. Berinde T. ș.a.,1976, *Întocmirea și analiza bilanșurilor energetice în industrie*, Ed. Tehnică, București
- [4]. Feldmann V. ș.a., 1976, *Măsuri practice de economisirea combustibilului și căldurii în industrie*, Ed. Tehnică, București
- [5]. Carabulea A. ș.a , 1962, *Modele de bilanșuri energetice reale și optime*, Ed. Academiei, Bucuresti
- [6]. Carabogdan, I.G. ș.a., 1986, *Bilanșuri energetice.Probleme și aplicații pentru ingineri*, Ed. Tehnică, București
- [7]. Badea A. ș.a., 2003, *Echipamente și instalații termice*, Ed.Tehnică, București
- [8]. Marinescu M., Ștefănescu D. ș.a.,1985, *Instalații de ardere*, Ed. Tehnică, București

EXPERIMENTAL BOOTH FOR DETERMINING GAS FLOW USING LOCAL HEATING TRANSITORY REGIME

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ABSTRACT

This paper represents an original research with the goal of applying the impulse method for gas flow measurement problems in special conditions.

Most of the flow measurements use the stationary regime and practically speaking, in many of these cases, there are some interventions in the flow sections with an active element or a special sensor. On that account, for avoiding the above mentioned inconvenient – the distortion of the flow sections - this paper presents an experimental booth proposed to be used for the gas flow measurement in a transitory regime without the above mentioned alteration.

The most important aspect of the experimental work when trying to accomplish a reliable flow measurement is the fact that all the conditions, environmental or non – environmental ones, have to be repeatable; there for, every parameter regarding the experimental part, must be precisely controlled, in this way, the obtained results should be characterized by a continuity, resulting the proper evolution of the works. This approach for measuring the gas flows has, as a central idea, the generation of a heat pulse and the reception of the results – the heat transfer, e.q. the temperature evolution along the flow, in the limit layer of the fluid volume. In this way, the gas flow will be determined without distortion in any way the flow section. This paper will present all the practical aspects and conditions in which this kind of experiments will be held, with all the needed equipments.

KEYWORDS: thermal flow meter, heat pulse, gas flow measurement, transitory regime

1. Theoretical aspects

For testing and calibrating a new gas flow sensor like the one that is currently under development, it is necessary to have an experimental booth that will provide the adjustment possibility for all the conditions and variables according to the original hypothesis.

After studying all the possibilities and variables that can influence the experiment, a first basic theoretical model of how the booth should look like, was proposed according to Figure 1.

All the components of the theoretical booth model will be described further after

presenting the main parts of the test booth.

The booth that is currently under the development for this specific flow sensor has four basic parts:

- The gas source (different gas tanks, for example in our case Oxygen, Nitrogen and Carbon)
- The part for setting all the experimental parameters, like the pressure of the gas inside the installation – consisting of a pressure regulator (that has already incorporated in it a special filter) or the flow of the gas with the help of a special needle valve – extremely precise

- The part for the calibration of the flow sensor consisting of an ultrasonic flow meter (from Bronkhorst in this case); the real gas flow that passes through the installation can be read on the flow meter and is set up by turning the needle valve
- The experimental part that consist of the thermal impulse source and the heating reception device

Many of the mentioned parts for this test booth, for example all of the components for the experimental part, have and will be handmade developed and manufactured especially for this experimental installation.

The figure 1 shows the theoretical approach regarding the experimental booth.

Regarding the list for all the components of this experimental booth theoretical approach, shown in Figure 1, please check the table 1.

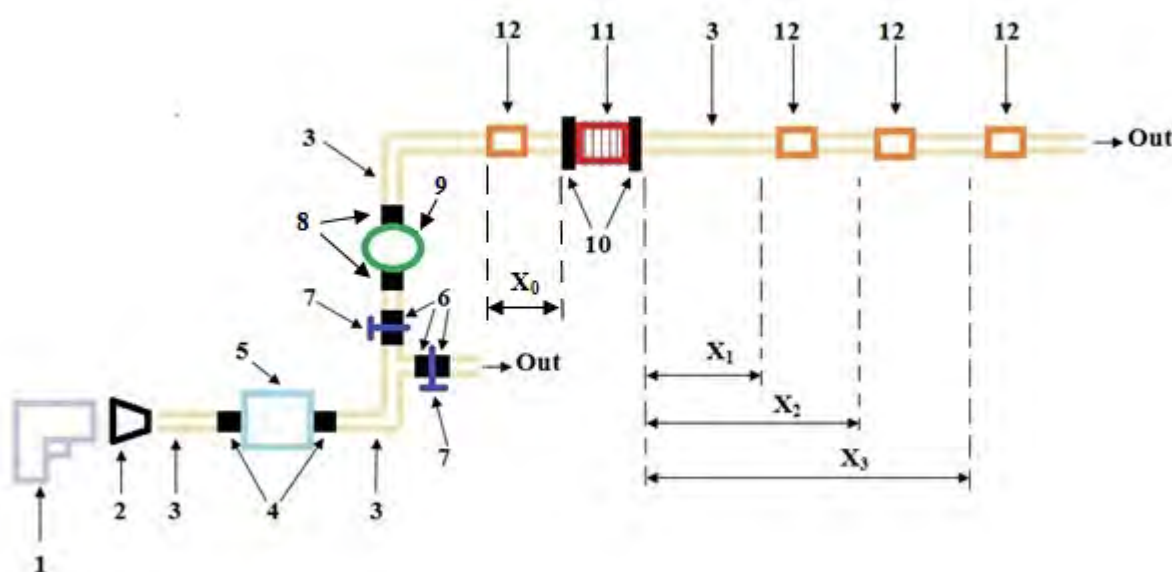


Fig. 1. Gas flow sensor experimental booth theoretical block scheme

Table 1. Theoretical test booth component list with individual description

Part No.	Component with a short description
1	Gas source: in the final stage there will be three 10 liter tanks, one for each gas (O ₂ , Nitrogen and CO ₂)
2	Adaptor between the gas source and the pipe
3	Regular $\Phi 15$ copper pipe
4	Threads or flanges for mounting the pressure regulator
5	A normal gas pressure regulator (preferably with built in filter) used for keeping the pressure in the installation constant

6	Threads for mounting the valve taps
7	Regular valve taps
8	Threads or flanges for mounting the gas flow meter
9	Regular gas flow meter used for calibrating the new sensor that is desired to be developed, in this case the flow meter is a mass flow meter from Bronkhorst tested to pressures up to 8 Bar
10	Flanges used especially for thermal isolation
11	Thermal impulse source that is a heating ring controlled by pulses made out of resistive materials that can support high temperatures

12	Detecting thermal pulse element, a special sensor that detects the heating impulse in the gas volume (thermocouples or special sensors)
X_0 , X_1 , X_2 , X_3	Distances between the thermal pulse source and the detecting element, distances well known after solving the mathematical model which describes the entire phenomena regarding the simple working principle of this flow sensor that is under development

2. Work in progress

As usual the practical approach for this experimental booth is a little bit different from the theoretical approach because of the specific used equipments.

At this time, no gases are used with this booth, only air. It is done in such a way for validating first the working principle of this new flow sensor and only afterwards to start doing the calibration of the new flow sensor for each gas type separately (Oxygen, Nitrogen and CO_2). For this matter, one of the gas sources at the moment is represented by a medical equipment that gives out an electronically adjustable air flow. The best air source that is used now, is an aquarium pump that gives a maximum flow of 15 liters per hour. Both of the mentioned equipments have a constant output pressure, so there's no need for the pressure regulator at the moment.



Fig. 2. The air sources

For having a specific flow through this installation, a special high precision needle valve is used before the flow meter. The real air flow is read with the help of a ball flow meter (specific for air, of course, up to 20 liters per hour) and is adjusted by turning the needle valve until the desired flow in the booth is reached.



Fig.3. The needle valve and the ball flow meter for the flow adjustment

Referring to the experimental part of this booth, everything is like in theory. First there is a 100 – 150 mm part for having a laminar flow inside the pipe. The length of this part is usually six times the inside diameter of the pipe (in our case $6 * 15 \text{ mm} = 90 \text{ mm}$), but the longer the better.

After that comes the thermal impulse source – a heating ring like a coil made out of a resistive wire.



Fig. 4. The thermal impulse source

It can heat up the stationary air inside it up to 120 degrees Celsius (more than sufficient for this application) in less than 50 seconds when having a power source of 20 Watts (20 Volts, 1 Amp).

The power source must be a time controlled one for the thermal source to generate heat pulses, not in a continuous way. For that matter, it is used a special source from Leaptronix that can be controlled by a PC with the help of Lab VIEW through a RS 232 port. The programme developed in Lab VIEW sets the duration of the time on and time off for the power source as a repeating cycle, thus generating the heat pulses from the thermal source.

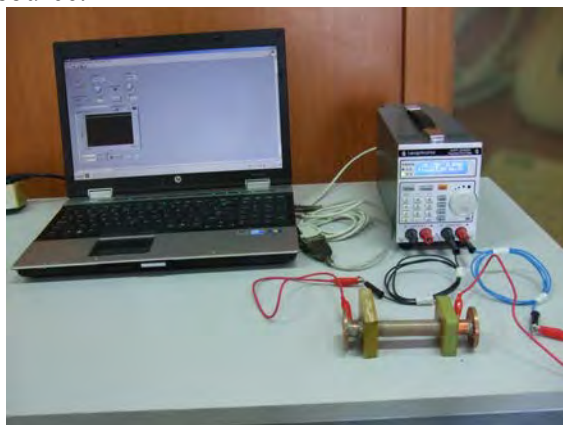


Fig. 5. The Lab VIEW controlled power source for generating the thermal pulses

After the thermal impulse source, there is the measurement part, where the temperature of the gas is measured in two or three specific points (located at a determined distance one from another) with the help of type K thermocouples, thus obtaining the raw data from which the flow will be calculated.

The only inconvenient regarding the experimental part was the fact that after some temperature measurements with an InfraRed Camera, isolation was needed.

Because the heat would transmit from the thermal source to the measurement part through the pipe walls, instead of determining the heated gas temperature, the

measured temperature was from the pipe walls.

This problem was solved by isolating the thermal source from the other parts, first of all from that 150 mm part for the laminar flow and second from the measurement part.

Two solutions were put to practice:

- The first one was to build flanges and between the flanges to put an isolation made out of Teflon
- The second one was to build out of Teflon special sleeves, for the parts not to have direct contact

Of course, in both cases the flow is undisturbed, still laminar, and also another thermal pulse source (heating ring like a coil) was built as a duplicate.



Fig. 6. The two experimental parts (one with flanges and the other one with sleeves)

3. Future work

Future work consists of working and testing the sensor and calibrating it for each of the three gases: Oxygen, Nitrogen and CO₂.

For that matter, first of all, the gas source will be a 10 liter tank for each gas separately (already bought from the company Tehnic Gaz Buzau); each gas tank has its own pressure reducing valve so the pressure regulator will not be needed. Second of all, the actual flow meter will be replaced with another ball flow meter according to the gas that will be used for experiments. The three flow meters (one for Oxygen, one for

Nitrogen and one for CO₂) will be provided by the company UTTIS Industrial Furnaces – Bucuresti, member of CECOF – European Committee of Industrial Furnace and Heating Equipment Associations.



Fig. 7. The three 10 liters gas tanks (Oxygen, Nitrogen and CO₂) with their valves

Another development for this experimental booth will be regarding the temperature measurement. A new equipment developed by the company National Semiconductor will be used for the automated DAQ part when wanting to measure the gas temperature. This equipment supports easily three K thermocouples that measure different temperatures simultaneously.

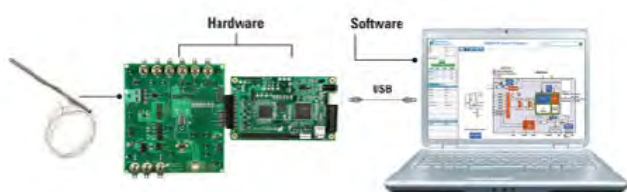


Fig. 8. National Semiconductor board

Also, instead of using K thermocouples for measuring the temperature, some new CRZ high tech temperature detectors from Hayashi Denko CO, Ltd Tokyo Japan will be used. The main advantage with these new sensors is represented by their dimensions,

they are very small (3 – 4 mm) and also very accurate. And already some measuring tests were done with the board from National Semiconductor and these temperature detectors and the results were good.



Fig. 9. The experimental booth

Acknowledgment

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References

- [1]. Gheorghe, G. (1978) *Masurarea debitelor de fluide*, Bucuresti: Editura Tehnica
- [2]. Iamandi, I., Petrescu, V., Sandu, L., Damian, R., Anton, A., Degeratu, M. (1985) *Hidraulica instalatiilor: Elemente de calcul si aplicatii*, Bucuresti: Editura Tehnica
- [3]. Motit, H., M., Ciocarlea – Vasilescu, A. (1988) *Debitmetrie industrială*, Bucuresti: Editura Tehnica
- [4]. Stefanescu, D., Marinescu, M., Ganea, I. (1986) *Termogazodinamica tehnica*, Bucuresti: Editura Tehnica
- [5]. Koizumi, H., Serizawa, M. (2008) *A microflowmeter based on the velocity measurement of a locally accelerated thermal flow in an upwardly directed Hagen – Poiseuille flow* Elsevier
- [6]. http://daniel-clark.net/documents/flow_meter.pdf

AN EFFICIENT TECHNOLOGY TO OBTAINING THE ALUMINIUM MASTER ALLOYS WITH REACTIVE ELEMENTS FOR ADVANCED REFINING OF THE FERROUS BATHS

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ABSTRACT

The favorable effect of aluminium and other reactive elements as simple deoxidizers for refining steel baths is known. By other hand the aluminium used as refining for ferrous baths present some difficulty. Also the literature references have shown once again that are effects obtained from the combined addition of two or more refining elements as complex deoxidizers. The obtaining of the complex aluminium alloys containing reactive elements by an efficient technology is difficult. In this paper is presented the solution for the making technologies of FeAl, FeAlMn, FeAlSiMn alloys. The maximum assimilation yields of elements at making aluminium alloys are ensured. Also this efficient technology allows the superior valorization of metallic scraps into products with added value.

KEYWORDS: aluminium master alloys, deoxidizer, reactive elements, silicon, manganese

1. Introduction

The increasing demands for products specification makes any non-metallic inclusions present in steel an important issue during the steelmaking process. There is a way to reduce the disadvantageous effects of non-metallic inclusions on the steel properties. The modification of inclusions create excellent conditions for its floating up and dissolving in the slag by the change in chemical composition of non-metallic inclusions during the steelmaking process. This can be achieved by steel treatment with deoxidizers with controlled composition. The literature references have shown once again that are effects obtained from the combined addition of two or more refining elements as complex deoxidizers are often greater than the added effects of the individual elements. In this case, the use of the aluminium alloyed with reactive elements is more effectively than the

singular elements addition. If alloying elements are simultaneously present in deoxidizers and these have a determined chemical composition in accordance with the utilization purpose, the refining capability of each element is increased because the complex non-metallic inclusions are formed and, the thermodynamic activity of each element that is present in the deoxidizing products is lower than their activity in the pure oxide. By this way, at equilibrium for a stable temperature, the oxygen content of the molten steel is lower [1, 2].

By other hand the aluminium used as refining for ferrous baths present some difficulty. The main problem of aluminium as a deoxidizer is the control of steadfastness of the refining process. The low density of aluminium, comparable with density of the steel and the slag, determines its float up and interaction with oxidizing atmosphere. As result the utilization yield of aluminium for refining action is low and variable. In

respect to aluminium the positive effect of complex refining alloys is explained by effect of the alloying elements on the aluminium deoxidizer properties. Especially the density and thermodynamic properties of the deoxidizers are improved. Also for refining process at utilization of these

complex alloys allows the modifying of the chemical composition for the deoxidizing products into wished direction [3].

The chemical composition for refining alloys used in the steelmaking practice is presented in Table 1 [4].

Table 1. Complex aluminium alloys for steel refining

Alloy	Chemical composition, %wt			
	Al	Mn	Si	Fe
AlFe40	20-50	-	-	Balance
AlFeMn15	10-20	45-75	-	Balance
AlFeMnSi	~10	40-60	15-20	Balance

In this paper is presented an efficient technology for making the alluminium master alloys. Simple aluminium alloys Al-Fe alloys and Al-Fe-Mn, respectively Al-Fe-Mn-Si as complex aluminium master were obtained. This is different from classical technology that is based on e lement extraction from raw material by carbothermal or metalothermal reductions in specifically electrical arc furnace. Moreover by this way lead at valorization of aluminium scraps and at increasing their recovery ratio into new materials with added value. The homogeneity of these alloys was confirmed by their phase structure.

2. Experimental method and materials

An efficient technology for obtaining the aluminium-iron alloys simple or alloyed with certain reactive elements is proposed.

This is based on the mixing the reactive elements in the aluminium liquid keeping a certain order and controllable parameters. The crucible induction furnace with neutral lining was been used. The following alloys were obtained: FeAl, FeAlMn, FeAlSiMn. The starting materials used were the aluminium scraps (premelted and casted as ingot) and steel scraps (obsolete scraps from steel sheets with following average chemical composition 0.15 %C, 0.48 %Mn, 0.20 %Si, 0.022 %S, and 0.028 % P). Also, the ferromanganese (minimum 80.00 %Mn, maximum 0.5 %C, 2 %Si, 0.03 %S, and 0.3 % P) and silicon-manganese (60-65 %Mn, 10-26 %Si) are added for obtaining FeMnAl, FeMnSiAl alloys. The diminishing the oxidation process of aluminium and the facility to remove the slag require the utilization of the protection flux. Its chemical composition is given in Table 2.

Table 2. Chemical composition of the protection flux for aluminium bath, %wt

NaCl	Na ₂ SO ₄	CaF ₂	Na ₃ AL F ₆	CaCO ₃	Na ₂ SiF ₆
40	20	25	5	5	5

3. Results and discussion

The obtaining of the complex aluminium alloys with controllable properties and content of reactive elements

is based on the ability to add these reactive elements and to adjust the chemical composition of aluminium alloys at melting. The correlation between the characteristics of aluminium, iron and the reactive elements

as solubility, oxidability, melting point etc. must be considered. Also technological parameters of making alloys must be accounted in the process.

Like as deoxidizing steel process with aluminium the main challenge for making process of the aluminium alloys is the assimilation of aluminium. The lower density of aluminium and the melting temperatures of aluminium and iron that are very different negatively influenced the making process of Al-Fe alloys. By other hand the aluminium display a higher tendency to oxidation concomitantly with

the increasing of the temperature. For this reason the melting of the aluminium solid in the iron bath lead to less assimilation yield of aluminium in the Al-Fe alloys. To obtain higher values of this parameter is necessary to establish the optimum flow sheet of making alloys (especially the introduction of the input materials components in the crucible of furnace). It is most important to take into account other properties of these elements. In this case most important is the solubility of Al in Fe. This can be analyzed from phase diagram of the binary system Fe-Al that is shown in Figure 1.

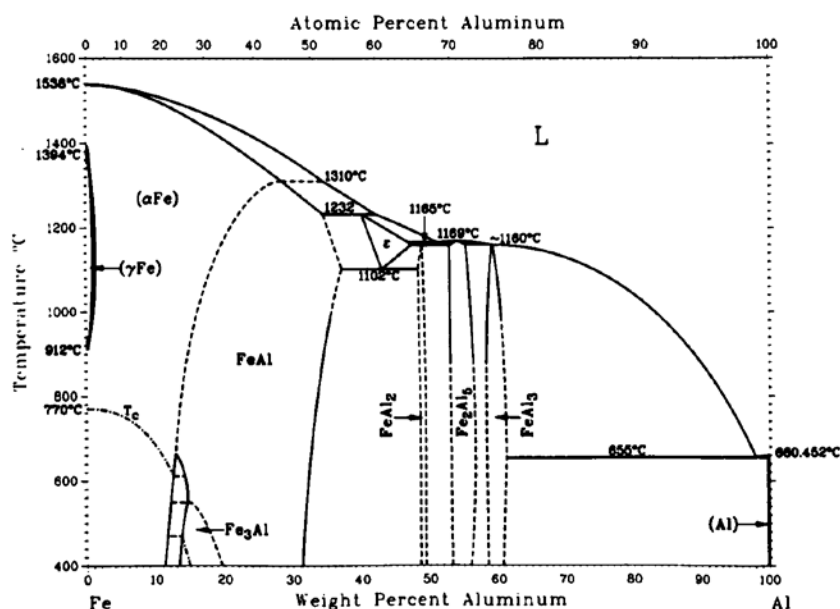


Fig. 1. Binary phase diagram of Fe/Al system [5, 6]

On the left hand side of the diagram it can be seen that the solubility of Al in Fe is in the range of several percent. Between Al and Fe there is a large mutual solubility, forming solutions with lower melting temperatures comparatively with melting temperature of Fe.

In accordance firstly a melt from the easier melting fusible component was obtained. At controllable temperature is immersion and melted in this bath in order other materials as ferrous scraps and then ferromanganese/silicon-manganese, Fig 2.

In the crucible of the furnace for starting an Al ingot is inserted. The

aluminium bath must be heated to controlled temperature to forestall unnecessary energy consumption, to hinder excessive oxidation and the gases saturation. The temperature recommended is $\sim 750^{\circ}\text{C}$. To protect the aluminium bath to interaction with atmosphere the protective flux must be added. Its quantity was established at range of 2...3% in relationship with the of aluminium ingot weight: 2/3 of this quantity was added along with input material and 1/3 on the surface of the aluminium bath. The gradually immersion of the preheated steel scraps starting when the aluminium bath has approximately 750°C .

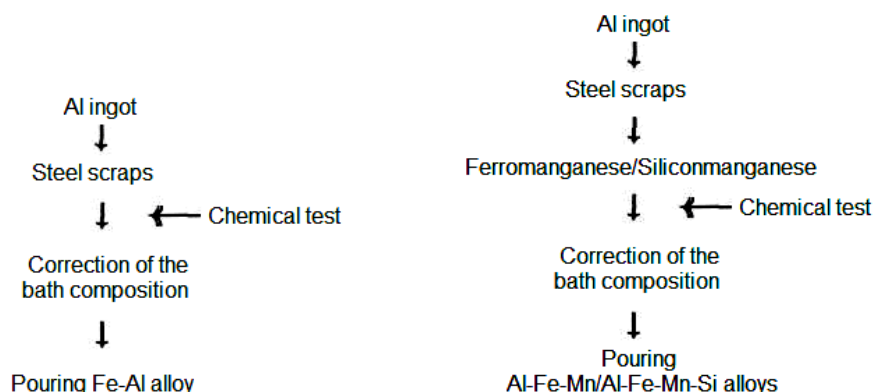


Fig 2. Flow of input materials to obtaining Fe-Al and Al-Fe-Mn alloys

In accordance with the solubility of Al in Fe, at this temperature the steel scraps that are mixed in the melted aluminium have been progressively dissolved into aluminium bath. Must be considered that before introduction into aluminium bath the steel sheet scraps were heated to 150-200 °C. The complete melting of these scraps occurs in the range of temperature 750-1250 °C. In these temperature conditions and with assistance work of the protective flux the assimilation degree of aluminium into Al-Fe alloy was higher (~85%). If is necessary to obtain the AlFeMn or

AlFeMn-Si alloys the ferromanganese or silicon-manganese were further immersed in the Al-Fe bath. For all alloys argon must

be used as degassing gazeous agent that has been blows in the melted alloys. The following parameters for blowing of the argon are imposed: pressure of argon 0.3 ... 0.5 daN/cm² and the volume of gas 2 ... 3 times the volume of subjected alloys.

The AlFe, AlFeMn and AFeMnSi alloys were obtained by respecting the parameters of technology that were before established. These are: input materials, flow sheet of process, and technological parameters (range of temperature, preheatings, argon for blowing, flux).

The chemical composition of some complex aluminium alloys obtained by this technology is given in Table 3.

Table 3. Chemical composition of complex aluminium alloys

Alloy	Casting temperature, °C	Chemical composition of alloys, %wt				Recovery yield of elements, %		
		Al	Mn	Si	Fe	Al	Mn	Si
Al-Fe	1230	40.81	-	-	balance	89.25	-	-
	1230	39.88	-	-	balance	86.33	-	-
Al-Fe-Mn	1490	10.34	55.23	-	balance	90.78	88.73	-
	1520	15.15	60.61	-	balance	87.97	87.68	-
Al-Fe-Mn-Si	1470	10.02	40.76	20.59	balance	90.34	97.21	85.45
	1490	9.95	40.80	20.83	balance	86.92	95.07	84.87

The homogeneity of the alloys obtaining was tested by chemical analyzes. Also this can be confirmed by

microstructural aspects. The microstructures of the aluminium alloys were discussed based on phase diagram of Al-Fe, Al-Mn-Fe

and Al-Mn-Si-Fe systems [5-8]. These are

presented in the Figure 3.

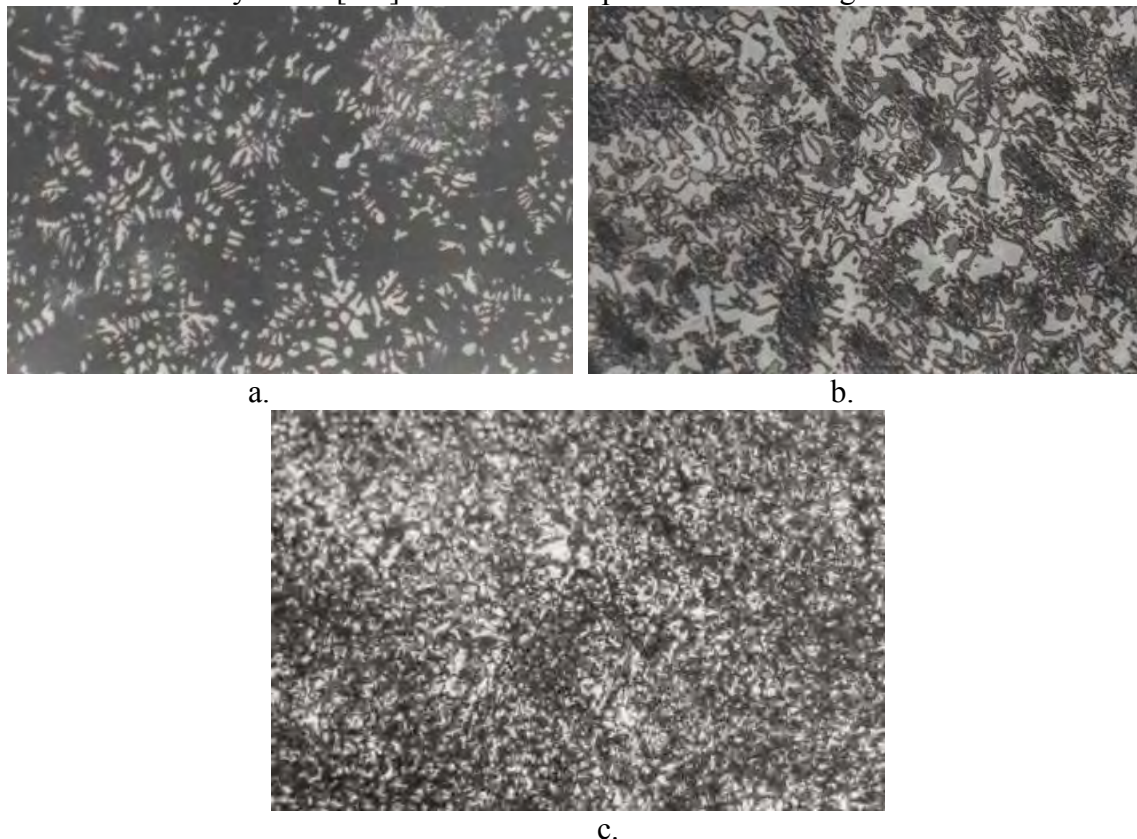


Fig. 3. Microstructure of alloys obtained (X150): a. FeAl, b. FeAlMn, c. FeAlMnSi

In correlation with the binary phase diagram of Fe/Al system the structure of this alloy is formed by α phase, eutectoid $\epsilon + \xi$ and ξ compound with a dendrite morphology. For AlFeMn alloy the solid solution, the eutectoid $\beta_{Mn} + \kappa$ and ξ compound with the dendrite morphology are present in the structure. The micrograph of AlFeMnSi alloy put in evidence the presence of the Fe_5Si_3 as binary compound and $Al_5Mn_{12}Si_7$, respectively Al_4Si_2Fe as ternary compounds.

4. Conclusions

The making technologies proposed in this paper require the physical, chemical and technological conditions to develop an optimum technological process.

This technology is more flexible because it can be regulated of specific conditions (input materials, furnaces) own to

each manufacturer. It is possible the production of these alloys into wished quantities. Also this has the possibility to adapt their chemical compositions in correlation with the metallurgical processes and properties of the steels. This is predictable, ensures the steadfastness of chemical composition.

The maximum assimilation yields of elements at making aluminium alloys are obtained. Also the complex composition of the alloys ensures higher using yields of the reactive elements at refining of steels.

This efficient technology allows the superior valorization of metallic scraps into products with added value.

References

- [1]. Fruehan R.J. *Making, Shaping and Treating of steel, Steel making and refining volume*, 11th Edition, AISE Steel Foundation, ed. United states steel. Co, 1998, p.767

- [2]. **Patent 5037609**, *Material for refining steel of multi-purpose application*, United States
- [3]. **Ciocan A.**, *Superior valorization of the metallic scraps for obtaining complex aluminium master alloys used in advanced refining of the steels*, Proceedings of Metal 2010, 18. - 20. 5. 2010, Roznov pod Radhostem, Czech Republic
- [4]. **Ciocan A.**, *Researches about new materials with content of reactive elements for the advanced refining of the steels*, PhD These, University "Dunărea de Jos" of Galați, 1994
- [5]. **Palm M.** *Concepts derived from phase diagram studies for the strengthening of Fe-Al-based alloys*, Intermetallics, Volume 13, Issue 12, December 2005, pages 1286-1295
- [6]. **Kubasciewski O.** *Iron—binary phase diagrams*, ed. Berlin: Springer, 1982
- [7]. **Raghavan V.**, *Al-Fe-Mn (Aluminum-Iron-Manganese)*, J. Phase Equilibria, Vol 15 (No. 4), 1994, p 410-411
- [8]. **Liu X.J., Hao S.M., Xu L.Y., Guo Y.F., and Chen H.**, *Experimental Study of the Phase Equilibria in the Fe-Mn-Al System*, Metall. Mater. Trans. A, Vol 27A, 1996, p 2429-2435

WAYS OF WORKING THE DATA OBTAINED THROUGH SEM TECHNOLOGY

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ABSTRACT

The article presents a series of methods of working the data obtained through Scanning Electron Microscopy technology. It shows the way in which the obtained data can be used and read through the Labview programming language. Emphasis is also laid on a series of advantages resulting from scanning by the direct contact or the non-contact method. SEM consists of a sharp microfabricated tip attached to a cantilever, which is scanned across a sample. The deflection of this cantilever is monitored using a laser and photodiode and is used to generate imaging or spectra of the surface. The SEM works in a number of different modes

KEYWORDS: technology, Scanning electron microscopy

1. Introduction

Scanning Electron Microscopy is a powerful surface analytical technique used in air, liquid or vacuum to generate very high-resolution images of a surface and can provide some topographic, chemical, mechanical, electrical information [15]. An SEM consists of a sharp microfabricated tip attached to a cantilever, which is scanned across a sample. The deflection of this cantilever is monitored using a laser and photodiode and is used to generate imaging or spectra of the surface. The SEM works in a number of different modes [15]. These include: **Contact mode.** The tip is kept in constant contact with the sample (with a force range of 1-1000 nN, it may be used with hard materials) and provides the basic mode for topography [15]; **Force modulation mode** The tip is kept in contact but a modulated signal is also applied which gives information on dynamic responses from surfaces. Phase and stiffness imaging are extracted from the modulated response signal. This is conducted in the frequency ranges of 10-20 kHz and 400-1000 kHz and modulation forces of

around 100 pN - 500 nN [5]; **Intermittent and non-contact imaging** The tip is oscillated normal to the surface enabling soft materials to be imaged for topography. This eliminates much of the shear force involved in the contact mode. Phase images are also taken in this mode [15]; **Force versus distance spectroscopy** The AFM applies forces from 50 μ N to 5 pN Newton to one spot on a surface to analyse material mechanical properties at surfaces. It either pushes into the surface to measure nanomechanical properties of a surface such as modulus and adhesion or pulls away from the surface for example to measure the forces associated with unfolding of proteins or the breaking of individual covalent bonds [15]. The hysteresis of the scanner can be controlled by use of closed-loop sensors. The deflection of the cantilever is measured using a laser and a position sensitive diode. The force acting on the sample is calculated from the product of the cantilever spring constant and the cantilever deflection.

The example below is a simple force-distance curve on a piece of silicon wafer [15].

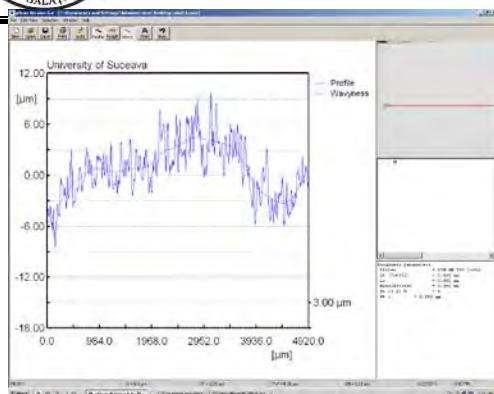


Fig. 1. A simple SEM force-distance curve on a silicon wafer

When a tip is far away from the surface no forces act, as the tip approaches a sample it experiences an attractive van der Waals force until it snaps onto the surface. [15]. For studies in ambient conditions this is promoted by a small neck of water, which condenses at very small separations. As the tip moves further the cantilever is deflected by the sample. As the tip is withdrawn, the small capillary layer of water and organics on the sample surface hold the tip longer than expected until the snap-out point is reached. This snap-out displacement is dependent on several factors such as the tip size, and the nature of the surface and ambient environment [15].

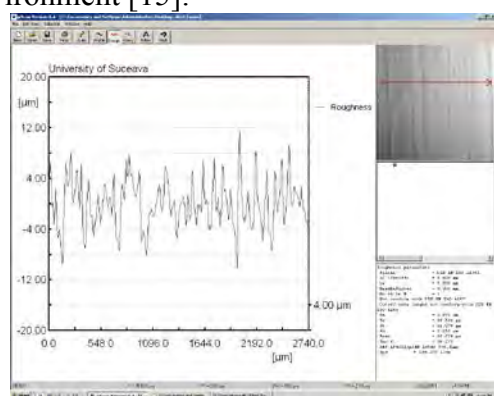


Fig. 2. Zoomed in region of a force-distance curve showing the snap-in event.

Thermally sprayed coatings are now used extensively in a variety of applications. However, their application has often preceded detailed knowledge or understanding of their corrosion mechanisms or rates. Previous studies involving plasma sprayed coatings [15] have shown that good

quality coatings, in terms of low porosity, are essential to protect the substrate from corrosion. There are many thermal spray processes available to date: the high velocity oxygen fuel (HVOF) process, which uses higher exhaust velocities and lower flame temperatures than other processes, can produce coatings of low porosity levels (1%) and avoids alteration of the mechanical properties of the substrate [7]. The corrosion characteristics of thermal sprayed coatings in static saline environments are extremely important where the flow of aqueous solution over components intermittently ceases. It has been established [1; 2] that where coatings are applied by a high-quality process and under stringent quality control procedures, the coatings can provide a very effective barrier to the substrate and prevent any corrosion from occurring. In this situation, however, it is very important to appreciate that corrosion of the coating can occur and that initiation and propagation of corrosion, associated with microstructural features of the composite system, are a real issue. For improvements to the coating corrosion resistance to be made, a full understanding of the corrosion rates and mechanisms, and in particular the substance of the metallic binder (in cermet systems), is required. In addition, an understanding of static corrosion behavior can help reveal the mechanisms of the coating degradation in erosion-corrosion environments. [9,10]. This article investigates the corrosion rates and mechanisms of two HVOF coatings (WC-Co-Cr and WC-Co).

2. Experimental procedure

Two HVOF sprayed coatings are studied in this work: a WCCo-Cr coating with nominal composition 86%WC10%Co-4% Cr, and a WC-Co coating with a nominal composition 86% WC-14% Co. The coatings were applied to a stainless steel substrate (UNS S31603). Specimens were soldered on the rear side to an electrical conducting wire and subsequently encapsulated in nonconducting resin. The exposed coated face of the specimen was then ground with

silicon carbide abrasive papers and polished to a 6 μm diamond finish. The main seawater constituents were 19300 ppm chloride, 11 000 ppm sodium, 2700 ppm sulfate, 1300 magnesium, 400 ppm calcium, 400 ppm potassium, and 150 ppm bicarbonate ions. The specimen-resin interfaces were sealed using Lacomit varnish (Agar Aids, UK) to prevent interference from the substrate. Electrochemical monitoring was carried out with a standard three-electrode cell, comprising a platinum auxiliary electrode and a saturated calomel reference electrode (SCE). Direct current (DC) anodic polarization tests were carried out after 1 h immersion in the seawater at 18 and 50 $^{\circ}\text{C}$. The seawater was left open to the atmosphere. Fig.1. Anodic polarization curves in static artificial seawater at 18 $^{\circ}\text{C}$ on WC-Co-Cr and WC-Co HVOF sprayed coatings. The potentiostat was used to scan the electrode potential of the coating samples from the free corrosion potential (E_{corr}) in the positive (anodic) direction until a current in the range of 500-700 $\mu\text{A}/\text{cm}^2$. In addition, an atomic force microscope (SEM) was used to map the topography of the coatings during accelerated corrosion tests. The SEM was configured to probe the surface under water and to record images during anodic polarization tests. Each image took 6 min to produce, during which time the potential had shifted by approximately 90 mV.

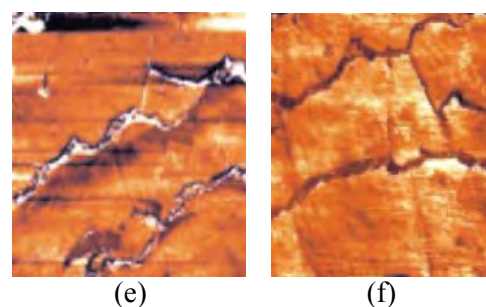
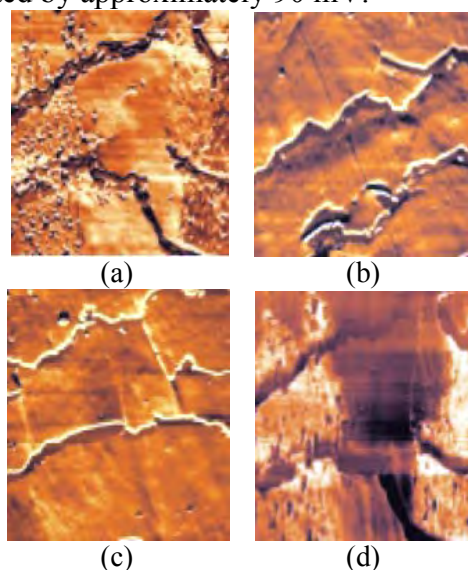


Fig 3. In situ SEM images (a) Polished coating prior to polarization; (b) points A to B; (c) points B to C; (d) points C to D; (e) points D to E; and (f) end of anodic polarization.

3. Results

During the decrease in current (points B to C), the matrix is dissolving at a steady rate, defining the hard phase particles more clearly (Fig. 3c).

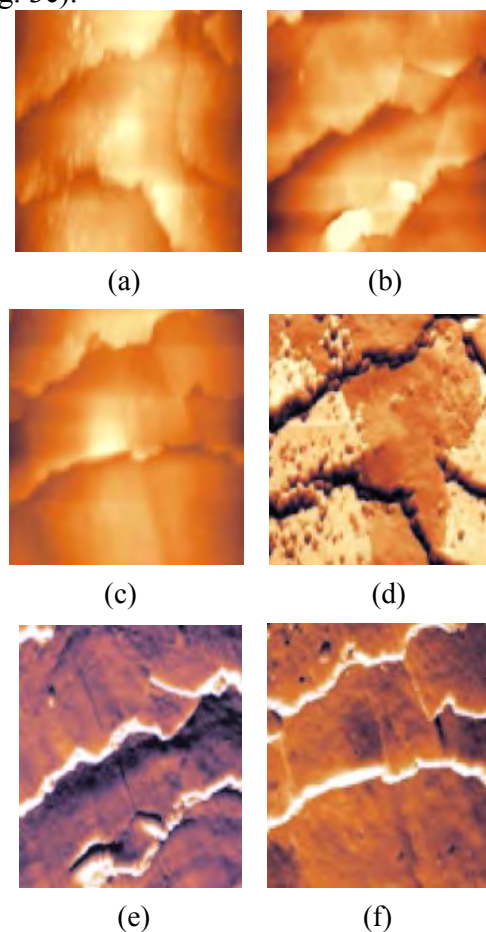


Fig. 4. In situ SEM images (a) Polished coating prior to polarization; (b) point B; (c) point C; (d) point D; and (e) end of anodic polarization.

As the current increases (points C to D in Fig. 3d), the matrix dissolves further, revealing the smaller hard phases from point D to E (Fig. 3e). At the end of the anodic polarization, areas where the matrix has dissolved in some regions and areas of attack around the matrix-hard phase interface can be seen (Fig. 3f). In a similar manner, the corrosion mechanisms during anodic polarization of the WC-Co-Cr coating were examined. Figure 4(a) shows the coating at the free corrosion potential with the light grey hard phases encased in the darker grey matrix. The rapid increase in current with the potential corresponds to dramatic matrix dissolution and leaves the hard phase protruding from the matrix (Fig. 4c). As the current stabilizes at point D, carbides begin to fall out from the matrix and leave voids behind (Fig. 4d). This progresses until the end of the scan at point E, where the matrix consists mainly of voids left by the carbide particles and a few carbides on the next layer are visible (Fig. 3e). After immersion in seawater for 1 h at 50°C, the kinetics of the anodic polarization processes are accentuated on both coatings.

4. Conclusion

The use of an SEM can aid the determination of corrosion mechanisms on a microscale. The addition of chromium to a cobalt matrix increases the corrosion resistance of a W C-based HVOF sprayed

cermet coating and its extent of this has been quantified. Although the WC-Co-Cr coating undergoes more localized attack at 18 °C, accentuated at the hard phase-matrix interface, the WC-Co has more uniform corrosion affecting the entire matrix. An increase in temperature results extensive dissolution of the cobalt matrix, whereas on the CoCr matrix more severe attack is further localized in regions not associated with any specific microstructural features.

References

- [1]. S.T. Tsai and H.C. Shih: *The Use of Thermal-Spray Coatings for Preventing Wet H₂S Cracking in HSLA Steel Plates*, Corros. Prev. Control, 1997, 44, pp. 42-48;
- [2]. R.J. Duncan and C.B. Thompson: "A Guide to Weld and Thermal Spray Hardfacing in the Pulp and Paper Industry. Part 2: Applications," Mater. Des., 1991, 11, pp. 71-75;
- [3]. C.B. Thompson and A. Garner: "Identification and Control of Wear in the Pulp and Paper Industry," Pulp Paper Can., 1986, 87, pp. 53-56;
- [4]. L. Pejryd, J. Wigren, D.J. Greving, J.R. Shadley, and E.F. Rybicki: "Residual Stresses as a Factor in the Selection of Tungsten Carbide Coatings for a Jet Engine Application," J. Therm. Spray Technol., 1995, 4, pp. 268-74;
- [5]. G. Binnig, C.F. Quate, and Ch. Gerber, *Scanning Electron Microscopy*, Phys. Rev. Lett. 56,930-933 (1986).
- [6]. G. Binnig, H. Rohrer, Ch. Gerber, and E. Weibel, *Surface studies by scanning tunneling microscopy*, Phys. Rev. Lett. 49, 57-61 (1982);
- [7]. M. Drozdov, G. Gur, Z. Atzmon, and W.D. Kaplan *Microstructural Evaluation of Al-Cu Intermetallic Phases in Wire-Bonding*

FLUX AGGLOMERATED FOR CHARGING WITH CIF OF SOME SURFACES RESISTANT TO USAGE

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ABSTRACT

The solid fluxes used in superficial hardening processes of steels using melting procedure with high frequency currents (CIF) have two purposes: to pickle and to alloy. The alloying processes are complex and differentiated depending on the pursue purpose. Thus, the enrichment of the usage layer with chrome and carbon is sufficient for accomplishing a good resistance to reduced stresses of usage by abrasion under charge, while adequate complex compositions are necessary for other types of usage. The flux achieved by the research team is used for hardening the active surfaces of tools by cold pressing processes, tools made of carbon steels, stressed by abrasion under medium pressure.

KEYWORDS: granular flux, usage of resistant surfaces, sediment

1. Introduction

The flux achieved by the research team is used for hardening the active surfaces of tools by cold pressing processes, tools made of carbon steels, stressed by abrasion under medium pressure.

In order to achieve this goal, I chose to obtain an agglomerated magnetic flux made of chrome carbides, metallic chrome, titan and graphite, having well determined proportions and a fluoroboric deoxidizer.

1.1. Generalities

The superficial hardening in high frequency currents (CIF), with additional material (MA) of highly used surfaces is a specialized procedure with limited applicability, non-pollutant and efficient.

Usage resistance and the tenacity of sediments are determined by the physical-chemical and technological features of fluxes and by the technological sediment parameters specific to the used equipment.

The flux achieved by the team of

authors, for the first time in our country, is designed to charging the active surfaces of tools by cold pressing processes submitted to abrasion usage exploitation under medium pressure. This is an agglomerated flux, mechanic mixing type, consisting of an alloy of chrome carbides, metallic chrome, titan, nickel and graphite, having well determined proportions and a fondant (deoxidizer) which becomes active at the temperature of the melting bath and of the mixing between MA (additional material) and MB (basic material).

2. Elaboration of flux

The performed researches aimed to achieve an agglomerated flux, compatible to a carbon steel at welding by melting CIF which is able to sediment an adherent alloy, rich in carbides of Fe - Ti type with minimum hardness of 55 HRC and a highly chemical activity at the melting temperature and liquid bath formation. The projected features of sediments are presented in table 1.

Table 1. The projected features of sediments

Chemical composition of MD [%]					Hardness MD [HRC]
C	Cr	Ni	Si	Ti	Min 55
2.0-3.5	18.0-24.0	2.0-4.0	2.0-3.0	Min 0.01	

2.1. Elaboration of alloying system

When elaborating the alloying system, the goal is to provide all elements necessary to the alloy by adding magnetic raw matters, powder with an adequate granulation of homogenous flow and float.

24 series of versions of the alloying system have been experimented in order to obtain the chemical composition and the

hardness, versions which led to the elaboration of experimental sediments for determining the content of chrome and silicon.

The experienced receipts have been calculated for dilution of max. 5% and a transfer coefficient of 90%.

The last 3 versions of dosage are presented in table 2.

Table 2. Versions of dosage

Composite in the receipt	Version of dosage / content %		
	22	23	24
Metallic chrome	25-30	25-30	10-15
Chrome carbide	40-50	60-70	65-75
Metallic nickel	10-15	2-8	2-8
Ferrosilicon 75	10-15	4-8	4-5
Ferrotitan 60	4-8	1-2	2-3

The chemical compositions spectrally determined, on achieved sediments, Fe basic programs and basic tools steels were framed within the limits of table 1 for version 24.

2.2. Elaborating the flux

The flux receipt has been chosen from

the manufacturer's patrimony [1], according to table 3. I used the two systems to achieve an experimental part of flux by dosage and homogenization and this part has been used to sediment some samples for tests, on the CIF installation.

Table 3. The flux receipt

Component in the receipt	Participation, in % mass
Dehydrated borax	1/3 din $35 \pm 10\%$
Boric acid	2/3 din $26 \pm 10\%$
Potassium hydroxide	$26 \pm 10\%$
Potassium fluoride	$\frac{1}{2}$ din $20 \pm 10\%$
Potassium tetrafluoro-borate	$\frac{1}{2}$ din $20 \pm 10\%$

3. Tests and measurements

The tests have been performed on specimens sampled from a sediment having the thickness of about 1,3 mm made on a carbon steel slightly alloyed with manganese.

3.1 Chemical composition

The chemical composition has been spectrally determined at the exterior level of the sediment. The obtained values are presented in table 4.

Table 4. Chemical composition

Chemical composition of MD, %					Hardness HRC MD %
C	Cr	Ni	Si	Ti	56, 57, 55
2.6	19.3	2.3	2.4	0.4	

3.2. Metallographic analysis

In order to perform a metallographic analysis, the sample has been transversally cut, with reference to the sediment's belts. Samples cut has been performed by electroerosion. After this cut, I removed by correction 3 mm of material, on thickness, of the surface resulted from cut.

The samples' surfaces resulted from the correction process have been metallographic prepared.

The structural examinations have been performed at two different sizes (scale no.1. fig.1.2.a. and scale no.2, fig.1.2.b.) at the metallographic optic microscope.

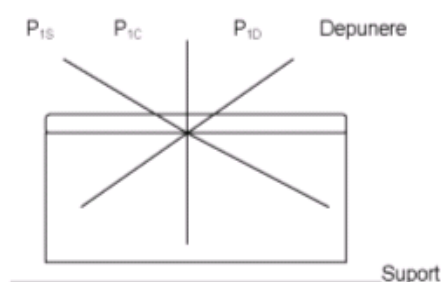


Fig. 1.1. Examination plan

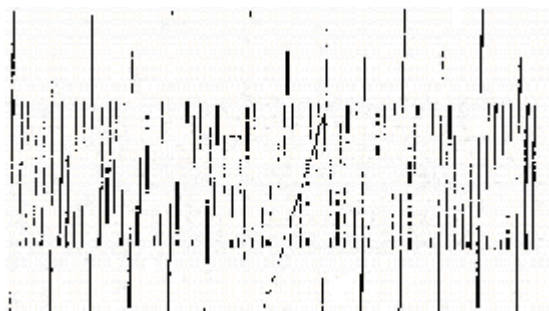


Fig. 1.2. a. Scale no. 1 1 Div = 0.01 mm



Fig. 1.2. b. Scale no. 2 1 Div = 0.01 mm

Fig. 1.3, 1.4, 1.5 present the structure of the support material, from the fusion surface to its exterior. Thus, the support's material has the ferito-perlite structure with high granulation in the proximity of joint, appropriate to the percentage $N = 2$ and with granulation of $N = 4$ at its exterior. The increase of granulation from the support's material is due to its overheating caused by

the great energy used to sediment. It should be noticed that the support's material has a structure that tends to a Widmannstatten structure, resulting mechanic features, except to the inappropriate hardness.

This fact could favour the avulsion of sediment during the exploitation process when this material is submitted to the shear stress.

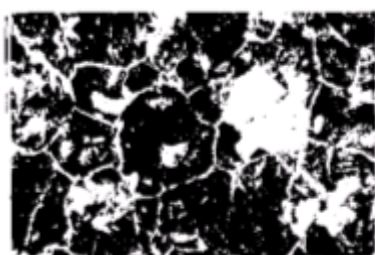


Fig. 1.3. High granulation

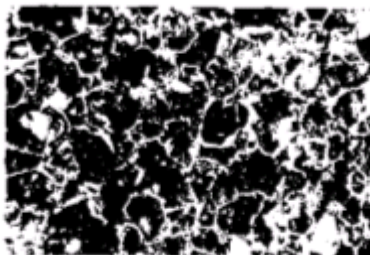


Fig.1.4. Central

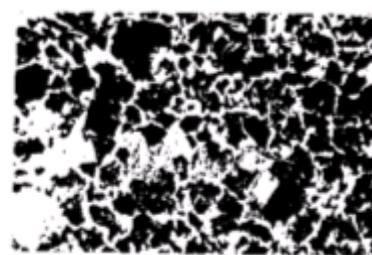


Fig.1.5. Granulation $N = 4$

In fig. 1.6., 1.7., and 1.8. I presented the material's structure submitted by welding, ledeburitic-type, made of perlite and carbides perpendicularly oriented on the solidification front. Thus, it is noticed that the submitted material has an homogenous structure on the entire thickness of sediment,

except to the pores with microscopic dimensions and some complex carbides having a dimension up to 0.2 mm. According to these figures, no microcracks, no penetrations and no micropores are present in the submitted material.

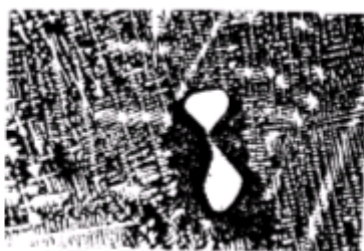


Fig.1.6. Ledeburitic sediment **Fig.1.7.** Sediment with imperfection **Fig.1.8.** Exterior ledeburitic Sediment

3.3. Analysis of material's hardness

I determined the material's hardness submitted by welding on its exterior surface and in sections on surfaces which have been metallographic examined.

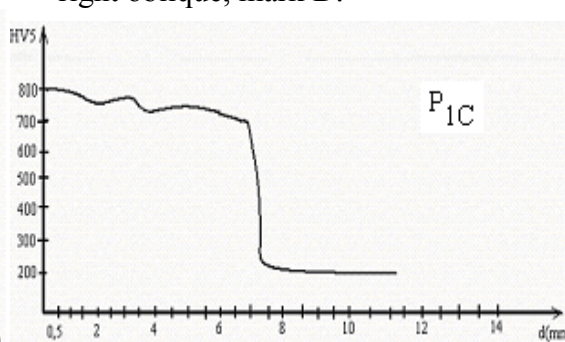
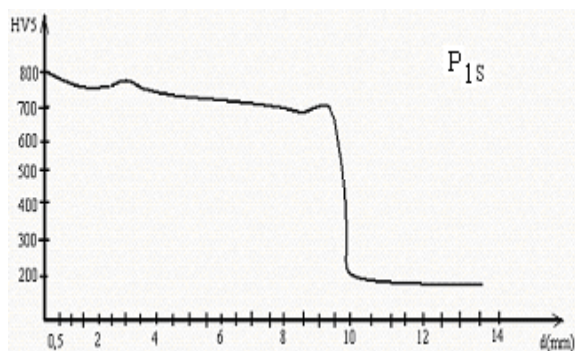
Likewise, in section, I also determined the hardness in the support's material, from the joint towards its exterior. The values of the hardness measurements, on the exterior surface of the submitted material are presented in table 5.

Table 5. Hardness

No. determination	Sample P ₁ , HRC
1	59
2	65
3	60
4	63
5	61
6	62
Average	61,6

In order to determine the hardness of the submitted material and to acknowledge the type of change, when passing towards the support material used for sediment, I proceeded according to sketch from fig.1.1.

Thus, I measured the hardness, HV₅, from the exterior surface of the submitted material towards the support material, according to three directions: one direction perpendicular on the joint area between the two materials, mark C; one direction at 45° left oblique, mark S; one direction at 45° right oblique, mark D.



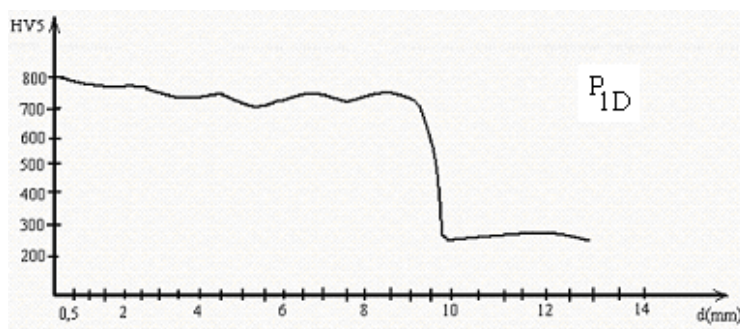


Fig.1.9. HV_5 hardness measured according to those three directions S, C and D

The printing point in order to observe the evolution of hardness along these directions has been 0.5 mm. The results of hardness measurements are presented in table 6.

Table 6. Measurements

Sample P ₁ , HV_5		
S	C	D
810	795	810
810	810	795
795	795	781
795	781	795
810	781	781
781	766	781
781	766	766
766	752	766
766	752	766
752	739	752
752	739	739
739	726	752
739	713	739
726	726	726
713	225	739
726	223	739
713	221	726
225	219	713
223	223	225
225	219	216
221	216	219
223	221	221
219	216	223
216	219	225
219		219
216		216

The measured hardness area presented graphically in figures P_{1S}, P_{1C}, P_{1D}. The hardness of complex carbides with size up to 0.2 mm presented in the submitted material is in average 1,087 (HV_5).

4. Conclusions

Based on the performed researches, the results are as follow:

- One metallo-ceramic flux for CIF sediment of some ledeburitic layers against usage, with associated hardness of about 60 HRC;

- One manufacturing technology during homogenization for the payment of the mechanic mixing type flux;

One new quality of bimetal structures determined by a small dilution, a good compatibility at sediment between MD (sediment material) and MB and an acceptable thickness of sediment for the application field.

Acknowledgement

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References

- [1]. I. Voiculescu, H. Binchiciu, *Achieving a family of coated ecologic rods for braying with alloys of silver*, Research report – Stage I, Contract RELANSIN 2023/2004, AMCSIT Polytechnique - SUDOTIM Timișoara, 2004.
- [2]. H. Binchiciu, *Charging by welding with the electric arch*, Technique Edition, Bucharest, 1992
- [3]. L. Milos, *Experimental researches on charging with hard alloys based on Fe of some marks stressed by strong abrasive usage*, UP Timișoara, contract no.486/1995
- [4]. Șerban, C.E. *Metallic materials science*; Edition Lux Libris, 2000
- [5]. Popescu, R. – *Science and technology of materials' process and manufacture*, Edition Lux Libris, 2009.

PHOSPHATE PASSIVATION SOLUTIONS ENHANCED BY CHEMICAL ADDITIVES FOR TREATMENT OF THE HOT DIP GALVANIZED STEEL

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ABSTRACT

To stabilize the surface of the galvanized steel it is important to apply a passivation treatment during its manufacturing. The general aim of the passivation treatment is to prevent the formation “storage stain” or “white rust”. For many decades, the chromium conversion treatments involving the use of chromic acid containing Cr⁶⁺ species have been used for their corrosion protection and adhesion promotion performances. Today all hexavalent chromates have been banned by the EC. Toxicological studies have evidenced the hazardous character of hexavalent chromium. Therefore more economical and environmentally friendly passivation solutions have been studied and used to replace the chrome passivations on galvanized steel.

Phosphate conversion coatings are commonly used on the galvanized steel. They form a thin protective film on steels surface. However, the formation of a stable and uniform coating for corrosion protection remains a challenge. More complexes passivating solutions with chemical activators added are the potential alternatives.

In this paper are presented the studies about such molybdate–phosphate passivation solutions as environmentally friendly alternative for chromium passivates. The results of treatments realized for different treatment times and more compositions were analyzed. Also the corrosion resistance of the passivated samples has been studied.

KEYWORDS: hot dip galvanized steel, molybdate–phosphate passivation film, corrosion resistance

1. Introduction

The protection of steel sheets is often obtained using a zinc coating by hot dip galvanizing technology. For inhibition of the formation “storage stain” or “white rust” on the surface of galvanizing steels must applied the passivating treatments. The reducing the corrosion rate of the zinc layer, in the past, a very common and popular way was chromate conversion coating based on Cr⁶⁺. This could increase the passivation tendency of zinc layer. However, hexavalent chromium is regarded as toxic and cancer-producing, there are environmental and

health risks associated with the use of chromate ions [1, 2].

Therefore, all hexavalent chromates have been banned by the EC and have been generally replaced by other chromium-free passivates [3 - 6].

As potential alternatives to hexavalent chromium was studied several passivating inhibitors like molybdates, tungstates, permanganates, vanadates, and organic compounds [7, 8]. The phosphating is one of the most important chemical conversion processes used for corrosion protection or painting primer for the galvanized layers [9 - 11]. Zinc phosphate is used as main

component for the passivating solutions. Molybdate can be added for the deposition of a superior zinc phosphate coating. This is an environmentally acceptable and effective corrosion inhibitor for galvanized steel [12, 13]. The molybdate additives into phosphate solution lead to accelerate the phosphating processes or to improve the corrosion resistance of phosphate coatings [14 - 16]. Molybdate films are amorphous, but they have cracks during a longer immersion [17]. As result were proposed molybdate-phosphate solutions. The molybdate-phosphate system was introduced by Tang et al. for corrosion protection of galvanized steel [18]. Other studies have been suggested that molybdate-phosphate based conversion coatings are an attractive alternative to chromate conversion coatings [19, 20]. For building films of significant thickness the presence of fluoride ions is also important [21].

In this paper are presented the results of study about the utilization of three molybdate-phosphate passivation solutions with different compositions to enhance the properties of coatings on the surface of galvanized steel sheets. The treatments realized at different concentrations and dipped times were analyzed. Also the corrosion resistance in sea water solution of the passivating samples has been studied and

discussed. Was make a comparative analyzes of corrosion rates for different passivation solutions and different times of exposure in corrosion medium.

2. Experimental method and materials

More series of rectangular galvanized steel sheet samples were used. Zinc protective coating was obtained by hot dip galvanized process. Before passivation the specimens were cleaned sequentially. The galvanized steel samples were degreased with acetone.

The surface that has been subjected to phosphating was rinsed with deionized water to remove any residue and non-adherent particles present on it. After rinsing the samples were dried. The zinc phosphate coating is applied by immersion of samples in a zinc phosphate solution. After the passivating film is deposited, the steel samples are removed from solution and then thoroughly rinsed and dried.

The solution used for coatings obtaining was prepared with zinc dihydrogen phosphate ($\text{Zn}(\text{H}_2\text{PO}_4)_2$). Also molybdate diamonium ($(\text{NH}_4)_2\text{MoO}_4$) as source of molybdenum ions was added. Fluotitanic acid (H_2TiF_6) for pH correction and source of active ion Ti for activation passivating process was added in solution.

Table 1. Composition of the phosphating solutions used in this work

Code of treatment solution	Zinc dihydrogen phosphate [g/L]	Fluotitanic acid [g/L]	Molybdate diamonium [g/L]
I	30	10	10
II	45	15	15
III	90	30	30

Three compositional variants for the passivation solution that has been applied on the surface of galvanized steel sheet samples are given in Table 1. The specimens were dipped in each passivating solution (open to air) at room temperature for 10, 15, 20, 30 and 60 seconds.

The corrosion properties of passivated samples have been tested by their exposing in the sea water solution as corrosion medium for different exposure times. The solution for corrosion tests have 27g/L NaCl, 6g/L MgCl_2 , 1g/L CaCl_2 , 1g/L KCl at pH = 6.5-7.2. The protective properties of the

molybdate–phosphate conversion coatings obtained for those three passivating solutions and different exposure times (168, 336, 504, 672 and, 840 h) have been evaluated by corrosion rates measurements.

3. Results and discussions

To evaluate the quality of molybdate–phosphate conversion coatings the physical characteristics as well as the performance in corrosive environment were determined.

Firstly was analyzed the physical characteristics of passivating films. To

determine the passivated coating thickness the determination of coating weight was adopted.

This method involves the determination of change in weight of a coated specimen after immersion in the treatment medium. The difference in weight after coating and before is divided by the surface area of sample in m^2 to obtain unit coating weight in g/m^2 .

The time evolution of the layer thickness corresponding to the samples dipped into the three solutions is presented in Table 2, respectively Figure 1.

Table 2. Passivated coating thickness as coating weight in g/m^2 at increasing immersion time

Immersion time in s	Coating thickness as coating weight in g/m^2 for:		
	Solution I	Solution II	Solution III
10	1.314	3.775	12.375
15	1.579	3.85	8.204
20	3.256	2.318	9.414
30	2.06	2.95	8.979
60	2.11	3.595	7.97

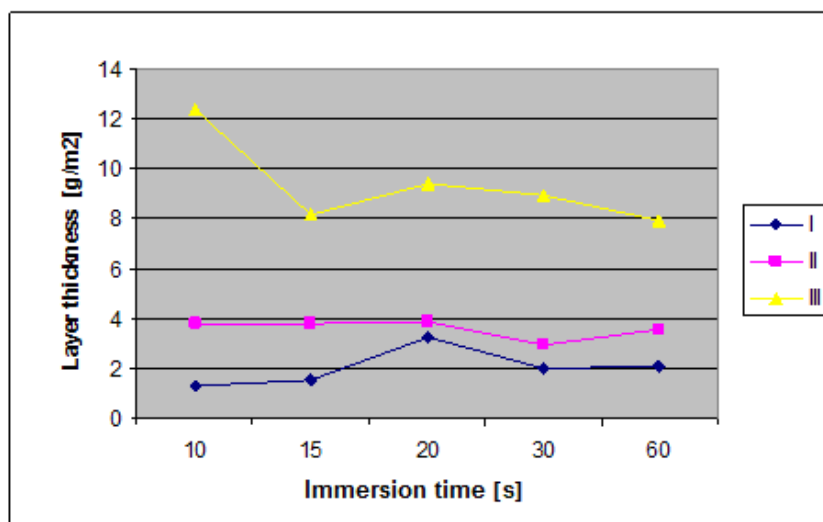


Fig. 1. Layer thickness of molybdate–phosphate conversion coatings as a function of duration of immersion for different passivating solutions

The thicknesses of conversion films obtained at different immersion times and the composition of the passivating solutions have been different. The thicker film was obtained for the solution III with higher phosphate and molybdate addition. At

prolongation of the immersion time a slowly reducing of the thicknesses of the layers was observed for all solutions.

For the treatments developed into all solutions the films were developed rapidly. In simple passivating solutions, phosphating

reaction tends to be slow owing to the polarization caused by the hydrogen evolved in the cathodic reaction. To achieve coating formation in a practicable time for classical phosphating solution, some mode of acceleration must be employed. For this study the chemical additives were added into zinc phosphate solution and their action was evidently.

Molybdenum and titanium compounds were added into phosphating bath as chemical accelerators. For all solutions after short immersion times (~15-20s) were obtained stable thicknesses for layers. The length of period for developing of a stable film corresponds with the first stage in coating formation (namely, the induction

stage) into classical phosphating process. For developing a stable layer is observed that the classical phosphating process involves more time.

The process for the coating formation care divided into four distinct stages: the induction stage, the commencement of film growth, the main exponential growth stage and the stage of linear increase in film growth [22].

The quality of passivating process for different solutions and immersion times was analyzed by examination of physical appearance of coated surfaces of samples. The surface morphologies of the molybdate-phosphate films are presented in the Figure 2-4.

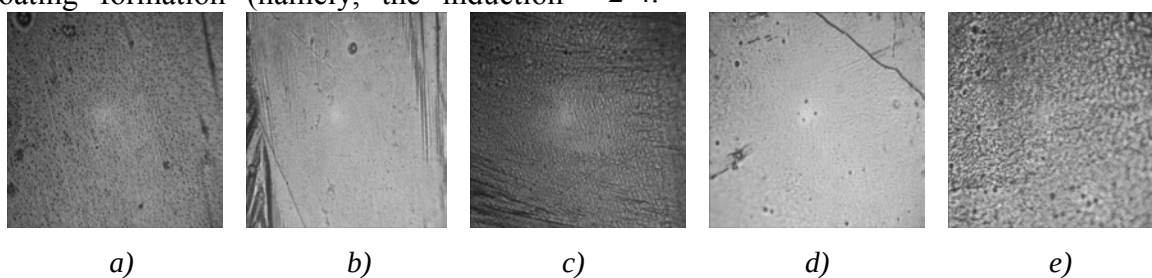


Fig. 2. Surface appearance of passivating layer for solution I at different immersion times: 10 (a), 15 (b), 20 (c), 30 (d) and, 60s (e)

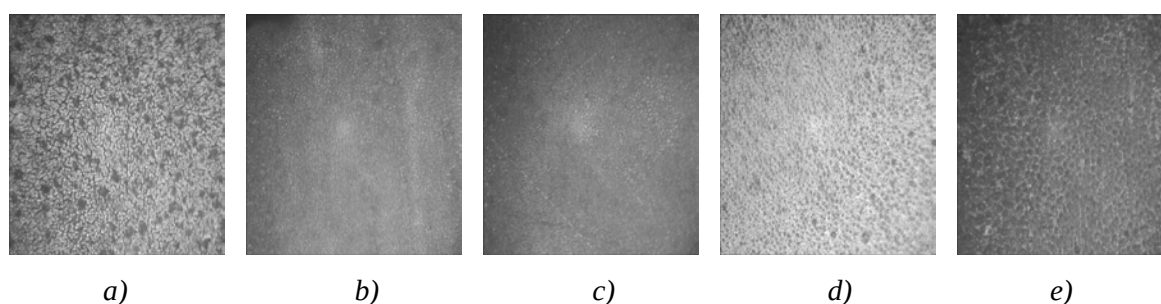


Fig.3. Surface appearance of passivating layer for solution II at different immersion times: 10 (a), 15 (b), 20 (c), 30 (d) and, 60s (e)

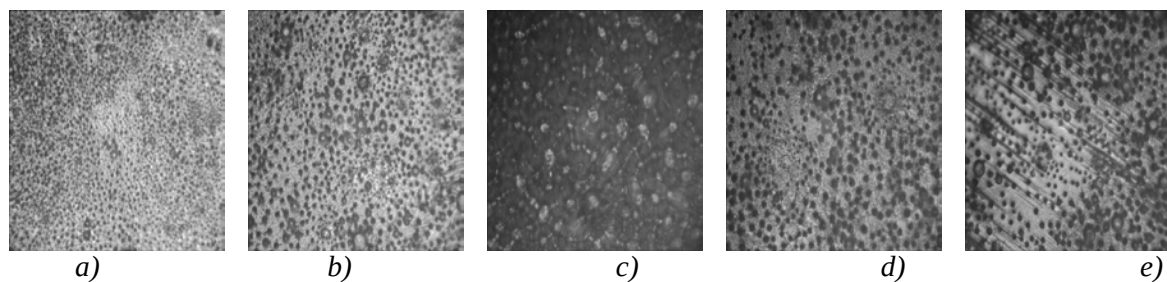


Fig.4. Surface appearance of passivating layer for solution III at different immersion times: 10 (a), 15 (b), 20 (c), 30 (d) and, 60s (e)

During the treatment the surface is in contact with the phosphate solution that dissolves a small amount of the coating. At the surface of the zinc, the attack of the zinc phosphate produces a localized increase in the pH, resulting in the precipitation and deposition of insoluble zinc phosphate crystals on the surface of the zinc coating. After some time of reaction developing, this crystallizing action leaves behind a continuous, relatively thick solid film of zinc phosphate.

The phosphate films on surface of hot dip galvanizing steel may range in colors from light gray to dark gray, depending on the type of bath and the grade of steel substrate used. The chemical additives can generated the depositions with other colors. The layers obtained in the experimental are have yellowish green color for solution I and green for solution III.

For solution I at all immersion times tested the passivating film obtained is uniform and adherent.

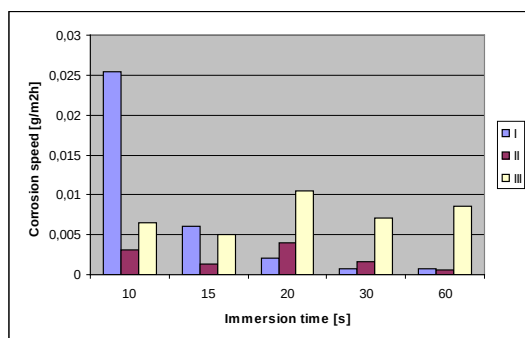
For obtaining an optimum surface appearance at dipping into solution II was necessary an immersion time in range of 15-20s. This is lower than the corresponding immersion in solution I. The solution III has a higher content of dihydrogen phosphate and as result the passivating reaction is more intensive. As result a thicker layer was developed. Because over 20s the layer becomes less uniform and adherent must be

established the optimum immersion time. In respect to these parameters of the passivating treatments (the composition of the solutions and immersion times) can concluded that a bigger thickness was obtained for a solution enriched in phosphate and for controllable immersion time. More phosphate addition negatively affects the coating. Sometimes for solution III was obtained non uniform and rough layers. Also uncovered areas were observed.

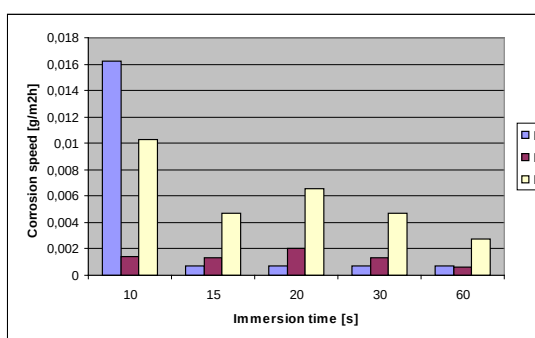
It is generally accepted that the composition of the phosphate layer has a strong influence on its chemical stability. For this reason in this study this was analyzed by corrosion tests at which were subjected the samples after the passivating treatments.

Is knows that the passivity (or reactivity) of the molybdate-phosphate layer at interaction with a corrosive medium is an important property of conversion layer. In order to determine the corrosion speeds in sea water medium the samples (obtained at different passivating treatments and different immersion times) were maintained at room temperature in sea water solution with 27g/L NaCl, 6g/L MgCl₂, 1g/L CaCl₂, 1g/L KCl, pH = 7.1.

The corrosion speeds were measured for different exposure times in corrosion medium: 168, 336, 504, 672 and 840 h. The results of experiment are given in comparison charts, Figure 5.



a.



b.

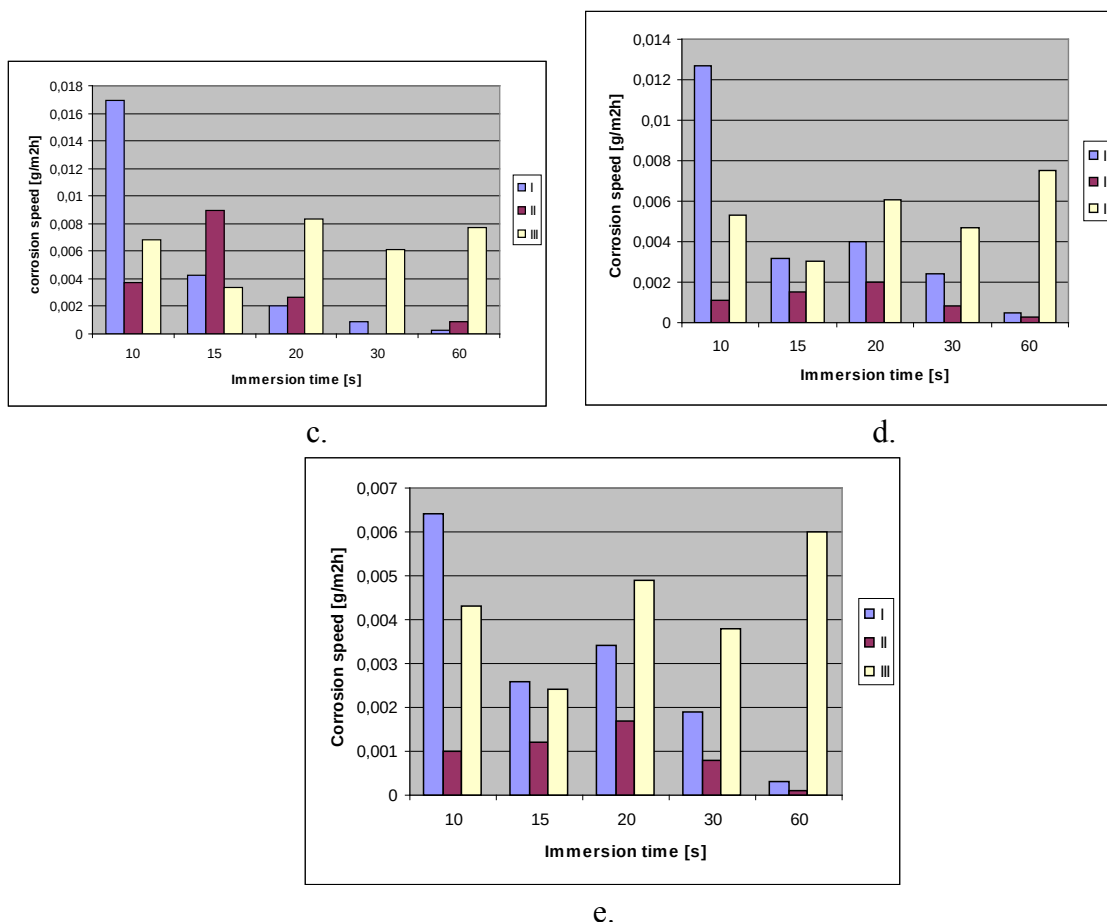


Fig.5. Comparison chart of corrosion speeds for different passivation solutions and different immersion times at variation of exposure time in corrosion medium: 168 (a), 336 (b), 504 (c), 672 (d) and, 840 hours (e)

By selecting the results for corrosion tests obtained for the three passivating solutions and variable immersion times in these solutions was possible to choose the better treatment, Figure 6. For solution III was obtained passivation layer the thickest but it did not show the best resistance to corrosion. This explication is done by the quality of the layer developed at higher phosphate content into passivating solution. Can be observed that for passivation solution with more molybdate-phosphate content the corrosion rate slowly decreases with exposure time into corrosion medium. For the other solutions the corrosion speeds are lower and appreciatively remain at these

lower values at prolongation of exposure time.

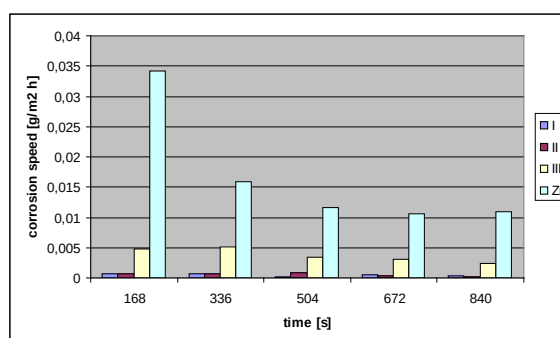


Fig.6. Variation of the corrosion speed as a function of the exposure time to the corrosive environment

4. Conclusions

The surface quality of the passivating hot dip galvanized steel sheet is important for its corrosion behavior.

The thickness of passivating coating obtained on galvanized steel surface varies with immersion times and phosphating compounds added. The addition of chemical additives influences the process. Comparatively with the classic process the times required for forming of continuous and solid molybdate-phosphate films were lower and their color was yellowish green or green. The passivating process was developed rapidly.

The thickness of molybdate-phosphate conversion coatings depends by chemical composition of the passivating solutions and by times of immersion.

The thickness of layer is higher for solution III, minimum for the solution I and, medium for solution II.

The solution with the following chemical composition zinc dihydrogen phosphate 45g/L fluotitanic acid 15g/L, molybdate diamonium 15g/L and immersion time of 60 second gives the best corrosion resistance. The appearance of the corroded surfaces for all the samples shows a general and uniform corrosion.

References

- [1]. Lunder O., Walmsley J.C., Mack P., and Nisancioglu K., *Formation and characterisation of a chromate conversion coating on AA6060 aluminium*, Corros. Sci., 2005, 47: 1604
- [2]. LIU Guangming, YU Fei, YANG Liu, TIAN Jihong, and DU Nan, *Cerium-tannic acid passivation treatment on galvanized steel*, Cerium-tannic acid passivation treatment on galvanized steel *Rare Metals*, Vol. 28, No. 3, Jun 2009, p. 284
- [3]. Hao J.J., An C.Q., and Mou S.H., *Advances in research on unchromium passivation of galvanized zinc layer*, Mater.Rev., 2003, 9 (17)
- [4]. Thierry L., Pommier N., *Hexavalent chromium-free passivation treatments in the automotive industry*, COVENTYA SAS, April 2003
- [5]. Yunying Fan, Yehua Jiang, Rong Zhou, *New passivating method to galvanized Zn coatings on steel substrate*, Advanced Materials Research Vols.163-167 (2011), pp.4555-4558
- [6]. Wang D. and Tang X., *A study of the film formation kinetics on zinc in different acidic corrosion inhibitor solutions by quartz crystal microbalance*, Corros. Sci., 2005, 9 (47): 2157
- [7]. Bexell U. and Grehk T.M., *A corrosion study of hot-dip galvanized steel sheet pre-treated with γ -mercaptopropyltrimethoxysilane*, Surf. Coat. Technol., 2007, 201: 4734
- [8]. Deflorian F., Rossi S., Fedrizzi L., and Bonora P.L., *EIS study of organic coating on zinc surface pretreated with environmentally friendly products*, Prog. Org. Coat., 2005, 52: 271.]. The phosphating is one of the most important chemical conversion processes used for corrosion protection or painting primer for the galvanized layers
- [9]. LORIN G. *Phosphating of metals: constitution, physical chemistry and technical applications of phosphating solutions* [M]. Hampton Hill: Finishing Publications, 1974: 146–155
- [10]. FREEMAN D B., *Phosphating and metal pre-treatment* [M]. New York: Industrial Press, 1986: 134–139
- [11]. RAUSCH W., *The phosphating of metals* [M]. Ohio: ASM International, 1990: 112–116.1–3
- [12]. VUKASOVICH M S, FARR J P G., *Molybdate in corrosion inhibition—A review* [J]. Mater Perform, 1986, 25(5): 9–18
- [13]. ARAMAKI K., *The inhibition effects of chromate-free, anion inhibitors on corrosion of zinc in aerated 0.5 mol/L NaCl* [J]. Corros.Sci, 2001, 43(3): 591–604
- [14]. Li Guang-yu, NIU Li-yuan, LIAN Jian-she, JIANG Zhong-hao. *A black phosphate coating for C1008 steel* [J]. Surf Coat Technol, 2004, 176(2): 215–221
- [15]. SALIBA-SILVA A M, DE OLIVEIRA M C L, COSTA I. *Effect of molybdate on phosphating of Nd-Fe-B magnets for corrosion protection* [J]. Mater Res Bull, 2005, 8(2): 147–150
- [16]. LIN Bi-lan, LU Jin-tang, KONG Gang, LIU Jun. *Growth and corrosion resistance of molybdate modified zinc phosphate conversion coatings on hot-dip galvanized steel* [J]. Trans Nonferrous Met Soc China, 2007, 17(4): 755–761
- [17]. LU Jin-tang, KONG Gang, CHEN Jin-hong, XU Qiao-yu, SUI Run-zhou. *Growth and corrosion behavior of molybdate passivation film on hot dip galvanized steel* [J]. Trans Nonferrous Met Soc China, 2003, 13(1): 145–148
- [18]. Tang T. and Beth-Nielsen G., *Molybdate-based alternatives to chromating as a passivation treatment for zinc*, Plat. Surf.Finish., 1994, 18 (11): 20



- [19]. **Ogle K., Tomandl A., Meddahi N., Wolpers M.**, *The alkaline stability of phosphate coatings I: ICP atomic emission spectroelectrochemistry*, Corrosion Science 46 (2004) pp.979–995
- [20]. **Ogle K., Bucheit R.**, *Conversion coatings*, in: A.J. Bard, M. Stratmann (Eds.), Encyclopedia of the Electrochemistry, vol. 5, Wiley-VCH, Weinheim, 2003, p. 460
- [21]. **Brooman E.W.**, *Chromium alloy plating*, ASM Handb Int. 5 (1994) 270
- [22]. **Sankara Narayanan T.S.N.**, *Surface Pretreatment By Phosphate Conversion Coatings. A REVIEW*, Rev.Adv.Mater.Sci. 9 (2005) 130-177

CONTRIBUTIONS ON THE TECHNOLOGY OF GENERATING THE COMMERCIAL TITANIUM POWDER

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ABSTRACT

The metallothermic method of generating the metals and alloys by reducing them to chemical compounds (salts, oxides) relies on the greatest affinity of the reducing metal to oxygen, chlorine, fluorine, etc., as against that of the reduced metal. I have proceeded to reduction using argon, magnesium, and calcium.

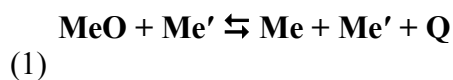
Selecting the reducing agent depends not only of the thermodynamic conditions, but also of its volatility, a physical property that, at the time of unfolding the thermal meal process at atmospheric pressure, must be minim. One of the most important factors I have considered when selecting the reducing agent was the technical and economic characteristic of the process, the extraction degree of the metal reduced, its quality, the reducing agent's price and the physical property of the other consumptions calculated per finished product unit.

For diminishing the reducing agent consumption, I proposed a combined process that assumed the following: firstly reducing the TiO_2 with magnesium, reducing with calcium, during the second phase, of the product that resulted subsequently.

KEYWORDS: metallothermic reduction, reducing agent

One of the most used methods for generating the titanium powder is the metallothermic reduction. The reduction reactions of non-reducible oxides, as well as of other chemical combinations with active metals active (Ca, Na, Mg, Al) or combinations of these ones (for example, calcium hydride), rely on the fact that the reducing metal (Me') has an affinity to oxygen greater than the oxidized metal. These reactions are used only in the case when the reduction involving carbon or gas (CO ; H_2) is not possible.

The reaction that is the basis of developing the reduction process by the metallothermic method is:



For priming the process in the reactor, the building of a temperature of minimum 700°C is necessary. The process develops

due to the heat released following the unfolding of reduction reactions, the work temperature varying thus between 700 and 1000°C .

For eliminating the possibility of oxidizing the final product, the reaction chambers have been filled with inactive gas. I have introduced the raw materials and the reducing agent (metal) in the reactor under the form of powder or agglomerates. Because after the reduction operation the powders are mixed with salts or halides of the reducing agent, I have removed the latter by washing them with acids and water.

The thermic method of generating the metals and alloys by reducing them from chemical compounds (salts, oxides), relies on the greatest affinity of the reducing metal to oxygen, chlorine, fluorine, etc., as against that of the reduced metal. I have proceeded to a reduction with the help of argon.

The method was disseminated broadly in the metallurgy for generating a whole range of rare metals in a pure state: Ti, Zr, Ta, Nb, Be etc., light metals: Rb, Cs, Mg, Ba, and metallic alloys (mainly with Fe or Al stick). It is used mainly in the iron alloys metallurgy area.

In a general form, the metallothermic reduction can be expressed with the help of the following equation:



(2)

where:

MeX – is the chemical combination subject to reduction;

Me' - reducing agent;

Q – thermal effect of the reaction.

The metallothermic reduction reaction is usually exothermic. Only those metals that generate compounds of the *Me'X* type can be used as reducing agent. Thus, this involves a significant decrease of the free enthalpy.

From the comparative analysis of free energies for forming oxides, chlorides and fluorides of different metals, at different temperatures, it was found that the greatest diminishment of this thermal – dynamic physical property was determined by the forming of calcium, magnesium, aluminum and sodium compounds.

Selecting the reducing agent depends not only of the thermodynamic conditions, but also of its volatility, a property that, for the developing of the metallothermic process at atmospheric pressure, must be minimal.

By using the reducing agents with a low boiling temperature, the reduction process occurs frequently in high pressures created by argon, a fact that leads on its turn to an increase of the device's complexity degree.

By aiming to generate the high purity titanium by reduction, it was necessary that the reducing agent does not form with the reduced metal stabile combinations, alloys or solid solutions, the reducing agent surplus and, as well, the reduced metal must remove the reaction by products fully.

One of the significant factors I have considered when selecting the reducing agent was the process's technical and economic characteristic, the extraction degree of the reduced metal, its quality, the reducing agent's price and the size of the other consumptions calculated per final product unit.

When analyzing the metallothermic process, I have considered the fact that during the reduction of one or another compound up to the pure metal phase, the reaction develops in several phases. These lead to the forming, for example, of lower oxides whose chemical stability is usually much higher than that corresponding to the higher oxides.

As consequence of the research, I have reached the conclusion that the metallic titanium cannot be generated by the direct reduction of TiO_2 with magnesium.

Next, I have calculated the value of the thermicity of the reduction reaction for titanium oxides (TiO_2).

For an adequate development of the metallothermic process, it is necessary to determine the difference between the forming heats of the **MeX** and **Me'** combinations, thus of the thermal effect corresponding to the reduction reaction.

For the free development of the reaction, the thermal effect (**Q**) must be sufficiently high. The quantity of heat *q* that is assigned to the load is named the process's thermicity.

It seems that the process's thermicity (specific thermal effect) is maximum for a stoichiometric ratio of the **MeX** and **Me'** compounds.

By the surplus of any compound, the thermicity diminishes due to the heat consumption for heating and melting the component surplus that does not participate in the reaction.

For the reaction



the expression of thermicity is

$$q = \frac{Q}{M_{MeX} + A_{Me'}}$$

$A_{Me'}$ - atomic weight of the reducing metal Me' .

(3)

where M_{MeX} – molecular weight of MeX ;

Table 1. Calculated value of the thermicity belonging to the reduction reaction for oxides

Oxide	Thermicity [kJ/g]	Oxide	Thermicity [kJ/g]	Oxide	Thermicity [kJ/g]
TiO ₂	1.596	Cr ₂ O ₃	2.562	Fe ₂ O ₃	3.990

Reducing agent – aluminum

The minimum value of thermicity depends not only of the thermal effect of the reaction and the general weight of the load, but also of a whole series of factors: size of particles belonging to the reacting components, oxidizing degree of metal, mixing degree of components, and thermal exchange surface.

The approximate calculus of temperature (T°C) reached during the development of the metallothermic reduction processes can be acquired by using the following equation:

$$T = \frac{Q_2 - Q_1}{E_1 + E_2} \cdot k$$

(4)

where: Q_1 [J/g_{equiv.}] – is the forming heat of MeX ;

Q_2 [J/g_{equiv.}] - combination heat of $Me'X$;

E_1 [g_{equiv.}] - equivalent weight of MeX ;

E_2 [g_{equiv.}] - equivalent weight of $Me'X$;

k - coefficient that considers the heat consumed for heating the weight of reacting

agents up to the melting temperature during its melting process, as well as the heat losses since the time of beginning the reaction and until the time of separating the metal of the slag (e.g. – in the aluminothermic process, $k = 13,23$).

The thermal effect of reactions is so great and they take place so violently that the throwing of part of the load outside the reactor can occur (if the reactor is not tightly sealed) or to destroying it (if it is tightly sealed).

In these cases, for mitigating the reaction, I have added to the load a certain quantity of CaCl₂ since the beginning that will take over part of the heat released by the reactions.

In this case, the thermal effect of the reduction reaction is insufficient for its autonomous development and so I have used the additional heating (with the oven) of containers with the load.

In Table 2, I have presented the melting and boiling temperatures of reducing agents and their combinations.

Table 2. Melting and boiling temperatures of reducing agents and their combinations [°C]

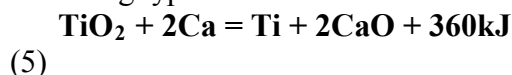
Element	Metal		Oxide	Chloride		Fluoride	
	T _{melting}	T _{boiling}	T _{melting}	T _{melting}	T _{boiling}	T _{melting}	T _{boiling}
Na	97.7	914	1000	800	1465	992	1704
Ca	851	1480	2570	782	2027	1418	2507
Mg	650	1126	2800	114	1418	1262	2227
Al	659	2330	2045	192.4	447	1040	1272

Then, I have proceeded to generating the titanium powder by reducing the TiO_2 with calcium.

The titanium is characterized by a great affinity to oxygen and that is why, for reducing the TiO_2 , the most active reducing agent, calcium, is used.

Due to the fact calcium has a great affinity to nitrogen and the metal resulting from metallothermic reduction will comprise also a great quantity of this element ($\geq 1\%$), a fact generated by the greater affinity of titanium as against the nitrogen. In connection to this, by the metallothermic reduction of TiO_2 with calcium, the reducing agent must have high purity, with nitrogen concentrations of maximum 0.05 – 0.15%, a requirement that was met by distilling it in vacuum.

The reduction of TiO_2 with calcium occurs after a general reaction of the following type:



In order to insure a reduction degree as advanced as possible, I have used a calcium surplus (25 - 100%), comparative with the necessary quantity indicated in the formula.

The process's thermicity (specific thermal effect) is approximately 2.2 kJ/g and that is why, for the adequate development of the reaction, an additional heating of the load was required.

For the reduction of TiO_2 , I have used temperatures in the range of 1000 - 1100°C. At these temperatures, calcium is found in liquid state ($T_{\text{melting}} = 851^\circ\text{C}$), thus insuring a very good contact with the oxide particles subject to reduction.

During the reaction, simultaneously with the forming of titanium crystals, calcium oxide formed that blocks the growth of metal particles, thus resulting titanium powders with sizes of 2-3 μm .

By the subsequent washing of the titanium powder generated by reduction (the washing is made for removing the surplus CaO or calcium particles) with water or low

acid solutions, the powder oxidized and its titanium concentration did not surpass 96-98%. Due to this, I have followed the leading of process thus that in the end the powder generated has coarser particles and is much more stable for oxidation.

To this end, in the initial load I have introduced, as fusing agent, CaCl_2 ($T_{\text{melting}} = 782^\circ\text{C}$) that, at reaction temperature, dissolves calcium oxides, transferring partially or fully the calcium in the melt. In such an option, generating a coarse titanium powder becomes possible; the powder has sizes above 10-15 μm .

The titanium generated by the metallothermic reduction method with calcium is characterized by the following:

98.5 - 99% Ti; 0.03 – 0.15% N_2 ; 0.2 – 0.3% O_2 ; 0.01 – 0.03% H_2 ; 0.1 – 0.2% Si; 0.01 – 0.05% C; 0.10 – 0.25% Fe; 0.05 – 0.15% Al; 0.1 – 0.3% Ca; Mg < 0.03%; 0.01 / 0.1% Cu.

At the temperature to which the process unfolds, in the presence of CaCl_2 , it was possible also a partial dissolving of TiO_2 , with the forming of some diminished proportions of TiCl_4 and of some lower titanium chlorides.

In order to avoid the possible oxidation and nitration of titanium, the reduction was achieved in reactors sealed tightly, made of refracting stainless steel. After loading and eliminating the air in the reactor, it was filled with argon. The process takes place in vacuum, thus that part of the calcium in the form of vapors will not be involved in the reaction, condensing on the reactor's lid.

I have put the briquetted load in the reactor. This improved the contact with the reducing agent and increased the loading degree of the retort.

For heating, I have used the oven with silicon carbide bars. After maintaining it one hour at a temperature of 1000 - 1100°C, the reactor was taken out of the oven, cooled down and then opened for extracting the agglomerate. I grinded and washed it in

water surplus in order to eliminate the heat that occurs in the process of “quenching” the calcium oxides, and then I washed it again in low acid solutions (acetic acid, hydrochloride acid or nitric acid) until the calcium chloride, the calcium hydrated oxides and the metallic calcium surplus were fully dissolved.

After drying, the powder was dried in a vacuum space, at 40 - 50°C.

For diminishing the reducing agent consumption, I have proposed a combined process that implies the following:

- firstly reducing TiO_2 with magnesium;
- reduction with calcium, during the second phase, of the product resulted previously.

As a conclusion:

- The metallic titanium cannot be generated by the direct reduction of TiO_2 with magnesium.
- The value of thermicity calculated for the adequate development of the metallothermic process is 3.990 KJ/g
- By using the fusing agent CaCl_2 , part of the heat released by the chemical reactions that occurred in ovens was taken over and, at the same time, I have heated the load additionally prior to putting it in the oven.

By using CaO in the generation process, at the same time with the crystals forming, I have obtained also the blocking of metal particles growth, thus resulting titanium powders with sizes of 2-3 μm .

Acknowledgement

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References

- [1]. Mohandas K S, *Unpublished research* (2003).
- [2]. Nohira T, Yasuda K, and Ito Y, *Nature Materials* 2 (2003) 397.
- [3]. Rodriguez P, and Mohandas K S, *Current Science* 81 (2001) 443.
- [4]. World Patent WO 02/40725 A2, 23 May (2002).
- [5]. Sadoway D R, *JOM* 53 (2001) 34.
- [6]. Gerdemann S J, *Adv Mater Processes* 159 (2001) 41.
- [7]. Haiyan Zheng, Toru H. Okabe – Direct production of titanium powder from titanium ore by Preform Reduction Process, Graduate, University of Tokyo, 2009;
- [8]. M. Cojocaru – Producerea și procesarea pulberilor metalice (Producing and processing metallic powders), MatrixRom Publishing House, Bucharest, 1997.

Cu-Ag-REAR METALS FOR WIRES: PROCESSING AND CHARACTERISATION

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ABSTRACT

Cu based alloy microalloyed with rear metals (RM) (in our case, sample with Nb) for wires were prepared by two different techniques arc-melting and mechanical alloying. Microstructure characterisation was carried out by SEM including EDX and X-ray measurements. Mechanical measurements at room temperature were performed and the results of materials obtained by different techniques are analysed.

Nanocrystalline microstructure it was observed and this is associated with fine grain refinement of CuAgRM material after both technologies.

KEYWORDS: Cu based alloy; arc-melting; mechanical alloying; microstructure; microhardness

1. Introduction

Cu based alloy microalloyed with Nb was produced using preparation conditions typically applied for manufacturing of bulk metallic glasses (BMGs) which is prepared by arc melting (AM) with cold drawing [1] and similar composed alloy prepared by powder metallurgical (PM) technique in order to study the microstructure and the mechanical properties

In the first technique called „in-situ” thermodynamical aspects and kinetic limitations on the specific solidification process of phase formation and it is strongly dominated by controlled diffusion mechanism [2]. A distribution of Ag dendrites in the Cu matrix can be achieved by casting. During cold drawing the Ag dendrites are deformed to fine filaments.

The second technique, PM is a new one which combine powder metallurgy, heat treatments and deformation mechanism. Some advantages of this technique are known: the microstructural features to be developed are independent from the size of sample. In this case, almost any geometry of the sample can be obtained depending only on the equipment that is used.

In the last period some studies shown remarkable advances have been made in the development and comprehensive understanding of Cu-Nb alloys, used for wires. Such wires can be

produced by casting with a logarithmic strain $\eta=15$ and leads to a finally obtained cross section of wire with 0.2 mm depending on their forming ability [3].

To outstanding the mechanism and the mechanical properties of Cu-Ag-RM alloys, one short description about the material obtained by arc melting and similar material obtained by PM, it will be presented in this work.

However, there are no detailed informations about the manufacturing of the materials because there are a substantial difference between sample preparation under clean laboratory conditions using high purity elements and in small quantities for wires preparation.

Consequently, the aim of this paper was to prepare and to investigate a common Cu-Ag-RM composition under optimum conditions concerning the cooling rate for special phase formation and the purity of the elements in different techniques to avoid unpredictable effects and to compare the microstructure and the mechanical properties of this before preparing wires from them [4, 5].

The conditions that we used here are typically used for obtaining wires with very good properties.

2. Experimental procedure

2.1. Arc-melting technique

A 50 g ingot of this alloys with nominal composition Cu-7Ag-0.05RM (at.%), with RM = Nb,

and purity > 99.9 wt.% for all elements, were prepared by arc melting in argon atmosphere. The ingots were remelted several times in order to achieve a homogeneous master alloy. From these ingots, cylindrical bulk samples with 2.5 mm diameter and 70mm length were prepared by centrifugal casting device in copper mould casting.

The structure of the samples was studied by X-ray diffraction (XRD) using a Philips PW 1050 diffractometer (CoK-radiation) and optical microscopy. Scanning electron microscope equipped with an X-ray spectrometer were employed for detailed microstructural analysis.

The microstructure was imaged using conventional SEM. The test conditions to figure out

the mechanical properties should be the same like those typically used for crystalline material [6]. Measurements of mechanical properties were performed at room-temperature and quasistatic conditions. According to the ASTM standard for micro hardness testing, cylinders with a length/diameter ratio of 2.5mm diameter were prepared from the cast samples. The specimens were tested with an SHIMADZU machine. The conditions of microhardness measurements according to Vickers HV 0.01 were: compressive force 10 N, time of load 10 s. Data obtained from microhardness testing machine were evaluated by software LECO.

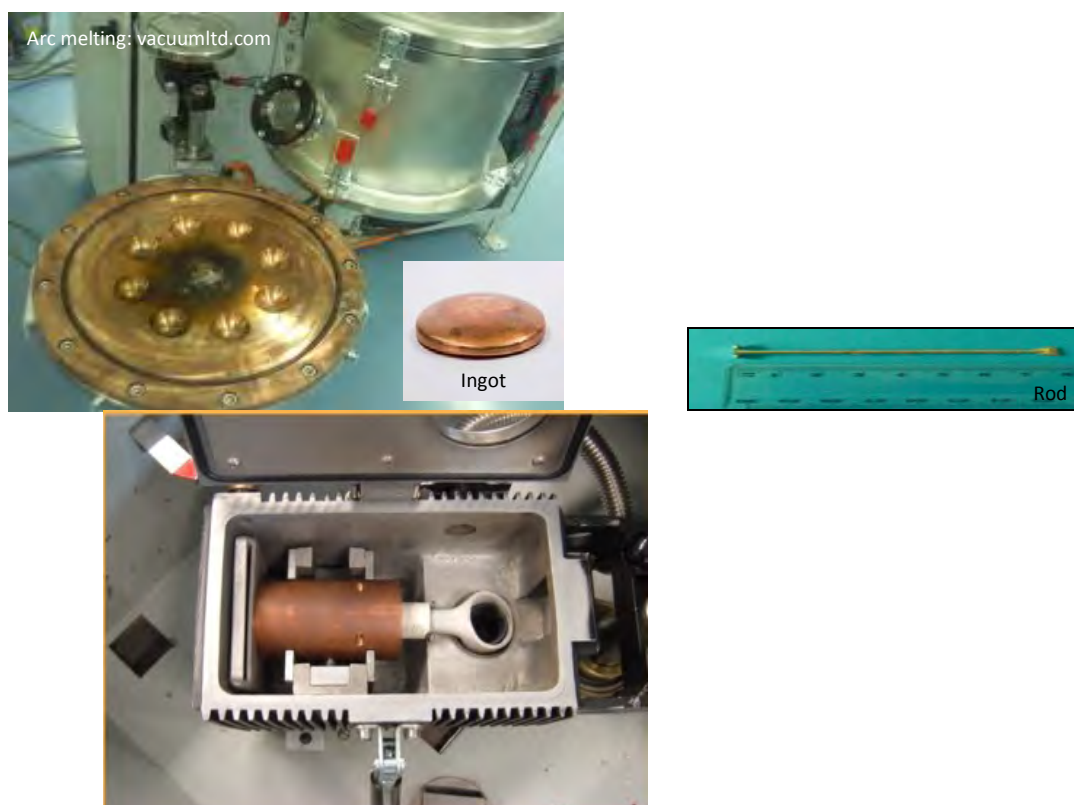


Fig.2. Arc melting for preparing ingot and centrifugal casting for preparing rod of Cu7Ag 0.05Nb

2.2. PM technique

Milling experiments starting from pure elemental powder mixtures (purity >99.9 wt. %) with nominal compositions Cu-7Ag-0.05RM (at.%), with RM = Nb and Cu, Ag were performed using a Retsch PM400 planetary ball mill and hardened steel balls and vials. No process control agent was used. The powders were milled for 30 h with a ball-to-powder mass ratio (BPR) of 13:1 and a milling intensity of 200 rpm cooling by liquid N₂ at liquid nitrogen temperature (77K) [7]. To avoid or minimize possible atmosphere contamination during milling, vial

charging and any subsequent sample handling was carried out in a glove box under purified argon atmosphere (less than 1 ppm O₂ and H₂O). The phases and the microstructure were characterized by X-ray diffraction (XRD) using a Philips PW 1050 diffractometer (CoK-radiation). The alloying was performed until complete solid solution of Ag and Nb within the Cu matrix has been achieved. The microstructure of the alloys was investigated by electron microscopy using a high-resolution scanning electron microscope (REM LEO 1530) with energy dispersive X-ray analysis (EDX) after different time of milling. From the SEM micrographs the size of the

alloying particles as well as the aspect ratio of the Nb filaments after deformation were determined. The lattice structure and the lattice constants (at room temperature) as well as the phase purity of the sample were investigated with an X-ray diffractometer (Philips, PW 1830) in Bragg Bretano geometry using

Co radiation. Based on the X-ray data the average grain size of Cu matrix was determined using Sherrer equation and Williamson-Hall plot. Microhardness by Vickers was performed by SHIMADZU machine at room-temperature and quasistatic conditions.



Fig. 3. Retsch machine and steel vials for preparing mixed powder of Cu7Ag 0.05Nb for compressed rods

3. Results and discussions

By arc-melting, CuAg forms a simple eutectic phase diagram with limited solubility. At binary Cu-7Ag alloy are detected two phases, namely a saturated Cu(Ag) solid solution and regions which show a reduced amount of Cu in comparison to the matrix. This situation changes for the Cu-7Ag-0.05Nb alloy. The addition of Nb leads to a slower decomposition reaction which in this case is found to be only continuous.

The grain boundary it was modify by the addition of a insoluble element like Nb.

This suppresses the diffusion along the grain boundary and hence enhances the formation of continuous precipitates [8]. Because of the specific solidification conditions in the arc-melter (relatively high cooling rate) and the particular composition with high carbon content a p phase formation it can be obtained. The reasons for the astonishing ductility of the arc-melted Cu-Ag alloy are likely manifold, which together give the capability for plastic deformation.

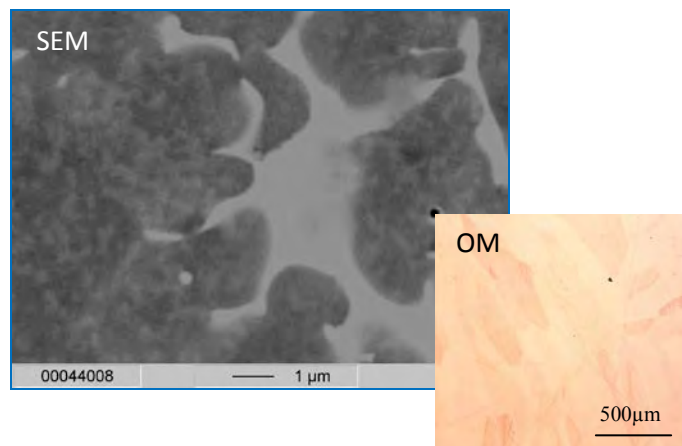
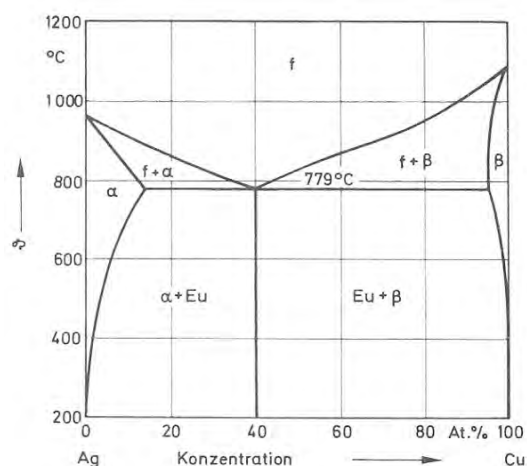


Fig.3. Phase diagram (a) of CuAg and precipitation modes as well as structure (c) and microstructures (b) of Cu7Ag 0.05Nb by arc melting with discontinuous precipitates (80-100HV)

Composition profiles measured by EDX (Fig. 3-b) show that the chemical composition frequently changes within a short distance (about once per $1\mu\text{m}$), indicate the formation of different very finely dispersed phases, which give the material its high strength and large ductility. Copper based materials leads to distinctively values of microhardness in surface.

At the second technique it was observed an intense mechanical alloying among all three phases (Cu, Ag, Nb) because of the high energy of ball milling. During milling time Nb shows a negligibly solubility in the solid state and it was observed niobium partly dissolves in the copper lattice during milling (fig. 4) [6]. The present investigation

demonstrates that this solubility can be improved to a strongly supersaturated Cu solid solution provided the appropriate mechanical alloying method is applied, by cryomilling. Scanning electron microscopy reveal a homogeneous single-phase microstructure after more then 10 hours of milling. Elemental Nb could no more be detected, indicating the formation of a metastable supersaturated Cu-Nb solid solution.

Cryomilling time influences the the graine size of elements and their miscibility. After cryomilling the structure of powder mixed is uniform. Microhardness increase with number of hours milling. (Fig. 5).

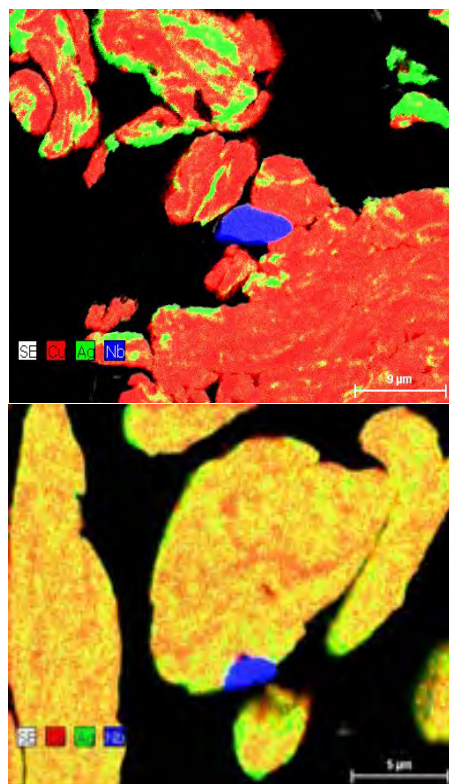
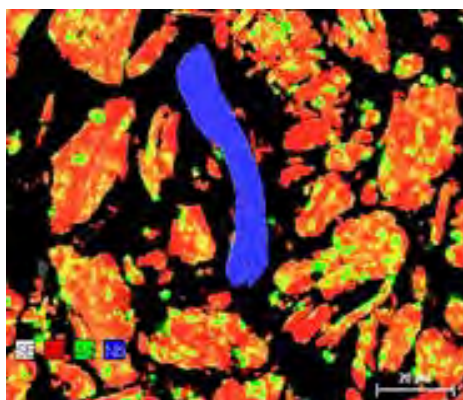


Fig. 4. SEM study of microstructure of Cu-7%Ag-0.05%Nb powder with mechanical alloying after 1h (a), 3h (b), 5h(c) and 10h(d) milling time

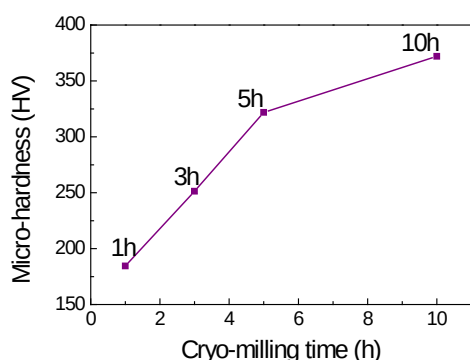


Fig. 5. Room-temperature microhardness curves for CuAgNb mechanical alloying samples. The inset shows how increases cryomilling time with microhardness curves of the alloy.

4. Conclusions

Conventional cast metallurgy cannot be applied on a large scale. Manufacturing of alloys from immiscible metal system can be carried out by using the following two techniques: rapid solidification (RS) and mechanical alloying (MA). By RS a fine distribution of two phases can be produced, but the formation of solid solution with a high content of the alloyed element is not possible. In contrast, by mechanical alloying, alloys with better homogeneity and a higher content of the alloyed element in solid solution can be manufactured. Due the high energy impact during milling, the region of solid state solution extends and alloys with very high homogeneity in the microstructure can be achieved by the use of under the appropriate conditions. In conclusion, applying preparation conditions typically used for the fabrication of bulk metallic glasses to the manufacturing of the Cu based alloy, superior mechanical properties have been achieved, due to the formation of a crystalline structure, with a ductile phase and finestructured Nb filamentary phase.

Also the work hardening behaviour of the crystalline alloy made by PM is excellent. Therefore, the most important benefit of this material is its distinct of uniform distribution of fine Nb particles in Cu-Ag matrix with very good plasticity, which is, as is known, a strong requisite for engineering applications.

Comparing the microhardness properties of crystalline metallic alloys obtained after two different techniques, arc-melting and PM, also the latter ones offer very interesting perspectives for novel applications as functional and structural materials for a variety of engineering applications when processed

under appropriate conditions. This opens new opportunities for the “processing for properties” of advanced materials with superior properties.

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References

- [1]. V.I. Pantsyrnyi, A.K. Shikov, A.D. Nikulin, A.E. Vorobova, E.A. Dergunova, A.G. Silaev, N.A. Bel'akov, I.I. Potapenko, IEEE Trans. Magn. 32 (4) (1996) 2866
- [2]. A. Inoue, T. Zhang, A. Takeuchi: Appl. Phys. Lett. 71 (1997) 464
- [3]. E. Botcharova, J. Freudenberger, A. Gaganov, Materials Science and Engineering A 416 (2006) 261–268
- [4]. X.H. Lin, W.L. Johnson, W.K. Rhim: Mater. Trans. JIM 38 (1997) 5
- [5]. A. Gebert, J. Eckert, L. Schultz: Acta Mater. 46 (1998) 5
- [6]. K. Werniewicz, U.Kuhn, N. Mattern, B. Bartusch, J. Eckert, J. Das, L. Schultz, T. Kulik: Acta. Mater. 55 3513 (2007)
- [7]. S. Ichikawa, K. Miyazawa, H. Ichinose, K. Ito, Nanostruct. Mater. 11(1999) 1301
- [8]. E.Bocharova, Ph.D. Thesis, TU Dresden, Germany, www.ifw-dresden.de/imw/theses/DrBocharova.pdf.

STUDY ON THE FINNING PROCESS DEFORMATION

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ABSTRACT

The fin stamping is the local plastic deformation of the metallic part of plat or strip applied in the aim of the imparting a fin, a recess, an inscription, an effigy etc. In the deformation process, in the case of the fin, the strain state is defined by the elongation strain in the transversal direction, the strain equal to zero in the long of the profile, and negative strain in the direction of the thickness. The elongation strain may be so great and the crack risk is, also, great. In the work is developed a study about the function of the fin profile and the value of the strain and strain rate in the aim of the calculus of the maximum value of the strain.

KEYWORD: plastic deformation, strain state, fin profile

1. Introduction

The fin stamping is the local plastic deformation of the metallic part of plat or strip, applied in the aim of the imparting a fin, a recess, an inscription, an effigy etc.

With a view to improving of the stability and the piece quality, in the deformation process the part is rigid fixed, on t he surfaces which are not deformed. As result the deformation has a local character, makes by the reduction of the thickness and not by the pulling of the material from the neighbor zones (as in case of the deep drawing). The thickness of the part decreases more intensive where the deformation intensity is greater. Consequently, at the fin stamping process, in the deformation zone, the great tensile stresses are developed and the rescue of crack appearance is great. From this reason the local deformation degree must be smaller of the admissible strain of the metallic material.

2. Analytical Study

We consider the cross section of the fin imparted in the deformed part rendered in figure 1.

In the analytical form the geometry of the relieved zone is described by a mathematical function $f(x)$.

In the hypothesis of the deformation without the pulling of the material from the neighbor zones the local deformation is defined by the relation:

$$\varepsilon = \frac{ds - dx}{dx} \quad (1)$$

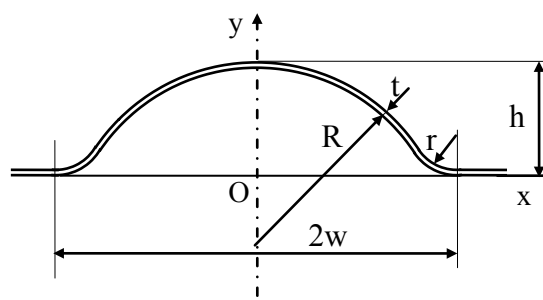


Fig. 1. The fin arch geometry

In this relation we denote ds the length of the curve arc resulted by deformation of the initial infinitesimal segment dx .

Haw:

$$dy = df(x) = f'dx \quad (2)$$

we have:

$$ds = \sqrt{dx^2 + dy^2} \quad (3)$$

Combining the equations (2) and (3) and finally the equation (1) we obtain:

$$\varepsilon = \sqrt{1 + f'^2} - 1 \quad (4)$$

At the given moment the strain rate is defined by the equation:

$$\dot{\varepsilon} = \frac{d}{dt} \left(\frac{ds - dx}{dx} \right)$$

Because dx is independent of the time the equation (5) becomes:

$$\dot{\varepsilon} = \frac{d}{dx} \left(\frac{ds}{dt} \right) \quad (5)$$

This equation shows that the strain rate depends of the speed of local length arc increasing.

The fin arch is composed of three circle arc: the principal circle arc of radius R and two lateral arcs of the radius r .

Because of the symmetry, according to the axis Oy , we consider the half of the fin, in accordance with the figure 2.

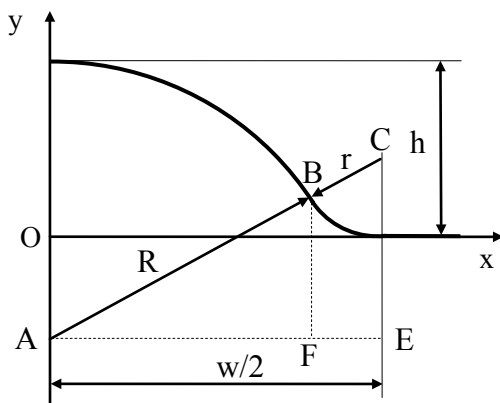


Fig. 2. Scheme of fin profile

The dimensions of the fin arch are: the breadth $2w$ and the height h . The thickness of the part is denoted t .

The correlation between the dimensions of the fin is established below.

We have the equation of the greater circle arc:

$$x^2 + (y + R - h)^2 = R^2 \quad (6)$$

For the small circle arc we have:

$$(x - w)^2 + (y - r)^2 = r^2 \quad (7)$$

The point B is inflexion point and, consequently, AB and BC straight segments

are collinear. We denote the coordinates a and b of the point B .

Form the condition $\triangle ABF \sim \triangle ACE$ we have:

$$\frac{BF}{R} = \frac{CE}{R + r}$$

and

$$\frac{b + R - h}{R} = \frac{R - h + r}{R + r}$$

Thus we have:

$$b = R \left(1 - \frac{h}{R + r} \right) + h - R \quad (8)$$

Form the constructive condition the dimensions R , h and r are known.

The coordinate a is determined from the equation:

$$a^2 + (b + R - h)^2 = R^2 \quad (9)$$

Consequently, the function of the fin is defined by the equation:

$$f(x) = \begin{cases} x^2 + (y + R - h)^2 = R^2 & \text{for } x \leq a \\ (x - w)^2 + (y - r)^2 = r^2 & \text{for } x > a \end{cases} \quad (10)$$

The breadth may be calculated with the equation:

$$w = 2\sqrt{h(2R - h + 2r)} \quad (11)$$

The function describes the mathematical expression of the fin curve in the final form.

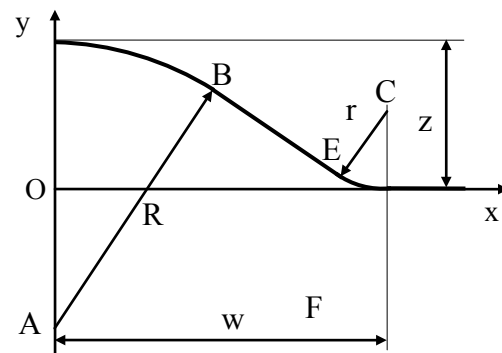


Fig. 3. Scheme of fin profile at the certain moment

In the effective deformation process the fin is developed step by step. At the certain moment, corresponding to the parameter z ,

being the penetration of the punch in the semi-product, the aspect of the fin corresponds with the form rendered in figure 3. The parameter z has values between 0 and h .

The profile of the deformed zone is composed by a circle arc of radius R with the superior point at z in the direction y , a circle arc of the radius r and the straight segment BE which joins the two circle arcs.

We consider the coordinates of the point $B(a,b)$ and for point $C(c,d)$.

The general mathematical expression of the function $f(x)$ is:

$$f(x) = \begin{cases} x^2 + (y + R - z)^2 = R^2 & \text{for } x \leq a \\ y = mx + n & \text{for } a < x \leq c \\ (x - w)^2 + (y - r)^2 = r^2 & \text{for } x > c \end{cases} \quad (12)$$

For calculate the coordinates a, b, c, d we will apply the following conditions:

1. The point B satisfies the first equation,

$$a^2 + (b + R - z)^2 = R^2 \quad (13)$$

2. The point C satisfies the third equation,

$$(c - w)^2 + (d - r)^2 = r^2 \quad (14)$$

3. The tangents at the circle arcs in the point B , respectively, C are equal. This condition is defined by expression

$$f'_1(a) = f'_3(c)$$

From this condition we have:

$$m = \frac{a}{b + R - z} = \frac{c - w}{d - r} \quad (15)$$

4. The fourth condition derived from the fact as the two tangents are situated in the same straight, that is the ordinate at the origin is the same. Thus we have:

$$b = \frac{c - w}{d - r} a + n$$

$$d = \frac{c - w}{d - r} c + n$$

and

$$b - d = \frac{c - w}{d - r} (a - c) \quad (16)$$

5. The breadth w is constant, indifferent of value of the parameter z . This condition has following mathematical expression:

$$w = c + \sqrt{2rd - d^2} \quad (17)$$

Because the value of coordinate d is small, for practically calculus may be neglected.

Solving the equation (13), (14), (15), (16) and (17) we will have completely defined the parametric function $f(x)$ of parameter z . Taking values for z from 0 until h we will define the aspects of the different moments of the deformation process. Thus, if we admit the movement of the mobile system of the press defined by speed v_0 , and that the speed is constant, we have the time increment, at the real moment, calculated with the relation:

$$\Delta t_i = \frac{\Delta z_i}{v_0} \quad (18)$$

The movement of the active element of the deformation die is defined by the iterative equation:

$$z_i = z_{i-1} + v_0 \cdot \Delta t_i \quad (19)$$

In the analytical form we have:

$$z = v_0 \cdot t \quad (20)$$

Using the equation (20) in the equations (12), (13), (14), (15), (16) we can define the function of the fin profile in function of the time, respectively:

$$f(x) = \begin{cases} x^2 + (y + R - v_0 \cdot t)^2 = R^2 & \text{for } x \leq a \\ y = mx + n & \text{for } a < x \leq c \\ (x - w)^2 + (y - r)^2 = r^2 & \text{for } x > c \end{cases} \quad (21)$$

In this equation we have:

$$a^2 + (b + R - v_0 \cdot t)^2 = R^2$$

$$m = \frac{a}{b + R - v_0 \cdot t} = \frac{c - w}{d - r} \quad (22)$$

The equations (14) and (16) have the same mathematical expressions.

In this mode we will study the evolution of deformation process in time, at the beginning of the movement of the punch until the final when the parameter z is equal to h .

3. Principles of Practical Calculus

In the figure 4 is showed the evolution of the deformed form of the part.

In the initial moment, the piece material is not deformed, in the deformation zone, and its geometry is defined by the straight segment AD .

In the deformation time the joint point B moves from the point A describes a trajectory defined of a mathematical function with maximum.

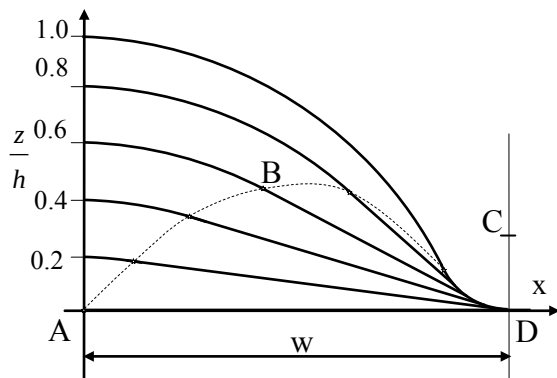


Fig. 4. Scheme of profile evolution of the deformation zone

Using the equation (4) we can define the strain rate according to the function $f(x)$ in the form:

$$\dot{\varepsilon} = \frac{d}{dt} \left(\sqrt{1 + f'^2} \right) \quad (23)$$

Thus, using the equations defined above we can calculate the strain rate in the any moment and any point of the deformed profile.

For a numerical case we consider the following values:

- R , the great radius of the profile, 20 mm;
- r , the small radius of the profile, 2 mm;
- h , the heath of the profile, 12 mm;
- v_0 , the punch movement speed, 10 mm/s.

We have:

$$w = 39 \text{ mm}$$

$$f(x) = \begin{cases} x^2 + (y + 20 - z)^2 = 400 & \text{for } x \leq a \\ y = mx + n & \text{for } a < x \leq c \\ (x - 39)^2 + (y - 2)^2 = 4 & \text{for } x > c \end{cases}$$

and conditions:

$$a^2 + (b + 20 - z)^2 = 400$$

$$(c - 39)^2 + (d - 2)^2 = 4$$

$$\frac{a}{b + 20 - z} = \frac{c - 39}{d - 2}$$

$$b - d = \frac{c - 39}{d - 2} (a - c)$$

$$c + 2\sqrt{d^2} = 39$$

From the last condition we have the factor c in function of the factor d , then, from the second condition we establish the factor d and using the first and third conditions we will establish the factors a and b .

Finally the function $f(x)$ is determined and the evolution of the profile of the fin, in the any time of deformation process, it was established.

4. Conclusions

The fin imparting in a part is a complex deformation process. In this process a great elongation occurs in the base of the thickness.

From this reason the establishing of the local deformation in the length of the part is necessary.

References

In this work we made an analytical study on the geometry of the imparted fin in the evolution of the deformation process.

It was established the mathematical function of the geometry of fin and the definition conditions, using the parameter of the movement of the punch.

The function of the fin profile is necessary for calculus of the deformation degree and strain rate in the long of the part in the any time of the deformation process.

The results have utility for predictive design calculus of this deformation process.

[1]. **Teodorescu, M. a.o.** – Elemente de proiectare a stantelor si matritelor, EDP, Bucuresti, 1977.

[2]. **Roamnovski, V.P.** - Stantarea si matritarea la rece, Ed. Tehn., Bucuresti, 1970.

[3]. **Lazarescu, I., Stetiu G.** – Proiectarea stantelor si matritelor, EDP, Bucuresti, 1973.

[4]. **Merchant, E.M.**, Mechanics of the metal cutting process, Journal of applied physics, MC Shaw, 2004.

[5]. **Jaspers, S.**, Material behavior in conditions similar to metal cutting: flow stress in the primary zone, Journal of Material Processing Technology, vol.122, Issues 2-3, March 2002, p.322-330.

[6]. **Nagîț, Gh., Braha, V.**, Bazele prelucrării prin deformare plastică, Ed. Tehnică, Chișinău, 2002.

[7]. ASM, Metals Handbook, vol.4, Forming, Ohio, SUA, 1969.

SPECTROPHOTOMETRIC DETERMINATION OF OS(VIII) WITH NITROSO R SALT AS CHROMOGENIC REAGENT

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ABSTRACT

Several methods have been reported for the spectrophotometric determination of osmium with various chromogenic reagents. Some of these reagents react slowly with osmium and conditions for obtaining reproducible colours are usually empirical.

In this context, a simple and sensitive spectrophotometric method for the determination of trace amounts of osmium(VIII) using disodium-1-nitroso-2-hydroxynaphthalene-3,6- disulphonate (Nitroso R salt) is described. The method is based on the formation of an Os–Nitroso R salt complex which exhibits two different colours as function of pH. Linear calibration graphs are obtained up to 60 µg/mL of the analyte at pH = 4.8. The stoichiometry of the complex is found to be 1: 4 by mole ratio method. The method is optimized and different analytical parameters were evaluated. For instance, the calculated values for the molar absorptivity are of $3.645 \cdot 10^3$ L/mol.cm (pH=0; $\lambda = 550$ nm) and $1.695 \cdot 10^3$ L/mol.cm (pH=4.8; $\lambda = 510$ nm), respectively. The proposed method should be valuable for the determination of osmium(VIII) with good accuracy and precision.

KEYWORDS: osmium, spectrophotometric determination, Nitroso R salt, chromogenic reagents

1. Introduction

Osmium is the rarest and a trace platinum–group element in the Earth’s crust; it is usually accompanied by many other elements. It is frequently used in small quantities in alloys where frictional wear must be minimized. These alloys are typically used in ballpoint pen tips, fountain pen tips, record player needles, electrical contacts and high pressure bearings. It is therefore not surprising that osmium is no longer considered industrially important, considering this list of applications. A less dated application of osmium is in the platinum/osmium (in a 90:10 ratio) alloy used in implants such as pacemakers and replacement valves. Osmium compounds are

used in many processes of organic synthesis. For example, heterometal complexes of osmium with chromium are efficient catalysts of alcohol oxidation, the reaction by-product being only water. Such reactions are promising in the so-called green chemistry [1]. Osmium compounds are used in medical, biological and tomographic studies. There are osmium compounds characterized by antitumor activity. Osmium containing reagents are promising for diagnostics of the presence of specific DNA nucleotide sequences [1].

The quantitative determination of osmium in complex samples usually demands considerable efforts at all stages of the analysis because Os is disposed to participate in redox processes and

dissolution of the samples can be accompanied by osmium losses as a result of incomplete dissolving and the formation of volatile OsO_4 . Unfortunately, the number of spectrophotometric methods providing rapid quantitative determination of osmium in real samples is rather small [1]. Spectrophotometric methods involving organic reagents (Table 1) are often used in the analytical practice, though most of these methods demand complicated sample preparation, e.g. preliminary separation of osmium in the form of tetroxide, or the extraction of coloured osmium compounds by means of organic solvents. Therefore the search for new accessible, selective and sensitive reagents, which would make it possible to determine the total osmium content, independently of the form of osmium in the analyte, is an very actual task.

Table 1. Chromogenic reagents for the spectrophotometric determination of osmium

Reagent	Remarks	Reference
Thiobenzhydrazides	The formed colored complexes are stable more than 12 hours and their molar absorptivities are in the 10^4 range.	[2]
Ethyl isobutrazine hydrochloride	The reagent reacts with Os(VIII) to form red complex species instantaneously in 2M HCl at $25 \pm 2^\circ\text{C}$	[3]
4-(2-pyridylazo)resorcinol	The orange – red mixed complex of Os absorbs light at $\lambda_{\text{max}} = 530\text{nm}$ with a molar absorptivity of $2.5 \cdot 10^4$ L/mol·cm	[4]
Pyrocatechol and hydroxyl amide	An ethanolic solution of pyrocatechol in the presence of hydroxyamide and Os(VIII) on heating at a pH between 7.0 and 9.0 gives a very sensitive color reaction.	[5]
5 – chloro – 2 – hydroxythio benzhydrazide	Beer's law was obeyed in the concentration range of 1.8 – 14.4 ppm of osmium in a chloroform solution at 510 nm. The molar	[6]

	absorptivity was $1.056 \cdot 10^4$ L/mol·cm.	
Carminic acid peroxide	The method is based on the osmium catalytic effect on the oxidation of carminic acid by hydrogen peroxide.	[7]
Basic dyes	The catalytic effect on the oxidation reactions on methylene blue, butylrhodamine B and Nile blue by KIO_4 are applied for the determination of Os(IV) in the acidic medium at $90 \pm 0.5^\circ\text{C}$.	[8]
Allyl thiourea	Os(VIII) forms a 1:1 complex with allylthiourea. Conformity to Beer's law was observed for up to $20\mu\text{g/mL}$ of osmium in acidic medium (molar absorptivity $2.17 \cdot 10^4$ L/mol·cm at 298nm)	[9]
Phenothiazine derivatives	Phenothiazine derivatives readily react with osmium in acid or buffer media to yield colored species which could be followed spectrophotometrically.	[10]
Phenanthrene quinone monoxime	Beer's law is obeyed in the concentration range of 1.0 – $10.9\mu\text{g}$ of osmium in 10 mL of chloroform.	[11]
Ethylene thiourea	The method is based on the formation of an instantaneous purple colored complex at room temperature in strongly acidic (pH=1) solution having absorption maximum at 490 nm.	[12]

The first attempts of spectrophotometric determination of osmium using Nitroso R salt as chromogenic reagent have been reported by S. Nath and R.P. Agarwal [13]. Their study was focused on the establishment of the optimum conditions of complex formation and Beer's law conformity.

Due to the fact that the speciality literature contains few informations regarding the complex formed between osmium and Nitroso - R salt, our aim was to carry out a detailed study on the conditions

of this complex formation. In this context, the influence of the solutions pH, heating time and the concentration of ligand and metallic ion have been studied.

2. Experimental

2.1. Reagents and apparatus

The experiments were performed with:

- Stock solution of osmium of 3mg/mL concentration which has been obtained by the dissolution of OsO_4 in 0.5M HCl. The working solutions were prepared by the dilution of the corresponding amount of the stock solution with bidistilled water at 25 mL.

- The aqueous solution of the Nitroso-R salt (NRS) with a concentration of 10^{-2}M

- The pH adjustments were made with the solutions of HCl, CH_3COOH and CH_3COONa

- The values of solutions pH were measured with an Radiometer pH M64 pH – meter.

- The absorbance of the solutions was measured on a 104D-WPA spectrophotometer, using glass cells of 1cm.

2.2. Methodology of determination

To a volume of maximum 5 mL of solution containing osmium (0.3-1.5mg) 10mL of Nitroso-R salt solution and 5 mL of buffer acetate(or a determined volume of 2N HCl) were added. Then, the mixture is heating on a bath water, for 2 hour s, at boiling. After cooling, the solution is quantitatively passed with bidistilled water into a flask of 25 mL and its absorbance is measured versus a blank sample.

3. Results and discussion

Due to the extraordinary chemical inertness of Os(VIII), the complex with nitroso-R salt is formed only after a continuous heating on a water bath at boiling

the minimum time of heating being of two hours. The complex is stable more than 24 hours.

In the case of Os–NRS complex, the change of absorbance as function of the solution pH (Figure 1) indicates a strong influence of the acidity on this complex formation and stability.

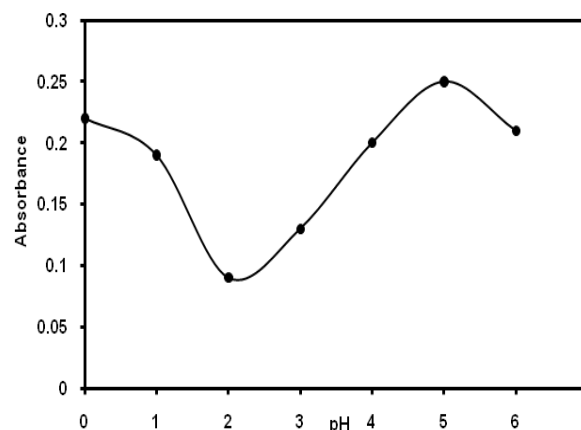


Fig.1. The effect of the solution pH on the Os–NRS complex ($C_{\text{Os}}=1.89 \times 10^{-4} \text{ mol/L}$; $C_{\text{SRN}}=10^{-2} \text{ mol/L}$)

According to Figure 1, it is obvious the existence of two ranges of pH in which the Os–NRS complex exhibits different colours. Thus, in hydrochloric solutions (pH=0) a violet color is obtained, while in acetate buffer solutions a green color with the absorption maximum at pH=5 is appeared.

In order to study the behavior of the Rh(III) and Os(VIII) mixture, the experiments were performed more in acetate medium.

The absorption spectra of the Os(VIII) complex at pH=0 and pH=4.8, by comparison with that of the Nitroso-R salt reagent are shown in Figure 2.

It can be seen from Figure 2 that the complex spectrum recorded at pH=0 exhibits an absorption maximum at $\lambda=550\text{nm}$. On the other hand, the spectrum from the acetate medium exhibits two maxima, at $\lambda=510\text{nm}$ and 620nm , respectively.

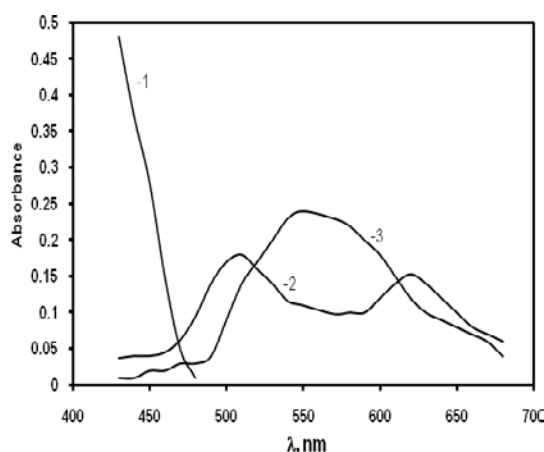


Fig. 2. Absorption spectra for: 1- Nitroso R salt reagent; 2-Os-NRS complex at pH= 4.8; 3- Os-NRS complex at pH=0. ($C_{Os} = 1.261 \times 10^{-4}$ mol/L; $C_{NRS} = 10^{-2}$ mol/L)

In order to establish the linearity range of the absorbance–osmium concentration dependence, the calibration curves were performed at pH=0 and pH=4.8, the absorbance measurements being accomplished at three wavelengths (Fig. 3).

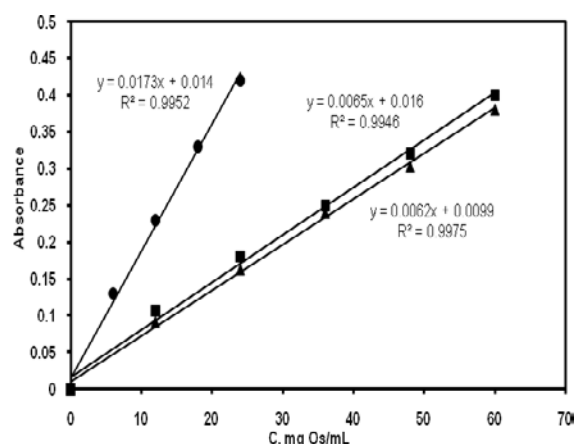


Fig. 3. The calibration curves at the determination of Os(VIII) with NRS pH= 0, $\lambda = 550$ nm (●); pH = 4.8, $\lambda = 510$ nm (■), $\lambda = 620$ nm (▲)

The statistical parameters characteristic to the calibration curves for the spectrophotometric determination of Os(VIII) with Nitroso–R salt as chromogenic reagent are listed in Table 2.

Table 2. Analytical parameters.

Reaction medium	pH = 0 ($\lambda = 550$)	pH = 4.8 ($\lambda = 510$)	pH = 4.8 ($\lambda = 620$)
Parameter			
Intercept	0.014	0.016	0.0099
Slope (L/μg)	$0.0173 \cdot 10^{-3}$	$0.0065 \cdot 10^{-3}$	$0.0062 \cdot 10^{-3}$
Correlation coefficient (R^2)	0.9935	0.9946	0.9975
RSD (%)	1.26	2.68	2.70
Linear dynamic range (μg/mL)	6- 24	12- 60	12- 60
Molar absorptivity (L/mol.cm)	$3.645 \cdot 10^3$	$1.695 \cdot 10^3$	$1.458 \cdot 10^3$

The composition of the Os–NRS complex has been established by the mole ratio method. This method involves the variation of the ligand amount, while the

amount of metal is keeping constant. The method was applied at pH=0 and 4.8, respectively (Figure 3 and Figure 4).

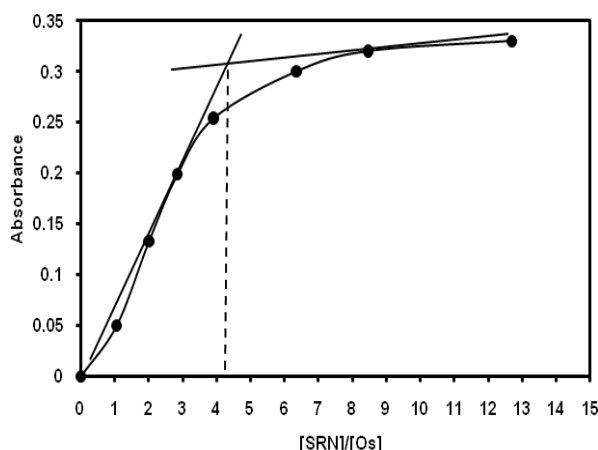


Fig.3. Establishment of the combination ratio for the Os–NRS complex. $C_{Os} = 0.1892 \times 10^{-3} \text{ mol/L}$; C_{NRS} – changing; $\lambda = 510 \text{ nm}$; $\text{pH} = 4.8$.

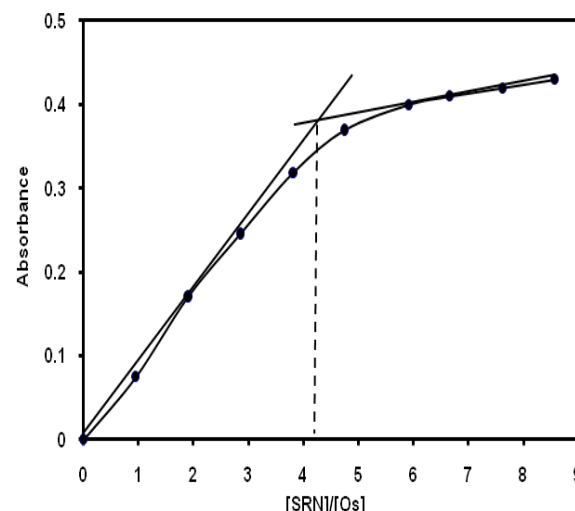


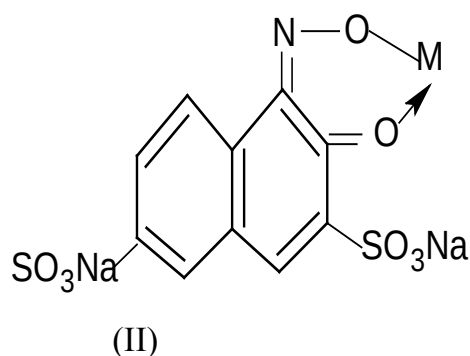
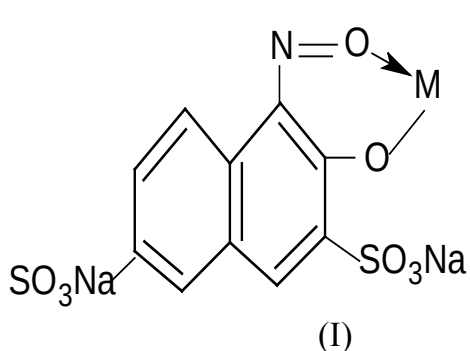
Fig.4. Establishment of the combination ratio for the Os–NRS complex formed in solutions of $\text{pH} = 0$; $C_{Os} = 0.1263 \times 10^{-3} \text{ mol/L}$; C_{NRS} – changing; $\lambda = 550 \text{ nm}$.

From the analysis of the obtained plots, it is obvious that by the metal–ligand interaction a complex with the combination ratio of 1Me: 4L is formed. The complex of green color formed at $\text{pH} = 4.8$ is characterized by a stability constant with the value of $\beta = 1.5203 \times 10^{15}$.

This combination ratio might be due to the fact that in the hydrochloric media OsO_4 is unstable and reduces at low states of oxidation.

According to the findings of the Losev and Kudrina researchers [14], as a result of the temperature increasing, in solution is formed the hexachlorosmat (IV) which by interaction with Nitroso–R salt leads to the formation of new Os–O bonds.

The most probable modality of osmium bonding would be the formation of the stable cycles I and II, corresponding to the enolic or cetonic form of the Nitroso–R salt.



4. Conclusions

- The complexation reaction between Os(VIII) and Nitroso–R salt depends

on the solution pH; the complex may be formed both in acidic medium of $\text{pH} = 0$ (hydrochloric solutions) and at $\text{pH} 4.8$ (acetate buffer)

- The products of the reaction are:
 - at pH=0 a complex of violet color having the maximum absorbance at $\lambda = 550\text{nm}$;
 - at pH=5, a green complex with the maximum absorbance at $\lambda_1 = 510\text{nm}$ and $\lambda_2 = 620\text{nm}$.
- The calibration curve is linear up to $60\mu\text{g/mL}$ at pH = 4.8.
- The composition of the Os–NRS complex, established by the mole ratio method, is of 1Os to 4NRS.
- The calculation of the stability complex of the Os–NRS complex leads to the value $\beta = 1.5203 \times 10^{15}$.

References

- [1]. D.B. Petrenko, O.A. Tyutyumuk, Yu.M. Dedkov, *Catalytic kinetic methods for determining osmium (review)*, Inorganic Materials 46(2010) 1493 – 1498.
- [2]. S.C. Shome, S. Nandy, A. Guhathakurta, N.C. Ghosh, H.R. Das, P.K. Gangopadhyay, *Spectrophotometric determination of ruthenium, rhenium, osmium and platinum with organic thiohydrazides*, Mikrochim Acta 70(1978) 343 – 357.
- [3]. A. Thimme Gowda, N.M. Made Gowda, *Spectrophotometric determination of osmium with ethylisobutrazine hydrochloride*, Microchimica Acta 88(1987)351 – 357.
- [4]. S. Dadfarnia, M. Shamsipur, *Extraction–spectrophotometric determination of osmium using 4–(2–pyridylazo) resorcinol*, Bull. Chem. Soc. Jpn. 64(1991)3063– 3066.
- [5]. M.K. Deb, N. Mishra, K.S. Patel, R.K. Mishra, *Sensitive spectrophotometric determination of osmium with pyrocatechol and hydroxyamide*, Analyst 116(1991) 323– 325.
- [6]. S.S. Sawant, *Sequential separation and spectrophotometric determination of osmium and platinum with 5–chloro–2–hydroxythiobenzhydrazide*, Anal. Sci. 25(2009) 813– 818.
- [7]. J.L. Manzoori, M.H. Sorouraddin, M. Amjadi, *Spectrophotometric determination of osmium based on its catalytic effect on the oxidation of carminic acid by hydrogen peroxide*, Talanta 53(2000) 61– 68.
- [8]. Q.E. Cao, Z.Li, J. Wang, C.Li, *Catalytic spectrophotometric determination of osmium based on oxidation of basic dyes*, Chem. Anal.(Warsaw) 47(2002) 701–712.
- [9]. B. Morelli, *Allylthiourea as a reagent for the spectrophotometric determination of osmium*, Analyst 111(1986)1289–1292.
- [10]. J. Seetharamappa, N. Motohashi, D. Kovala–Demertzi, *Application of phenothiazine derivatives and other compounds for the determination of metals in various samples*, Current Drug Targets 7(2006) 1107–1121.
- [11]. A. Wasey, R.K. Bansal, B.K. Puri, *Spectrophotometric determination of iridium(III) and osmium(VIII) with phenanthrenequinone monoxime after extraction into molten naphthalene*, Microchimica Acta 82(1984) 211 – 220.
- [12]. B. Joseph, S. John, M. Prajila, A. Joseph, *Spectrophotometric determination of osmium(VIII) in trace amounts using ethylene thiourea(ETU) as chromogenic reagent*, Indian Journal of Chemical Technology 18(2011) 113 –117
- [13]. C. Paduraru, Ph. D. Thesis „Analytical Chemistry of Platinum Metals” (2005)
- [14]. V.N. Losev, Yu. V. Kudrina, A.K. Trofimchuk, P.N. Komozin, *Features of the sorptive extraction of osmium in different states with silica gels chemically modified with mercapto and disulfide groups*, J. Anal. Chem. 59(2004) 546 - 551

EXPERIMENTAL RESEARCHES ON THE LOBE DEFORMATION PROCESS

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ABSTRACT

In this work are presented the physical model, experimental conditions and researches concerning the lobe process. In this aim it was worked a physical experimental system composed of the deformation die, hydraulic press and the data acquisition system – resistive force transducer, electronic tensometer Spider 8, and computer. The experiments are focused to the establishing of the force variation in the tome of deformation process.

KEYWORD: plastic deformation, force, physical model

1. Introduction

The force at the lobe deformation process is, generally, calculated with the empirical mathematical expressions. One of these is showed above [1]:

$$F = k \cdot p \cdot S \quad (1)$$

In this relation k is coefficient which values are rendered in the table 1, p – the pressure applied on the material and S is the plan surface of the lobe (table 2).

Table 1. Values of the coefficient k

Advised values of coefficient k	
$t \leq 1 \text{ mm}$	$t = 1 - 1.5 \text{ mm}$
0.7 – 0.8	1.0 – 1.6

Table 2. Values of the pressure, p

Pressure p [daN/mm ²], for:		
Light steel	Brass	Aluminum
30 – 40	20 – 25	10 – 20

For evaluation of the deformation force we can consider the maximum values of the deformation degree.

Thus at the final moment of the deformation process we have the maximum

strain in the superior section of the lobe (fig.1).

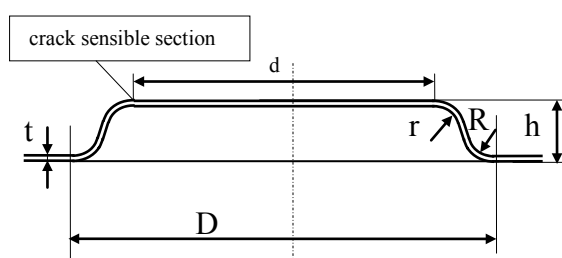


Fig. 1. Scheme of the stamped lobe

Effective dimensions of the stamped lobe are: D of 24 mm, d of 18 mm, h of 5 mm, R of 2 mm, r of 1 mm.

In this section the strain has the maximum value $\varepsilon_{\max}$ what may be calculated in function of the local decreasing of the thickness [2].

Between the strain and real stress there is a correlation defined by the hardening equation.

For example:

$$\sigma = \sigma_0 + \sigma_1 \cdot \varepsilon^n \quad (2)$$

Where σ_0 is the yield stress in the actual deformation conditions, σ_1 -constant, and n is the hardening coefficient.

Thus for maximum value of the strain results the maximum value of the stress, respectively:

$$\sigma_{\max} = \sigma_0 + \sigma_1 \cdot \varepsilon_{\max}^n \quad (3)$$

Using the equation (3) we can write:

$$F_{\max} = S \cdot (\sigma_0 + \sigma_1 \cdot \varepsilon_{\max}^n) \quad (4)$$

In this equation S is the effective value of the cross area in the superior section of the part, respectively:

$$S = l \cdot t_{ef} \quad (5)$$

where l ($l = \pi \cdot d_b$) is the length of lobe bottom and t_{ef} is effective value of the thickness in this section.

In the practical calculus we can use a relation:

$$F_{\max} = k_1 \cdot S_0 \cdot \sigma_r \quad (6)$$

In this relation S_0 is the initial area of the superior section (for thickness t_0), σ_r is the conventional maximum tensile stress and k_1 is a coefficient with values approach unit.

2. Experimental conditions

The aim of this work is the establishing in the experimental way the variation of the force at the lobe stamping process.



Fig. 2. The experimental lobe die:
 1-hydraulic press, 2-lobe die, 3-resistive force transducer

The laboratory conditions of the lobe stamping are the follows:

- the proves are cut from steel strip for sever drawing deep, with 0.6 mm of thickness,
- the lobe die showed in the figure 2,
- force resistive transducer,
- the data acquisition system



Fig. 3. General view of the experimental system

3. Experimental results

The experimental program had following objectives:

- establishing the force variation;
- visualizing the microstructure aspect;
- estimation of crack sensible section.

The dimensions of proves were: the length of 80 mm and the breath of 30 mm. In each prove were stamped two lobes.

For example, in the figure 4 is showed one stamped sample.



Fig.4. Example of stamped prove

For establishing the sensible crack section we prepared a micrographic prove and analyze the variation of the thickness.

In the section of the diameter d the thickness of the sample presents a visible decreasing (fig. 5).

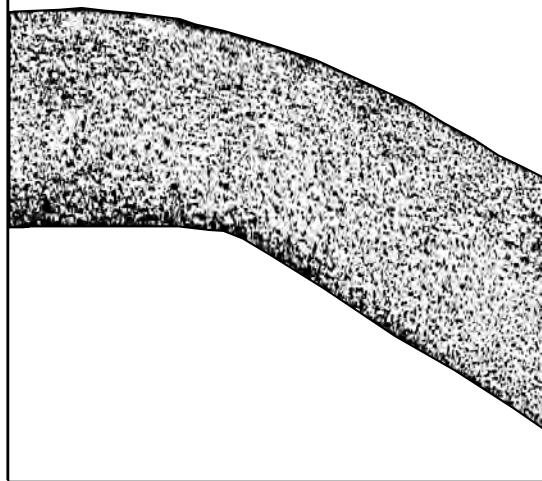


Fig. 5. Aspect of stamped sample section
 ($\times 50$, Nital 5)

The decreasing of the thickness in the critical section is of 80% approximately. Moreover, in this zone the structural hardening of the material has a great intensity.

In figure 6 is showed the variation of the microstructure in the sensible crack section. Because the level of the deformation degree is great the microstructure is strong influenced.

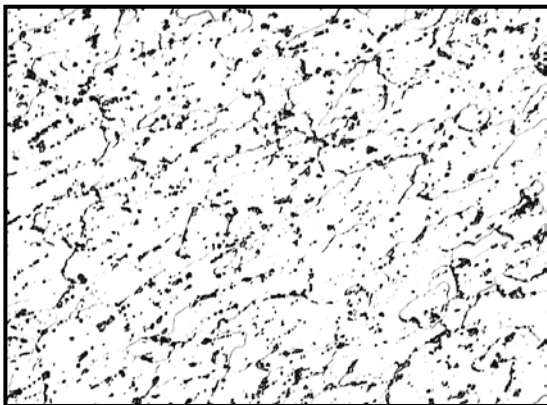


Fig. 6. Aspect of crystalline grains in critical section, ($\times 250$, Nital 5)

The crystalline grains are much deformed. Consequently, local hardening intensity is great and the probability of the cracks appearance in this zone is very great.

Variation of the force in the time of the lobe stamping process is showed in the figure 7.

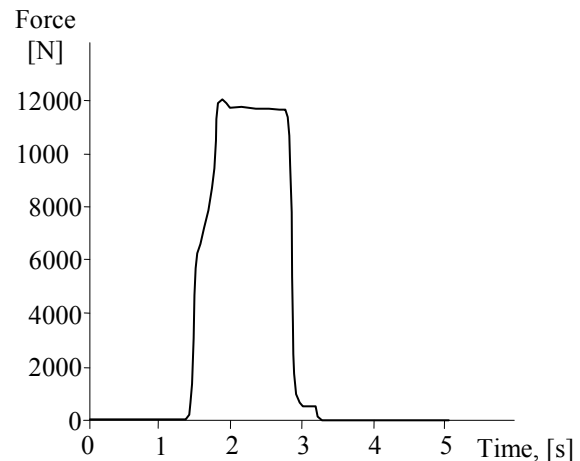


Fig. 7. Variation of force in the stamping process

The force rapidly increases until the maximum value of 11190N, then it maintains at this value when the change of the movement sense.

The stress, in the sensible crack section, may be calculates in the function of the maximum value of the force using the above relation:

$$\sigma = \frac{F_{\max}}{\pi \cdot d \cdot t} \quad (7)$$

In the actually conditions we have the level of the tensile strain in the critical section

$$\sigma = 329.97 \text{ N/mm}^2$$

that is 97.05 % of the conventional tensile stress σ_r of the material.

Considering the hardening coefficient by the plastic deformation the real maximum stress, corresponding of the maximum deformation degree, is equal of 566.6 N/mm^2 .

Thus the effective maximum stress at the lobe stamping process is 58.23% of the real maximum tensile stress of the material. Consequently, in the practical data conditions not will appear the cracks.

The technological coefficient of the lobe stamping process, in the given case is calculated as the ratio between the length of the unfolded form of the deformation zone and L and the diameter D of same zone.

$$C = \frac{L}{D} \quad (8)$$

We have

$$L = 2 \left[\frac{\pi}{2} (R + r) + 2 \right] + d \quad (9)$$

respectively,

$$C = \frac{2}{D} \left[\frac{\pi}{2} (R + r) + 2 \right] + \frac{d}{D} \quad (10)$$

In the data conditions we have $C=1.309$.

The cumulated deformation degree may be calculated as the logarithmic form, respectively:

$$\varepsilon = \ln \frac{L}{D} = 0.269$$

Result a great value of the cumulated deformation degree. The local deformation degree can be with 20-25% greater of the cumulated deformation degree.

This result confirms that the material has a good reserve for plastic deformation and the risk of cracks appearance is small.

4. Conclusions

The lobe stamping is a deformation process based on the local elongation of the material without the traction of this from the neighbor zone. Consequently, the elongation, at lobe stamping, takes place in the base of the thickness. In the long of the lobe profile the dimension increases and the thickness decreases. In the point where the increasing of dimension, in length direction,

is greater, the decreasing intensity of thickness is smaller.

This fact must be known in the aim to forestall the crack appearance.

In this sense may be established the critical value of the deformation degree. The level of the deformation intensity, in the practical conditions, is defined by the deformation coefficient C , or the logarithmic strain.

The experiments systematized in this paper show the variation of the force in the time of the lobe deformation process, the variation of the thickness, specially, in the critical zone and the variation of the microstructure of material.

In the critical section of the deformed zone the crystalline grains are deformed very much.

The experimental results and the calculated values of the maximum real stress and the maximum deformation degree show that the cracks generation has a reduced probability.

References

- [1]. Teodorescu, M. a.o. – *Elemente de proiectare a stantelor si matritelor*, EDP, Bucuresti, 1977.
- [2]. Roamnovski, V.P. - *Stantarea si matritarea la rece*, Ed. Tehn., Bucuresti, 1970.
- [3]. Lazarescu, I., Stetiu G. – *Proiectarea stantelor si matritelor*, EDP, Bucuresti, 1973.
- [4]. Merchant, E.M., *Mechanics of the metal cutting process*, Journal of applied physics, MC Shaw, 2004.
- [5]. Jaspers, S., *Material behavior in conditions similar to metal cutting: flow stress in the primary zone*, Journal of Material Processing Technology, vol.122, Issues 2-3, March 2002, p.322-330.
- [6]. ASM, *Metals Handbook*, vol.4, Forming, Ohio, SUA, 1969.

THE PRE-BIBLICAL METALLURGICAL ART ON THE BIBLICAL TERRITORY

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ABSTRACT

The Old Testament describes in details the metallurgical achievements, both in the period before the conquest and colonization of the promised land (mostly related to the manufacturing of the Tabernacle, in this sense, the gold chandelier with seven branches, also known as the menorah, is an exceptional example), and the period after the conquest and colonization of the promised land (the sea of bronze pillars Boaz and Jachin, the 10 golden candlesticks with seven arms, etc., famous artifacts of Solomon's Temple facilities, are good examples). Question: at that time, did the Jews held the technical and technological knowledge necessary to do things in order to reach the great achievements of metallurgical processes described in the Old Testament? This article tries to answer this question.

KEYWORDS: Canaan, pre-biblical metallurgy, casting, lost wax casting, Nahal Mishmar's Treasure.

1. Introduction

Even before it was colonized by the Jews, The Promised Land – known as Canaan it was habited by other peoples (Canaanites, Amorites, Philistines, etc.). At that time, those people already had a certain degree of culture and civilization, including a high level of metallurgical creativity and development. As a result of the contact with these people, the Israelites were able to absorb technology, in addition to technological knowledge that they already had from the previous period, which also includes the Egyptian slavery period; exception is the iron manufacturing¹. For requirements subject matter, the pre-biblical time is the chalcolithic period (or Copper Age, 4500-3300 BC). For the two reference coordinates – time (the pre-biblical period) /geographical area/(Canaan) - based on

archaeological material, will be presented two things with connection to the metallurgical aspects: (1) casting as a wide use pre-biblical metallurgical process, and (2) the treasure from Nahal Mishmar.

2. Casting, a wide use pre-biblical metallurgical process

Before it was colonized by the Israelites, the land of Canaan was inhabited by other peoples. These people had reached a high level of metallurgical development and creativity. For example, in Canaanite temples were discovered many statues casted in bronze, mostly small size. An example is the figurine in Figure 1, dated sec. 17 BC: in figure 1a², we can see the original casting mold, made of stone; figure 1b is a statue of a worship idol, cast in modern conditions in the original stone mold.

¹ A good example is the conflict with the Philistines, described in Kings1

² The mold was discovered following excavations near Naharya (northern Israel), in a place where was a Canaanite temple.



Fig 1. Canaanite religious idol

In pre-biblical times, casting was one of the most important technological processes, used for the fabrication of copper objects. General scheme of development of processes for manufacturing objects by casting is shown in Figure 2. The raw material used was copper ore, which may contain impurities of arsenic³. As reference, the mineral exists in appreciable quantities as carbonate- malachite, $\text{Cu}_2\text{CO}_3(\text{OH})_2$. The process used was pyro-metallurgical: thermal dissociation in a coal bed at temperatures of 700 °C.⁴

³ The Nahal Mishmar's treasure – the most artifacts on copper-arsenic bronze - constitutes an eloquent example.

⁴ The melting process is carried out in two phases: (*)carbonate dissociation: $\text{Cu}_2\text{CO}_3(\text{OH})_2 \rightarrow 2\text{CuO} + \text{CO}_2 \uparrow + \text{H}_2\text{O} \uparrow$ and (**)metal oxide dissociation: $2\text{CuO} \rightarrow 2\text{Cu} + \text{O}_2 \uparrow$

The first two activities in the scheme shown in Figure 1, is de facto extractive metallurgy. The result, after melting, is a mass of clay which included copper grains⁵.

The casting was done in disposable forms (sand, wax models, etc.) or forms with multiple uses (stone), etc., to a wide range of uses: cult and ornament objects, work tools (knives, chisels, axes, etc.), etc.

Lost Wax Casting process is one of the oldest techniques of casting metal - about 5000 years [2, 3, and 4]. Initially, the process was used for idols, ornaments, jewelry, etc.

But it seems that the Middle East has the first use of this process. In the Middle East, the Lost Wax Casting process has been used increasingly wider in Mesopotamia and Sumer (for statues made of copper and later bronze) since 3500 years BC; something later, the method is found in Anatolia. The ancients quickly understood the advantages of the process: obtaining artifacts with complex configurations, versatility, repeatability, minimal finishing operations, the technique can be used for a large variety of metals and alloys (copper, gold, silver, bronze, etc.), etc.⁶

The majority of artifacts belonging to the Treasury from Nahal Mishmar were made by Lost Wax Casting process. Made no later than 3700 years BC, this means that the first use of this process in the region was for the artifacts discovered in Nahal Mishmar.

⁵ The slug will be eliminated later - totally or partially, and the copper granules obtained, following the melting procedure.

⁶ In antiquity, the technique was known in India, China, Thailand, was used by Greeks and Romans, Aztecs and Mayans, but also in Mexico and the African population near the Benin bay. Many pieces found in the Pharaoh Tutankhamen tomb (1333-1324 BC), were also made through this process.

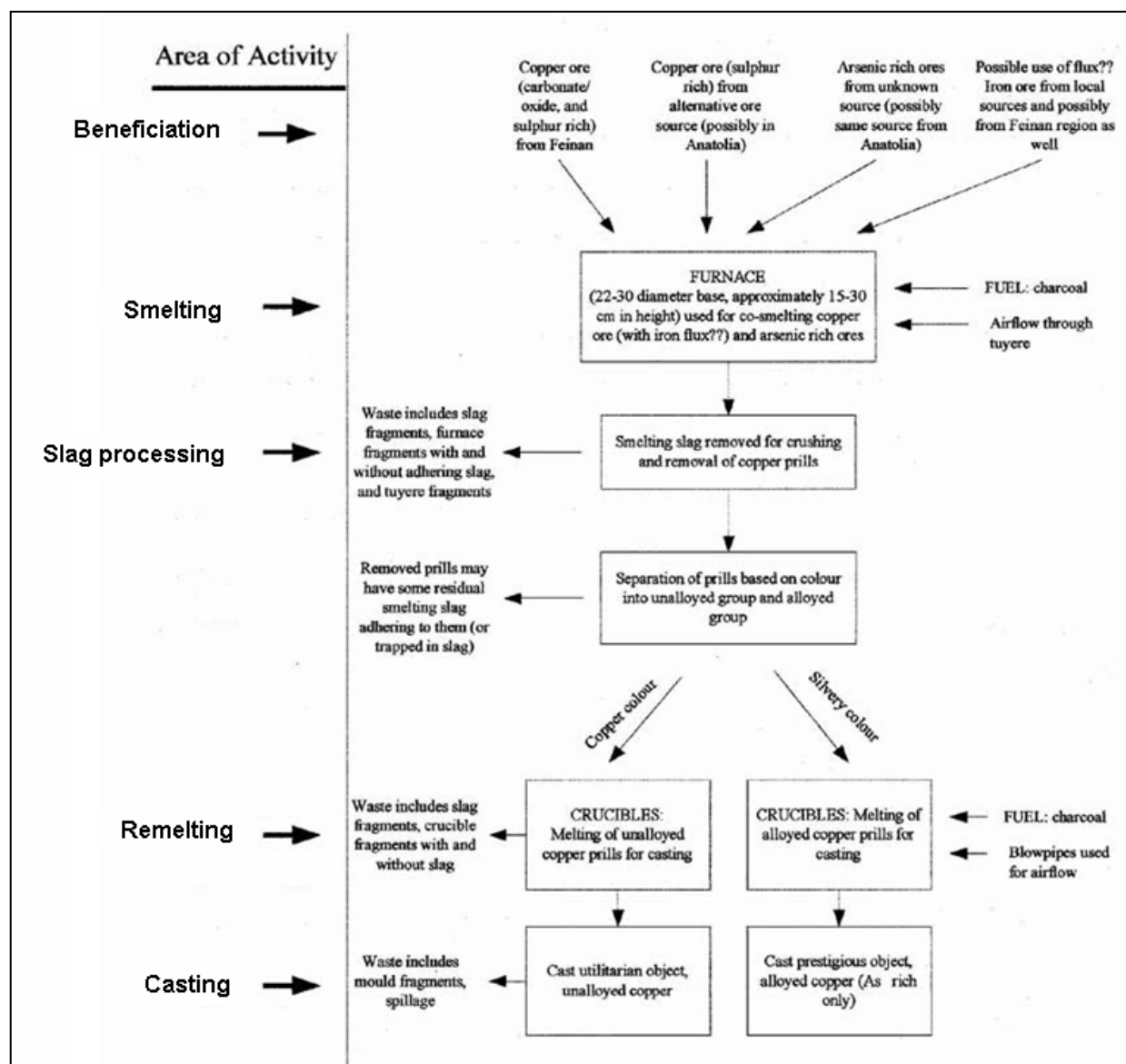


Fig. 2. General scheme for manufactured artifacts by casting process.

3. The Treasure from Nahal Mishmar

We are in 1961. The team of archaeologists led by Pesach Bar Master, was engaged in the search for possible additional scrolls in the Judean Desert, near the Dead Sea, where manuscripts from famous Oumran were discovered.

The geographical point at coordinates 31 ° 38 '0.93 "N 35 ° 36' 4.34" E - point located between Masada and Ein Gedi - is a cave accessible with difficulty, today called the Nahal Mishmar's Treasure.

In this cave were discovered 442 objects, wrapped in a mattress of straw, a real treasure, Figure 3.



Fig. 3. *Treasure of Nahal Mishmar*
Left: at finding time right: after preservation

This treasure is the largest group of ancient copper objects, found so far in the Middle East. Among these objects, 429 were made of copper-arsenic alloy (4-12% arsenic). This arsenic-bronze is the first alloy in the history of civilization [6]. 10 crowns, 256 mace heads, 118 scepters, 16 work tools chisel shaped were inventoried. Also, the thesaurus contains a set of objects of other materials: six of hematite, five of

hippopotamus ivory and one of elephant ivory.

Their esthetics is exceptional and they are so sophisticated that in many cases, modern artisans are surprised. The shape and decoration of each artifact is unusual. Many are so strange that it defies accurate definition. An additional aspect: each artifact is in itself unique, given that there are no two identical objects.



Fig. 4. *Examples of artifacts from the Nahal Mishmar's treasure*

Some additional examples are in figure 4: a crown (center), a two-headed (left), a scepter with three-deer heads (right)⁷.

⁷ An explanation accepted by most researchers is that the objects found were objects of worship and belonged to Ein Gedi temple discovered. This temple is known in literature as Chalcolithic Temple, and the distance from Nahal Mishmar - Ein Gedi is about 12 km. Researchers believe that at the time of reference, for reasons of insecurity, the objects were transferred temporarily from Ein Gedi temple in a temporary place of refuge, the cave from Nahal Mishmar. The reason for insecurity is not well defined, but depositors should have to return the treasure back to Ein Gedi. The fact is that they did not return it, and the treasury had to wait for the team of archaeologists led by Pesach.

The fact that 338 of objects represent deities, deity's head, scepters, supports the hypothesis that the antique warehouse complex was used for ceremonial and religious needs. The metal particles were studied for geo-chemistry-mineralogy. For this purpose, a variety of methods of investigation were used: SEM equipped with EDS (morphology and chemistry), ICP-AFS (chemical analysis), XRD (mineralogical composition).

A few results:

- Chemical analysis of most minerals: 40.5% Cu, 10% As, 4% CaO, 2% P₂O₅, 6.7% Al₂O₃, 25.3% SiO₂, 1.5% Fe₂O₃, 1.8% Na₂O, 1.2% K₂O, 1.1% TiO₂, 0.3% SO₃, 0.4% MgO, 2700 ppm Zn, 1600 ppm Mn, 400 ppm Ba, 360 ppm Pb, 100 ppm Ag, 55 ppm V, 25 ppm Sb.
- EDS analysis results of mineral elements: 71% Cu and 29% As.
- copper was associated with other minerals rich in arsenic [koutekit (Cu₅As₂) domeikite (Cu₃As)]

and sulfur [Covelit (CuS)].

- Carbon-14 dating of the reed mat in which the objects were wrapped suggests that it dates to at least 3700 BC.

Artifacts are particularly beautiful, with complex geometry, which explains the skill, professionalism and experience of Canaan artisans⁸. Saas notes [7]: *The treasures from the Judean Desert represent the acme of the metallurgical skill of Chalcolithic artisans, working from 4500 to 3150 B.C.E., when copper and copper-arsenic alloys were first widely used in the Near East ...*

In parallel, it should be emphasized the combination of primitive art, religion and metallurgy, striking in this case.

Many of the artifacts were made by Lost Wax Casting process. Also, additional procedures were used: casting in open forms, casting in closed forms, etc. Several types of artifacts - and their sections - are shown in Figure 5.



Fig. 5. Some examples of artifacts types from the Nahal Mishmar's treasure

⁸ Today, the artifacts are exhibited at the Israel Museum in Jerusalem, Department of Antiquities.

As mentioned before, the material from which artifacts were made from the treasury of the Nahal Mishmar - arsenic bronze - is the first alloy in the history of civilization developed about 4000 years BC. Arsenic is a rare element in the earth's crust: its abundance is at about $5 \times 10^{-4}\%$ estimated. However, it often accompanies ores of gold, silver, lead and copper, thus becoming a by-product. Perhaps at first, this bronze was made by accident, likely caused by the similarity of colors both metalliferous ores and green-light the flame when heating in the furnace. One thing is sure: both "metallurgical" ancient and user - that could even be one and the same person - quickly realized that the pieces made of arsenic bronze has both technological properties (casting and forging capability) and use properties (toughness, hardness) superior, compared to the similar parts made of copper.

Regarding the previous question: did the Jews of that time held technical and technological knowledge necessary to do things of the great achievements of metallurgical order described in the Old Testament?

An affirmative answer can be given: the Jews came in contact with people who held a high level of metallurgical development and creativity, which allowed the technological knowledge assimilation.

4. Conclusions

- In the pre-biblical times, casting was a widely used metallurgical process
- Pre-biblical peoples have held a high level

of development and metallurgical creativity

- By contact with these people, the Israelites - in addition to technological knowledge already held in previous periods - could absorb metallurgical technology
- Metallurgical achievements described in the Old Testament had the necessary technological knowledge support, to be materialized.

References

- [1]. **S. Moisa**, *Biblia si Metalurgia* (in Romanian), Editura Galaxia Gutenberg, 2011
- [2]. http://www.goldbulletin.org/assets/file/goldbulletin/downloads/Hunt_2_13.pdf L. B. Hunt, *The long history of lost wax casting*.
- [3]. **Moorey, P. R. S.**, (1988). *Early Metallurgy in Mesopotamia*, in *The Beginning of the Use of Metals and Alloys*. Paper from the *Second International Conference on the Beginning of the Use of Metals and Alloys*, Zhengzhou, China, 21-26 October 1986., ed. R. Maddin Cambridge, Massachusetts & London, England: The MIT Press.
- [4]. **Muhly, J. D.**, (1988). *The Beginnings of Metallurgy in the Old World*, in *The Beginning of the Use of Metals and Alloys*. Paper from the *Second International Conference on the Beginning of the Use of Metals and Alloys*, Zhengzhou, China, 21-26 October 1986., ed. R. Maddin Cambridge, Massachusetts & London, England: The MIT Press.
- [5]. **Moorey, P. R. S.**, *The Chalcolithic Hoard from Nahal Mishmar, Israel*, in *World Archaeology* vol. 20 (1988), pg. 171-189
- [6]. **S. Ilani, A. Rosenfeld**, *Ore source of arsenic copper tools from Israel during Chalcolithic and Early Bronze ages*, in *Terra Nova*, vol. 6 (1994), pag. 177-179
- [7]. **S. L. Saas**, *The Substance of Civilization*, Arcade Publishing, New York, 1998, pag. 59.

STUDY AND RESEARCHES ON THE HOLE BORDER PROCESS

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ABSTRACT

The hole border is a plastic deformation process applied of the metallic part by plat in the aim of the realization a collar through expansion of a hole or a part border. In the deformation process, in the case of hole expansion, the strain state is defined by the elongation strain in the circumference direction. The strain is zero at the base of the deformed collar and has the maximum value at the border surface of the collar. The elongation strain may be so great and the crack risk is, also, great. In the work is developed a study about the variation of the strain in the long of the collar in function of the ratio between the hole diameter and collar diameter.

KEYWORD: plastic deformation, hole border, expansion

1. Introduction

The hole border is the local stamping plastic deformation of the metallic part, by plat or strip, applied in the aim of obtaining a collar through expansion of the border hole, prior perforated (fig.1a,b), or of the border piece (fig.1c).

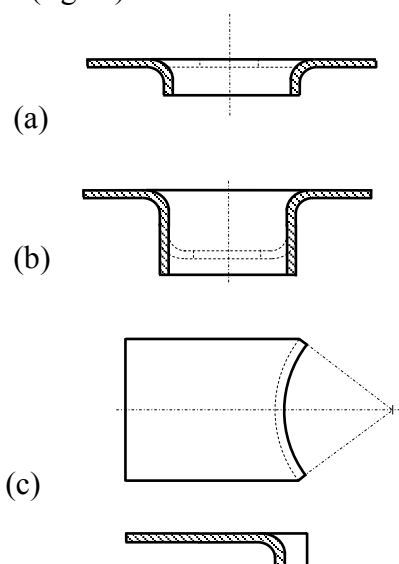


Fig. 1. Variants of the stamping border: a-case of plane piece, b-case of the deep drawing part, c-case of the border piece

In the deformation process the strain state is defined by the elongation strain, ε_1 in

the circumference direction and the strain ε_2 in the direction of the thickness. In the radial direction the strain ε_3 is equal of zero (fig.2). Thus between the two strains, different of zero, is the following relation:

$$\varepsilon_1 = -\varepsilon_2$$

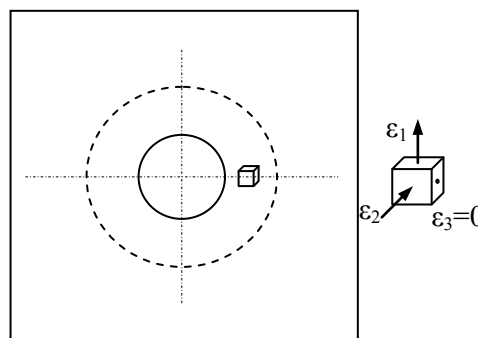


Fig. 2. Scheme of strains state

In the long of the collar the strain ε_1 is variable. The strain is zero at the base of the deformed collar and has the maximum value at the border surface of the collar.

The elongation strain may be so great and the crack risk is, also, great. In the work is developed a study about the variation of the strain in the long of the collar in function of the ratio between the hole diameter and collar diameter.

2. Evaluation of the local deformation

In the hypothesis defined above the deformation in the circumferential direction, at the given moment, for the border hole, is calculated with the following equation:

$$\varepsilon_j = \ln \frac{d_j}{d_0} \quad (1)$$

In this relation d_j is the diameter of the hole at the given moment and d_0 is the diameter of hole at the initial moment (fig.3).

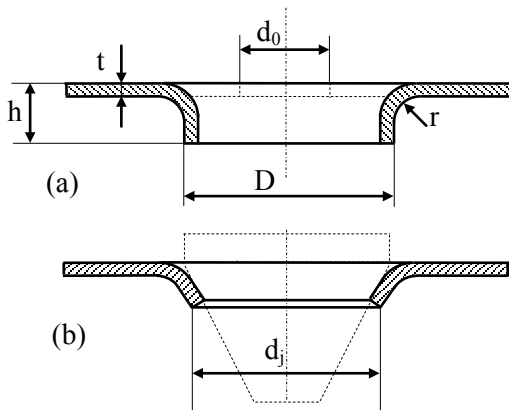


Fig. 3. Geometry at the given moment:
a-the final form, b-momentary form

The maximum value of this deformation

is:

$$\varepsilon_{\max} = \ln \frac{D}{d_0} \quad (2)$$

We denote d_{ij} the certain diameter between the d_0 and D .

The deformation degree (strain) at this position is:

$$\varepsilon_{ij} = \ln \frac{d_{ij}}{d_0} \quad (3)$$

The value of the diameter d_{ij} may be established in function of the geometry of the punch. The form of the active zone of the punch may be conical, spherical or parabolic.

Case of conical punch. The phases of the deformation process are showed in figure 4. We admit the material is in contact with the active surface of the punch (fig.4).

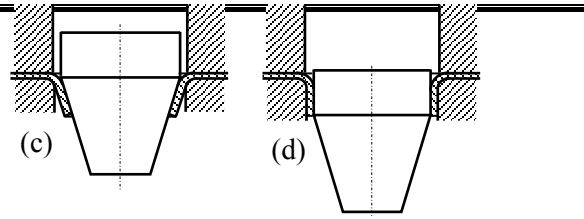
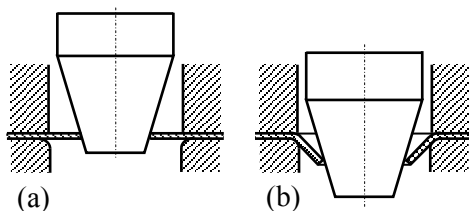


Fig. 4. Phases of the deformation process: a-initial, b,c-intermediate, d-final phase

At the beginning of the process the punch attains the part, at the level of the hole outline (fig.4a), acts on the material and induces the deformation without contact between the surface of piece and active surface of the punch (fig.4b). Then the surface of the material comes in the contact with the punch surface (fig.4c) and finally a calibration process takes place (fig.4.d).

Because of the great, relatively, tensile stresses the form of the deformed zone is maintained conical. Also, the length of the radial dimension of deformed zone is constant.

In these conditions the geometry of the half collar, at the different moments of the deformation process, has the aspect rendered in figure 5.

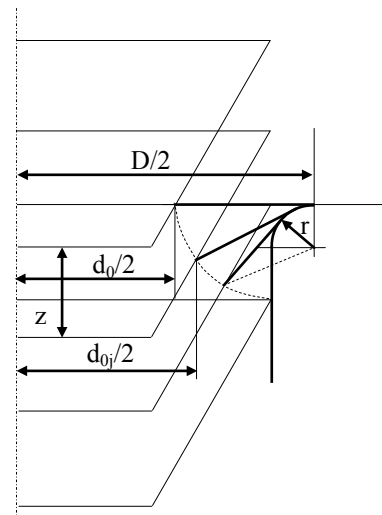


Fig. 5. Collar wall aspect at different phases of the deformation process

Because in the deformation process the material covers the border of the die without gliding, the point M_0 describes the evolvent of the arc of radius r . The segment MN is constant and, consequently, the point N_0

develops, also, an evolventic curve. This curve (fig.6) is the trajectory of the border point of the collar at the time of the deformation process.

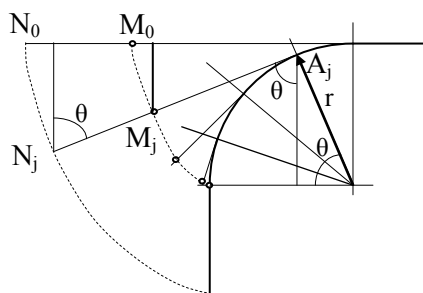


Fig. 6. Trajectory of the collar border

Thus, we can establish the diameter of the border collar, at the route of the stamping process, and of course, the value of maximum strain in any time of the deformation.

Because the coordinates of the point M_j are defined by parametric equations:

$$\begin{aligned}\xi &= r(\cos \theta + \theta \sin \theta) \\ \eta &= r(\sin \theta - \theta \cos \theta)\end{aligned}\quad (4)$$

which correspond at the coordinates of the reference point A_j :

$$\begin{aligned}x &= r \cos \theta \\ y &= r \sin \theta\end{aligned}\quad (5)$$

In the next paper we will show the analytical study on the distribution of the strains, strain rates and stress states.

3. Experimental conditions

In this work we show the experimental results concerning the variation of the force at the hole border by stamping process.

The laboratory conditions of the hole border are the follows:

- the proves are cut from steel strip for sever drawing deep, with 1.0 mm of thickness,
- the experimental die is showed in the figure 7,
- force resistive transducer,
- the data acquisition system,

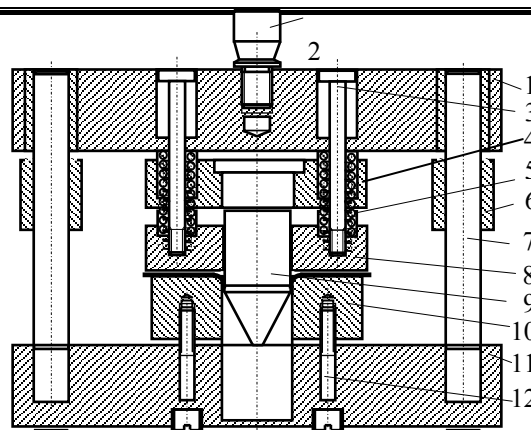


Fig. 7. The experimental die:

1-superior plate, 2-spigot, 3-screwed bolt, 4-port-punch plate, 5-helicoidal spring, 6-guiding jack, 7-guiding column, 8-fastening plate, 9-punch, 10-active plate, 11-base plate, 12-screw

4. Experimental results

The experimental program had following objectives:

- establishing the force variation;
- visualizing the microstructure aspect;
- estimation of critical strain.

The dimensions of proves were: the length of 80 mm and the breath of 30 mm. In each prove were stamped two holes of 12mm in diameter. Then hole border was effectuated.

For example, in the figure 8 are showed stamped samples.



Fig. 8. Examples of stamped proves

In the figures 9 and 10 we showed an example of the structure of material, in the deformed zone.

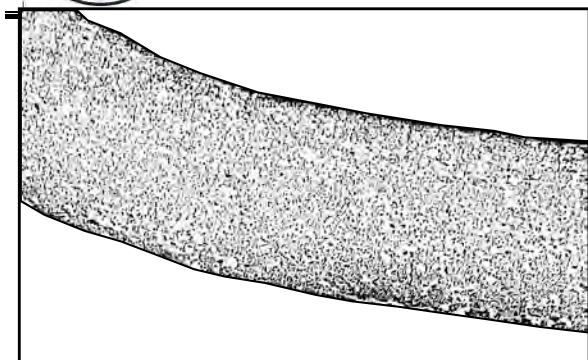


Fig. 9. Aspect of stamped sample section ($\times 50$, Nital 5)

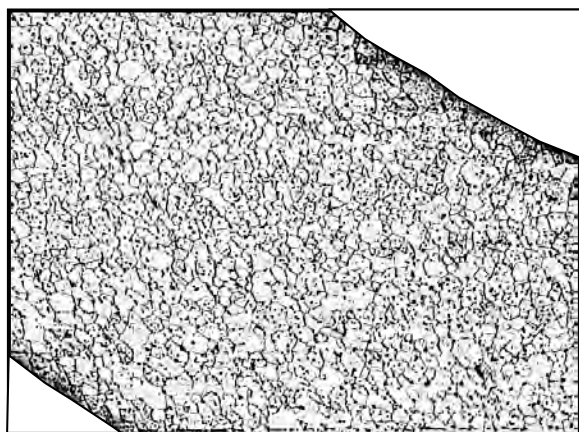


Fig. 10. Aspect of microstructure in deformed zone, ($\times 100$, Nital 5)

In the wall of the deformed zone the crystalline grains are practically non-deformed.

In the corner of the expanded collar the crystalline grains are sensible deformed, specially, in the interior surface (fig. 11).

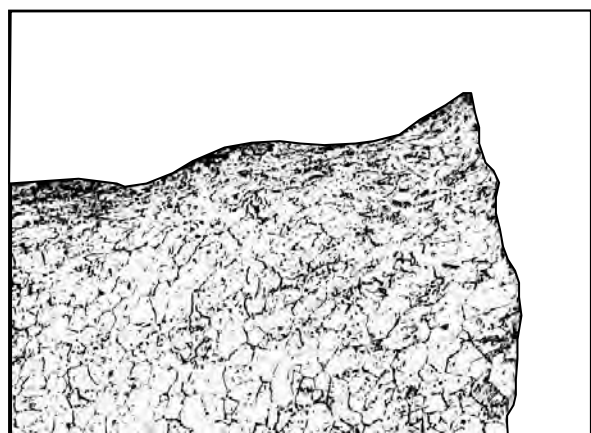


Fig. 11. Aspect of crystalline grains in corner of the reflected collar, ($\times 200$, Nital 5)

The maximum strain, in the really conditions, is 0.51. The border coefficient, defined by the equation:

$$m_b = \frac{d}{D} = 0.60$$

The values of the border coefficient are advised in the specialty literature in function of real; deformation conditions [1]. For example, in case of the light steel and the spherical or conical punch we have the values written in the table 1.

Table 1. Values of the border coefficient

Hole work mode	Relative thickness, $(t/d) \times 100$						
	1	3	6.5	12.5	20	35	100
Boring	0.70	0.52	0.40	0.33	0.30	0.25	0.20
Perforating	0.75	0.57	0.48	0.44	0.42	0.42	-

In laboratory conditions we have relative thickness of 8.33. By interpolation we obtain the advised value of the border coefficient of 0.3767. Because the real border coefficient is greater of the advised coefficient the deformation was effectuated in good conditions, without fissures or cracks. Variation of the force in the time of the lobe stamping process is showed in figure 12. The force has a complex variation because of the first phase the material is free, in the space between the punch and active die. When the maximum diameter of the active surface of the punch attains the superior surface of the active plate the material is in contact with the surface of the punch (see figure 4c) and deformation of the material is more difficult.

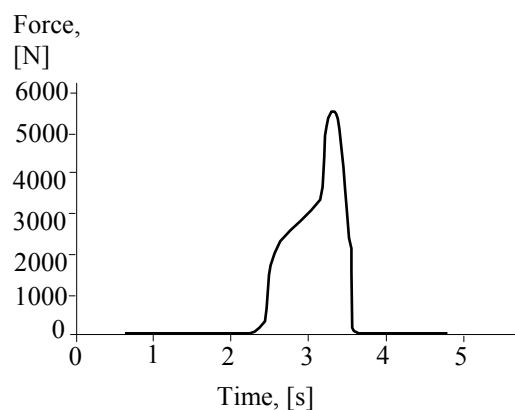


Fig. 12. Variation of force in the stamping process

Consequently, the force increases intense, relatively, reaches a maximum value then decreases until zero.

5. Conclusions

The border stamping is a deformation process based on the circumferential elongation and bending of the material in round of a hole prior worked. In the circumferential direction the dimension increases and the thickness decreases. This fact must be known in the aim to forestall the crack appearance.

In this sense may be established the critical value of the deformation degree. The level of the deformation intensity, in the practical conditions, is defined by the border coefficient m_r .

The experiments systematized in this paper show the variation of the geometry of

deformation zone, the force in the time of the border deformation process and the variation of the microstructure of material.

In the border deformed zone the crystalline grains are much deformed, relatively.

References

- [1]. Teodorescu, M. a.o. – *Elemente de proiectare a stantelor si matritelor*, EDP, Bucuresti, 1977.
- [2]. Roamnovski, V.P. - *Stantarea si matritarea la rece*, Ed. Tehn., Bucuresti, 1970.
- [3]. Lazarescu, I., Stetiu G. – *Proiectarea stantelor si matritelor*, EDP, Bucuresti, 1973.
- [4]. Merchant, E.M., *Mechanics of the metal cutting process*, Journal of applied physics, MC Shaw, 2004.
- [5]. Jaspers, S., *Material behaviour in conditions similar to metal cutting: flow stress in the primar zone*, Journal of Material Processing Technology, vol.122, Issues 2-3, March 2002, p.322-330.
- [6]. ASM, *Metals Handbook*, vol.4, Forming, Ohio, SUA, 1969.

INFLUENCE OF ECAP PASSES ON SPD PROCESS PARAMETERS AND MATERIAL PROPERTIES

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ABSTRACT

Samples of an aluminum alloy were subjected to an equal channel angular pressing (ECAP) at room temperature for five passes. For the several specimens severe plastic deformation process was interrupted to observe the material flow. Also are studied the force variation in SPD process microstructure and hardness in different zones of deformed sample. The paper highlights a way to obtain ultrafine grained aluminum alloy. The nanostructured prismatic shape may be processed in specific products like wires or rolled strip.

KEYWORD: Severe Plastic Deformation (SPD), Equal Channel Angular Pressing (ECAP), grain refinement, aluminum alloys

1. Introduction

Nowadays processes with severe plastic deformation (SPD) can be defined as metallic materials forming processed in which an ultra large plastic strain is applied into bulk specimens in order to create ultra fine especially nanocrystalline structures [1-3].

Mechanical behavior of a material is dependent on the microstructure of material. Refinement of grain size is increasing yield stress. That was confirmed by many experimental results, meaning that mechanical behavior of a metallic alloys may be different if its grain size changes.

The severe plastic deformation was defined as metallic material process were a high degree plastic deformation is induced at low temperature (lower than recrystallisation temperature).

Conventional process as rolling, forging and extrusion, allow plastic strain generally less about 2.0. In order to impose an extremely large strain on the bulk metal without changing the shape, many SPD processes, have been developed. Various

SPD processes such as equal channel angular extrusion or pressing (ECAE, ECAP), high pressure torsion (HPT), accumulate roll bonding (ARB), repetitive corrugation and straitening (RCS), cycling extrusion compression (CEC) have been developed. Segal in 1977 proposed in the first time this process in order to create ultrafine grained materials. [1].

ECAE is one of the major methods among the groups of severe plastic deformation technique.

ECAE can be performed on specimens repeatedly for increasing the cumulative strain amount in condition that the specimen's cross section shape does no change after this severe deformation process.

2. Experimental procedures

The study was carried out on a commercial aluminum alloy A319 supplied in 10 mm rolled plate.

The ECAE die for extrusion (samples of 10x10 mm) was designed and machined. It consists of two parts: the body die within a

channel with a length of 10x10 mm and the cover. The inner angle ϕ is 90° and the outer angle ψ , 13° .

The material for body die is OLC 45 mark. The drilled holes in body die were threaded, the cover also was drilling but the holes are not threaded. After both components have been rectified, they were subjected to the quenching operation.

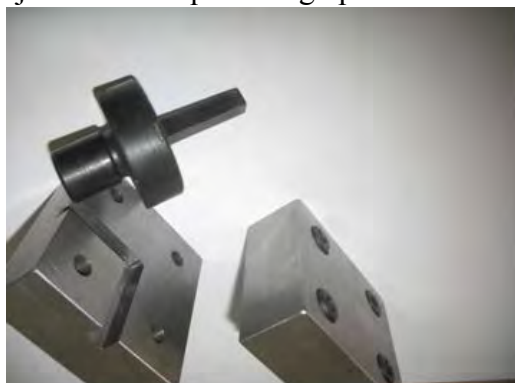


Fig. 1. ECAE die and plunger

After quenching the die and cover both have been tempered. Since the channel was not very fine faces, it was subjected polishing with abrasive paper. Joining of die and cover has to be perfect and done with 4 bolts metric 8. Punch was made of tool steel in turning operation.

The specimens shape 55x10x10 mm was obtained by machining. Before SPD samples were lubricated throughout the lateral surface with a mixed graphite powder in oil to reduce friction in SPD process. After each pass the samples were adjusted dimensional on metallographic paper to be inserted again in the ECAE die. The road used for the SPD was route named A.

The test program consisted of severe plastic deformation of aluminum two samples with the dimensions specified above. The first sample was obtained in incomplete ECAE process. The linear displacement of punch on the first pass was set so that to be able to observe all specific areas ECAE SPD (fig.2). The second sample was subjected to five complete cycles SPD.

ECAE process was developed on a laboratory 20 t f hydraulic press. One limit switch is used to set the punch stroke and protect the force transducer.

After severe deformation the samples were subjected to metallographic analysis. On each sample were made microhardness studies

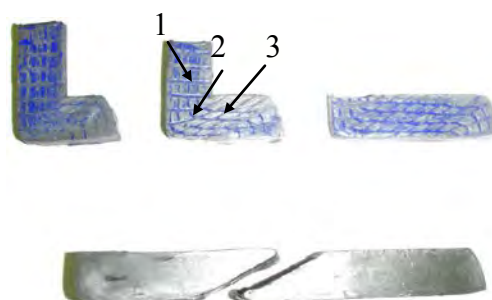


Fig. 2. The specific shape of ECAE specimens on different stages of SPD process

The chemical composition was determined with a X ray spectrometer.

The microstructural study has been carried out using an optical microscope Olympus BX45 with digital image acquisition. The samples surface has been metallographic prepared and etched.

The hardness Vickers has been carried out using a hardness testing machine 5kgf load.

3. Results and discussions

The chemical composition of the samples are: Si-6.1, Mn- 4.98, Mg-1.27, Fe-2.1, Zn- 0.57, Cu- 0.67, rest Al (wt%)

The calculation of ECAE deformation degree

The interior angle Φ is designed 90° the outside angle Ψ is 13 degrees.

Substituting in the equation:

$$\varepsilon_{total} = \frac{1}{\sqrt{3}} \left[2ctg\left(\frac{\Phi + \Psi}{2}\right) + \Psi \cos ec\left(\frac{\Phi}{2} + \frac{\Psi}{2}\right) \right]$$

We will have

$\epsilon_{\text{total}}=1.07$ for each ECAE pass.

Determining the number of passes influence on variation in the ECAE force

Numerical data were obtained from Hottinger Spider 8 acquisition system (time in second and micrometer/ meter – signal, corrected with constant transducer to achieved force in Newton's). The acquisition sample rate was set at 60Hz. Plots force versus time is shown in figures 3.

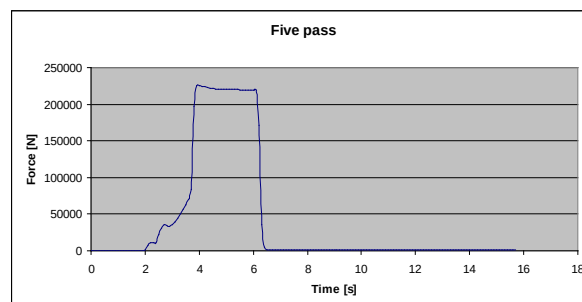
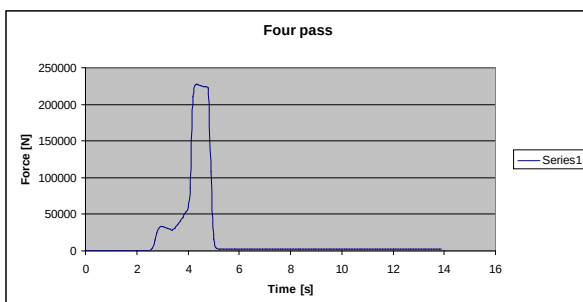
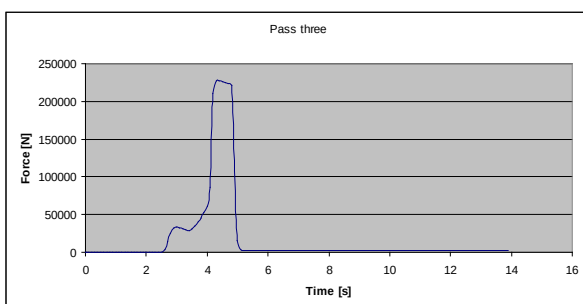
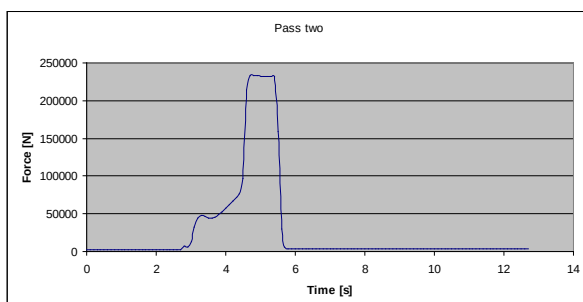
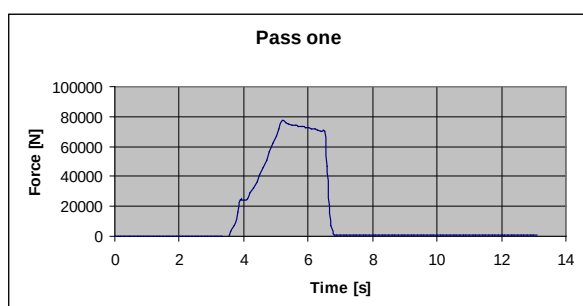


Fig.3. Force versus time plots on different ECAE passes

The plots show a slowly force increasing in the first part of ECAE process because pressing. The material has now tight contact with die. Start from this moment is observed a rapidly increase friction force respectively SPD force. When the force variation achieves a maximum the SPD process is complete. This behavior is similar for all SPD passes.

The effective degree of deformation provided by ECAE die in one pass, used during the experiments is 1.07. After five passes the cumulative level of deformation is 5.35. In table 1 is presented data on the maximum force on each pass. The pressure values are around 2GPa.

Table1

No ECAE pass	Accumulated effective strain	Maximum force [N]	Pressure [GPa]
1	1.07	77018.2198	0.770182
2	2.14	233144.7366	2.331447
3	3.21	226941.9269	2.269419
4	4.28	210670.7886	2.106708
5	5.35	225481.1203	2.254811

The maximum force versus ECAE passes plotted in Figure 4. It may be noted that after the first pass the maximum force peak was 77,018kN and then force increases to 233.14kN with a slight oscillation at levels around.

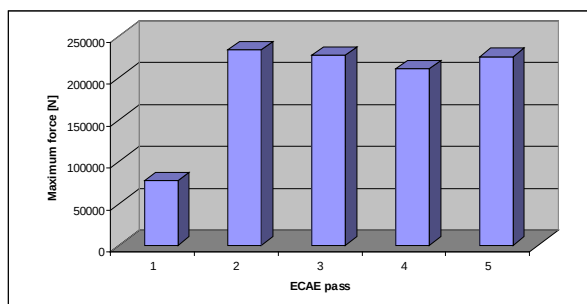


Fig.4. Maximum Force on ECAE pass

In figure 5 is represented the variation of pressure with the accumulate deformation degree. The maximum plot is depicted at 2.33 GPa. The pressure is stabilized at this value for the next passes.

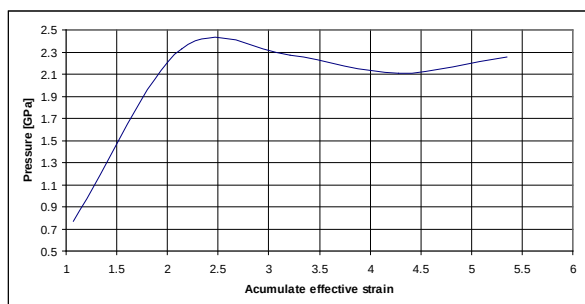


Fig.5. Pressure versus accumulate effective strain plot

ECAE is a way to obtain ultrafine grained aluminum alloy. Severe plastic deformation processes can lead to the formation of ultrafine grains and crystalline nanostructures in conditions of repetitive large plastic deformations. The optical micrographic structure of sample lie in as received state reveals an α solid solution consists of a coarse grain and fine precipitated intermetallic compound of magnesium and manganese. A solid solution structure is shown in polyhedral grains with sharp edges elementary fcc cells. The literature highlights through methods of X ray diffraction and TEM intermetallic compounds such as Mg_2Si and Mg_2Al_3 insoluble particles of dark areas. Areas with light gray contours are considered to be particles $MnAl_6$ [5].

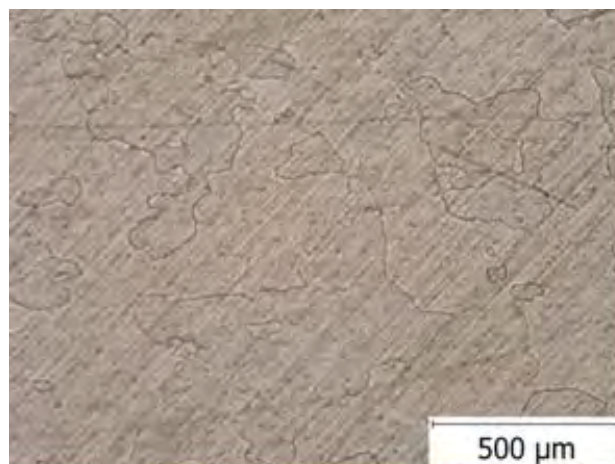


Fig.6. O.M. as received specimen

In a first-pass partially deformed sample allows analysis of how plastic deformation occurs in the ECAE process. Rectangular shaped sample placed in the mold is partially deformed.

The shape of studied ECAE samples has a *boot* aspect (fig.2). Optical microscopy shows sample three areas:

1. Upper zone, the entry in the die and it supports only the friction (fig.6.a)
2. Severe deformation zone, shear, situated at the intersection of L planes of the die in the length a designated of the arc outer angle Y (fig.6.b)
3. Exit area after plastic SPD (fig.6.c)

Although the material denoted by upper zone is not deformed yet can be notice texture of α solid solution in longitudinal section on the external surface of the sample which is in contact with the die. The grains observed on specimen are elongated and also have dark colored particles of intermetallic compounds. Texture comes only because of friction with the die walls although prismatic sample was lubricated before deformation over the entire longitudinal contact with the die. A possible reason for the occurrence of texture is the effect of friction can not be totally excluded. The results obtained through optical microscopy are consistent with those of previously published works [4]

Some authors provide initial polished with alumina solution.

Plastic deformation occurs almost monotonous in region near the intersection of the two planes of the die. Successive shear occurring inside crystalline grains. Strip line structure of the first area of friction with the die is now refined, in this zone of exit area after plastic deformation. It is noteworthy that give crystalline solid

solution grains supports a sinusoid crimping process besides grinding.

After five successive passes on the route denoted A, accumulative deformation degree 5.35 was achieved. The micrographs show the presence of an elongated structures associated with an ultrafine structure where the grain boundaries is missing. In accordance with the literature, applying severe deformation degree more than 5 occur nanocrystalline grain structure.

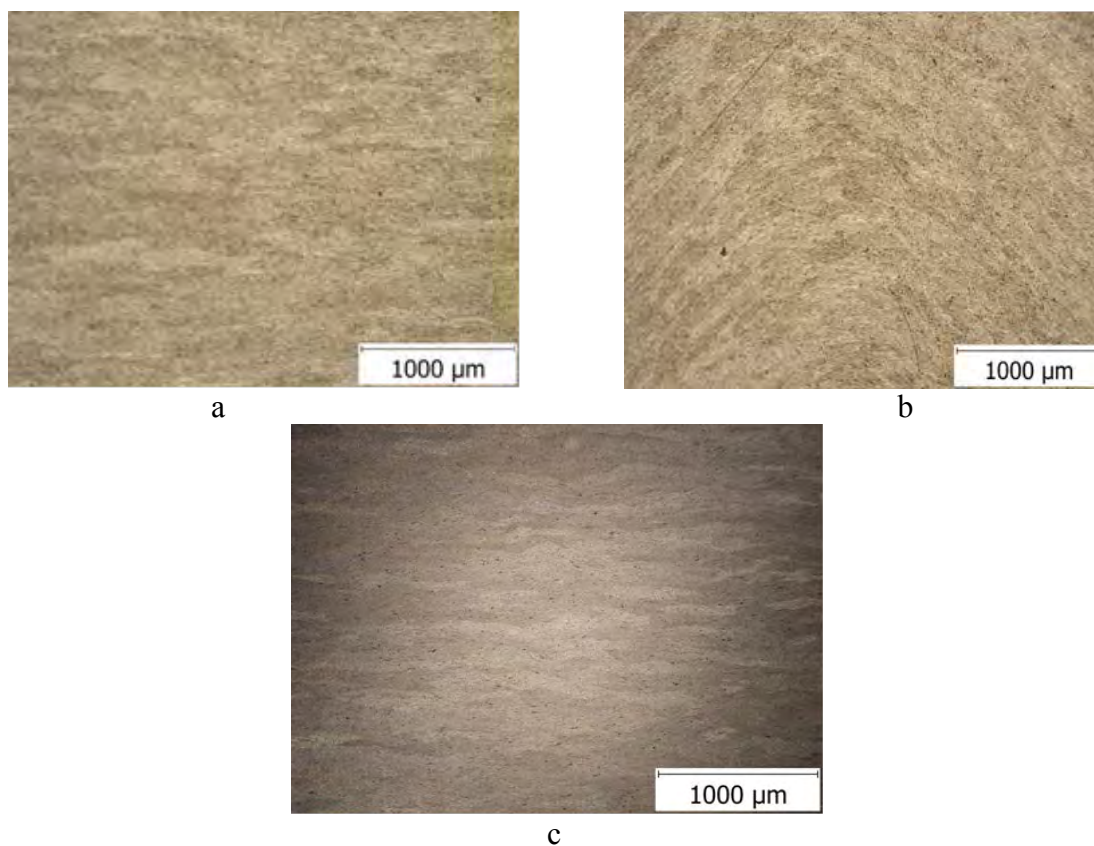


Fig. 7. Optical micrographs in the defined specific ECAE zones

After severe plastic deformation, insoluble phase particles, dark colored and light gray, magnesium and manganese were refined.

Some authors consider that some of them dissolve in solid solution due to thermal effects accompanying ECAE process that. The thermal effect takes place in successive severe ECAE deformation cycles.



Fig. 8. Optical micrograph 5 passes sample

Structure evidenced through light microscopy only allows the study of material flow texture. The central area of the sample shows lines that are parallel to the direction texture vertical extrusion 45 ° angle.



Fig. 9. Optical micrograph 5 passes sample (left and right sample edges)

The end edges of the sample area after five successive passages severely deformed ECAE highlighted circular turns forming texture (figure 7). The turns occur at the left on the specimen end and starting right at the exit part.

The hardness obtained on specimen five ECAE passes is very similar with low carbon steel. Sample rich Vickers hardness upper 1200 MPa, 4.65 times more than as received material.

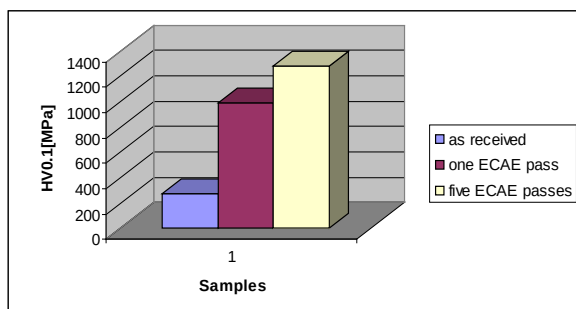


Fig. 10. Vickers Microhardness on different state of material

ECAE process consists in pressing the specimens to a die with two equal cross section channels. The plastic deformation occurs in the share deformation zone at

channels intersection. For one pass the deformation degree depends on de noted inner angle θ and outer angle Y . For ECAE process was defined four basic routes. In this study route A was used. That means pressing the sample without rotation. The process was repeated five times to increase the strain amount by cumulative plastic deformation. For this alloy two maximum three passes are necessary for gain ultrafine structure and increase hardness more then four time.

Conventional plastic deformation processes achieve large strain reducing the cross section. Multi pass ECAE allow ultra large plastic strain without changing in cross section specimens.

4. Conclusion

The microstructure and mechanical properties are influenced by parameters of the deformation process (speed, pressure, extrusion angle, number of passes) and for that those parameters have to be determined and controlled for each system of alloys [6]. The characteristic features of the SPD process are the following:

- plastic deformation is produced predominantly by a shearing process,
- the cross section remains virtually unchanged
- material integrity is not affected,
- parameters of severe plastic deformation process are optimized in order to get a substantial grain refinements,
- the process permanently change the mechanical properties.
- nanostructuring by SPD can be applied to any type of alloy

The basic mechanism involves initial coarse grain subdivision in much smaller areas subgrain and cells in shear plane. Equivalent cumulative deformation strain change the bulk structures depending on the material microstructure and deformation conditions imposed. A repetitive process ECAE is a way to achieve large plastic deformation and obtain bulk nanostructure

maintaining a constant cross section. The nanostructured prismatic shape may be processed in specific products like wires or rolled strip.

References

- [1]. **A. Azushima (1), R. Kopp, A. Korhonen, D.Y. Yang, F.M. Icar, G.D. Lahoti, P.G. Roche, J. Yanagimoto, N. Tsuji, A. Rosochowski, A. Yanagida**, *Severe plastic deformation (SPD) processes for metals*, CIRP Annals - Manufacturing Technology, journal homepage: <http://ees.elsevier.com/cirp/default.asp>, p.716-735
- [2]. **D. Nagarajan, Uday Chakkingal, P. Venugopal**, *Influence of cold extrusion on the microstructure and mechanical properties of an aluminium alloy previously subjected to equal channel angular pressing*, Journal of Materials Processing Technology 182 (2007) 363–368.
- [3] **A.A. Gazder, F. Dalla, Torre, C.F. Gu, C.H.J. Davies, E.V. Pereloma**, *Microstructure and texture evolution of bcc and fcc metals subjected to equal channel angular extrusion*, Materials Science and Engineering A 415 (2006) 126–139
- [4]. **Terence G. Langdon** *The principles of grain refinement in equal-channel angular pressing*, Materials Science and Engineering A xxx (2006) xxx–xxx
- [5]. **Mumin Sahin H. Erol Akata, Kaan Ozel**, *An experimental study on joining of severe plastic deformed*, Materials and Design xxx (2006) xxx–xxx
- [6]. **Francisco M. Braz, Karimbi K. Mahesh, Rui J. C. Silva, Carmela Gurau, Gheorghe Gurau**, *XRD study of the transformation characteristics of severely plastic deformed Ni-Ti SMAs*, Fernandes1Physica status solidi (c), Volume 7, Issue 5, pages 1348–1350, May 2010, DOI: 10.1002/pssc.200983371

INCREASING THE SLABS QUALITY BY IMPROVING THE CONTINUOUS CASTING TECHNOLOGY

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ABSTRACT

This paper provides an innovative solution on how the quality of the slabs is attained by improving the continuous casting technology. All of this can be achieved only by modifying and upgrading the tundish and the perforation's prediction system.

KEYWORDS: continuous casting, moulds, turbostop

1. Introduction

The cooling is done by a free fall in to a metallic shape without bottom.

The casting speed represents the speed of the slab who is insurance by mold for continuous casting is the mold who

insurance the solidification and the create of the slab shape.

Figure 1 depicts the working principle of continuous casting.

This form is called proceedings casting in mold.

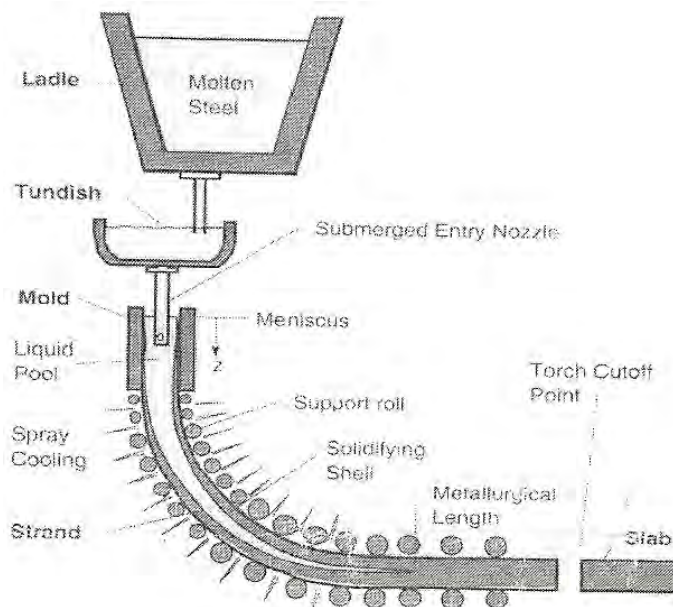


Fig.1. Continuous casting installation

The molds can come in different types: made by welding or casting from copper, steel, aluminum or graphite. The mold is characterized by a great liquid alloy that uses a water circuit, under pressure.

2. Phenomena scheme at continuous casting

The continuous casting is characterized by a great productivity and competitively.

This method introduces a large number of automatization steps during the casting process.

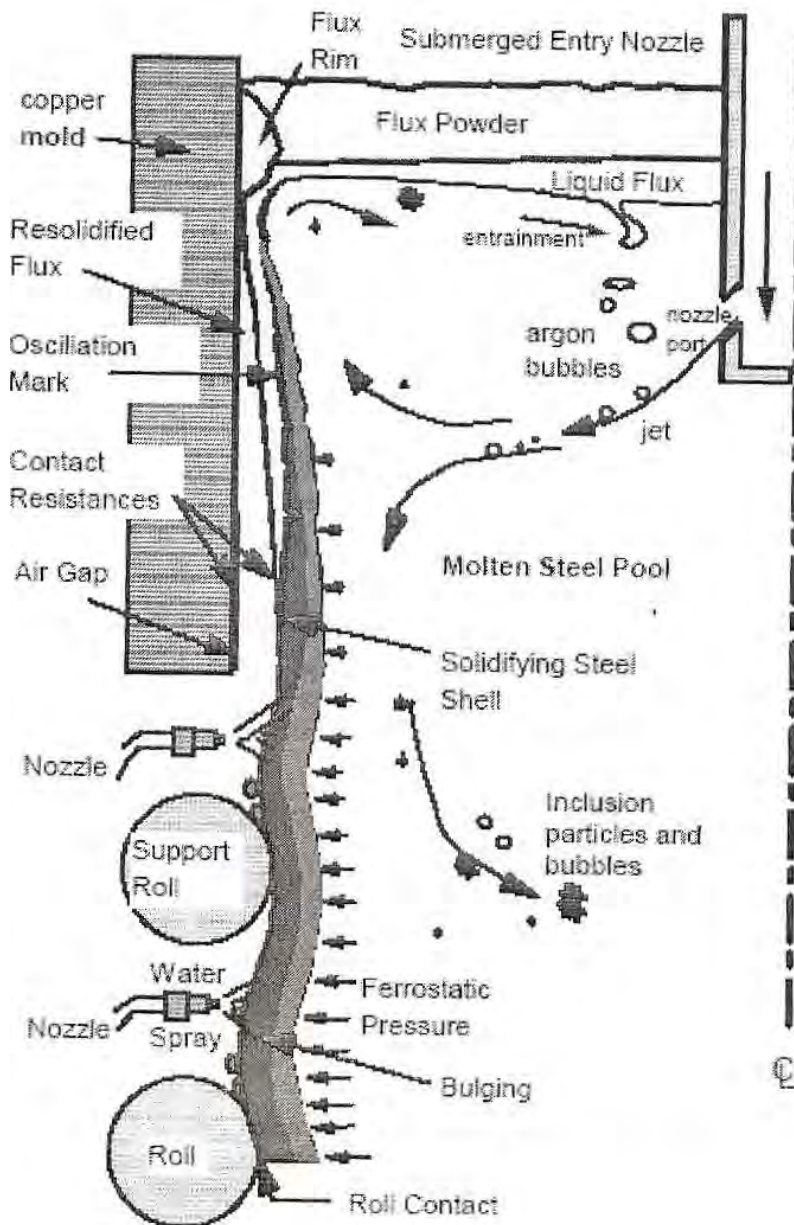


Fig.2. Schematic of flow phenomena in mold region of continuous casting process

3. Improving the continuous casting technology

3.1. Modifying the configuration of the distributor

Tundish's role is to take the liquid alloy from the ladle and distribute it on the hardware threads while ensuring a constant

flow, a decrease of turbulence during the flow and a diminishing of the nonmetallic and gaseous inclusions number.

To improve the quality of the casting and implicitly the quality of the ingot casting, the tundish's configuration was changed and mended together with the control conditions of the casting machine.

The basic tundish was replaced by a baffle tundish and subsequently the one with turbostop was introduced.

The operating principle of the turbostop is depicted in Figure 3.

In Figure 4 it can be observed that after using the turbostop, at the impact with the tundish's lining, the velocity distribution is more uniform and the casting takes place at lower turbulences.

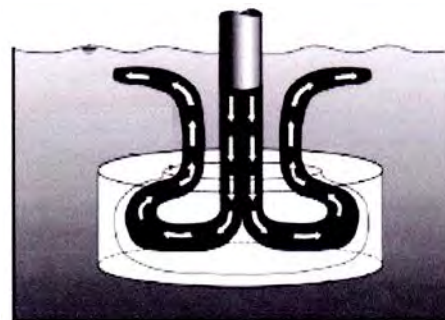
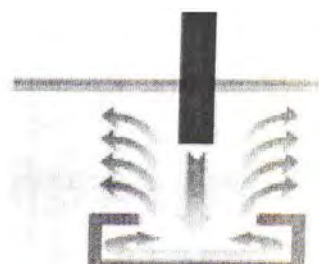


Fig.3. Turbostop's working principle



a. Impact on lining
 - high turbulence level
 - distribution with a non-uniform speed



b. Turbostop
 - low turbulence level
 - distribution with a uniform speed

Fig.4. Difference between the basic tundish and turbostop

First, in industry the basic distributor was replaced with the chicanes distributor. The main advantage was that the chicanes were redirecting the baffles inclusions. As the turbulences were still significant and some of the inclusions were still returning into the liquid steel bath, the turbostop was added to the tundish. The purpose of the turbostop was: to reduce the flow's fluctuations, to redirect the flow of the steel to the top side and to improve the separation of inclusions.

After changing the distributor with turbostop system the following progresses could be observed:

- avoid splashing steel phenomena and to entrain air bubbles seen in early casting;
- reduction of the tundish's refractory lining erosion;
- stream is redirected back to the top side, where is dispersed at the surface of the

metal bath. In this way no turbulences and waves appear on the surface of the metal bath.

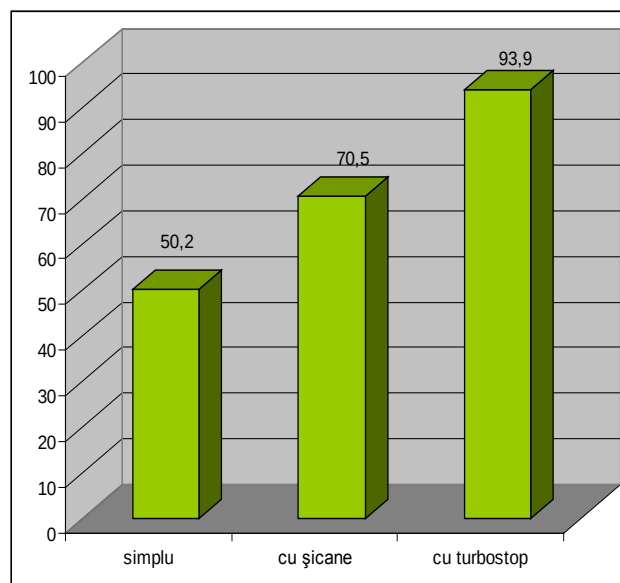


Fig.5. Removal efficiency of inclusions for the 3 types of distributors

The coverage flow of the metal bath remains intact.

- it increases the particle removal from 50% for simple tundish to 70% for the chicanes distributor till over 93% for the distributor equipped with the turbostop, done by assimilating the inclusions from the slag layer.

Because the configuration of the tundish has changed due to the adding of the baffles and the turbostop, the number of inclusions and the fluctuations has dropped. This has led to an increased quality of cast ingot.

Through experiments it could be observed that there is increased efficiency when using the turbostop as impact board and also it reduces the incidents present when using old chicanes.

By controlling the trajectory and velocity of the steel's flow it can be avoided the castings avoid removing of casting dust from the surface of the tundish. This leads to

better protection of the liquid alloy against re-oxidation.

3.2. Automatic level control of the crystallized and prediction of the perforation

The need to be aligned with higher standards and the need to improve the quality have imposed the usage of a prediction system for perforation together with an automatic level control system of the crystallizer.

In automatic control of the continuous casting machine very small variations can occur, about 1 mm, compared with manual control where the variations are approximately 6 mm. This leads to a significant reduction in number of defects that may be present on the surface of the slabs cast continuously.

The differences of level variations before and after the modifications are to be seen in the following graphs.

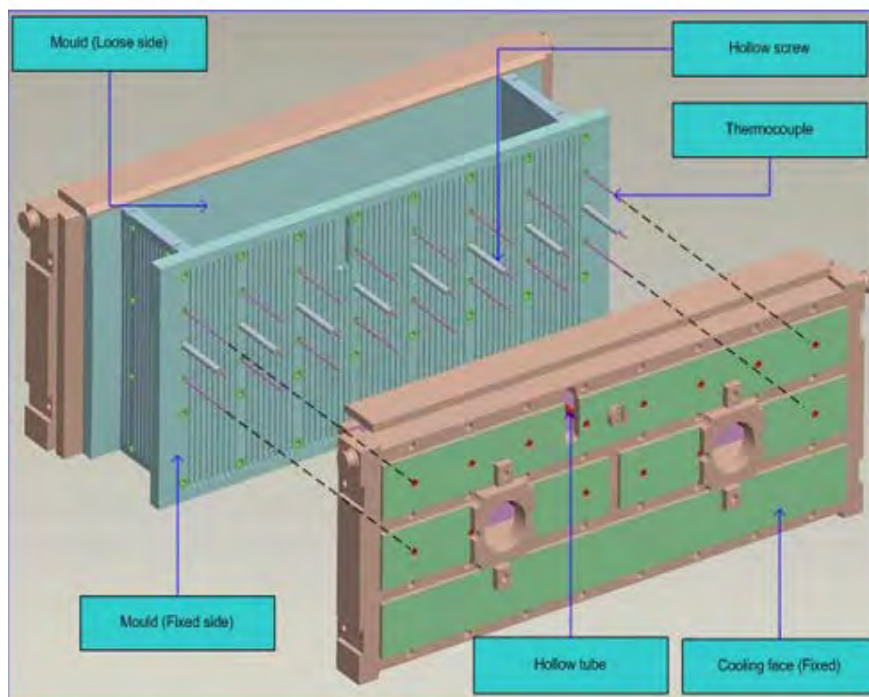


Fig.6. Location of thermocouples in the plates of the crystallizer

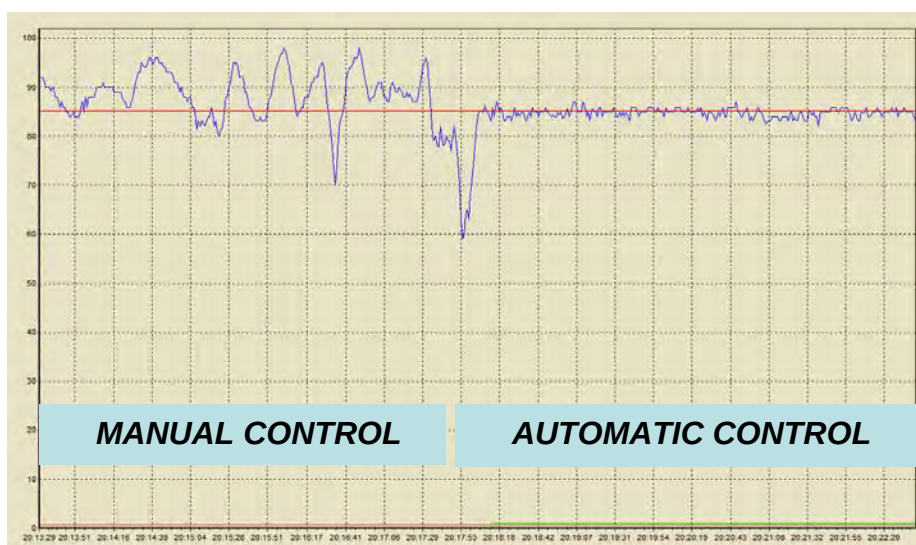


Fig.7. The difference between the automatic and manual level

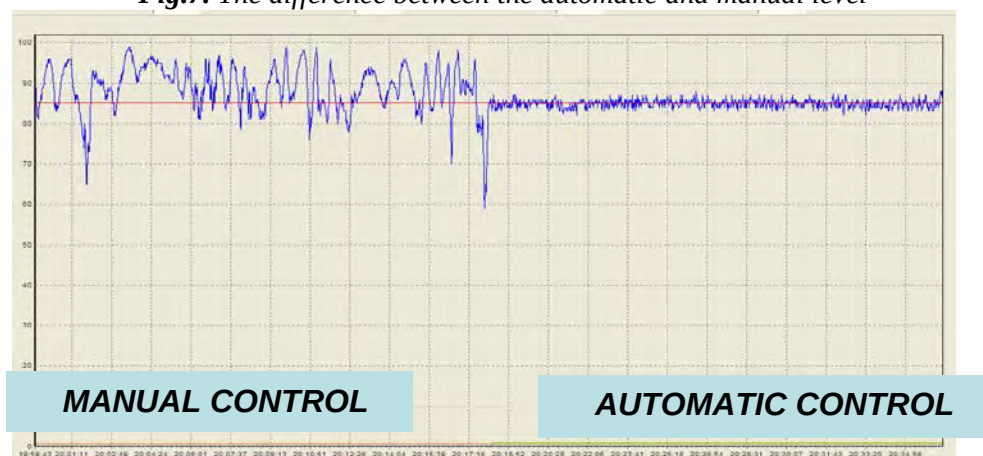


Fig. 8. System of maintaining constant the level inside the crystallizer

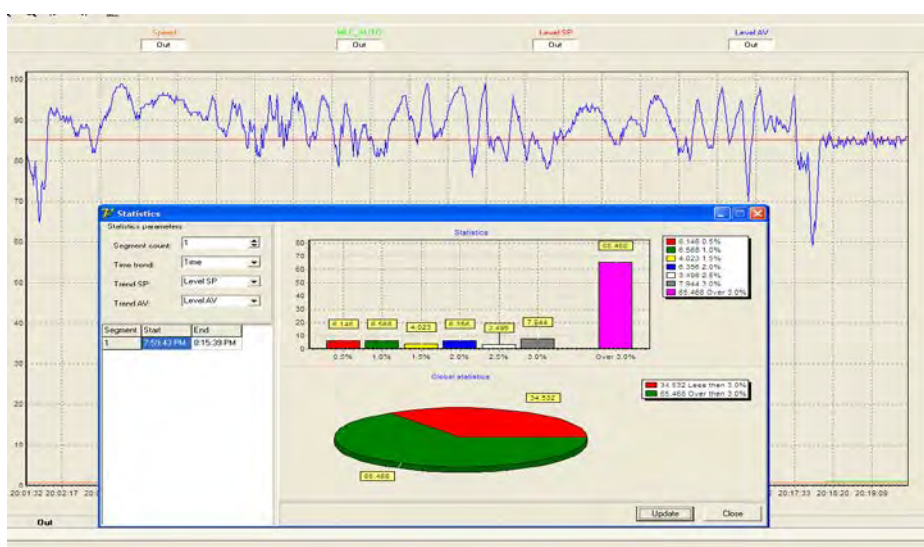


Fig.9. Manual casting

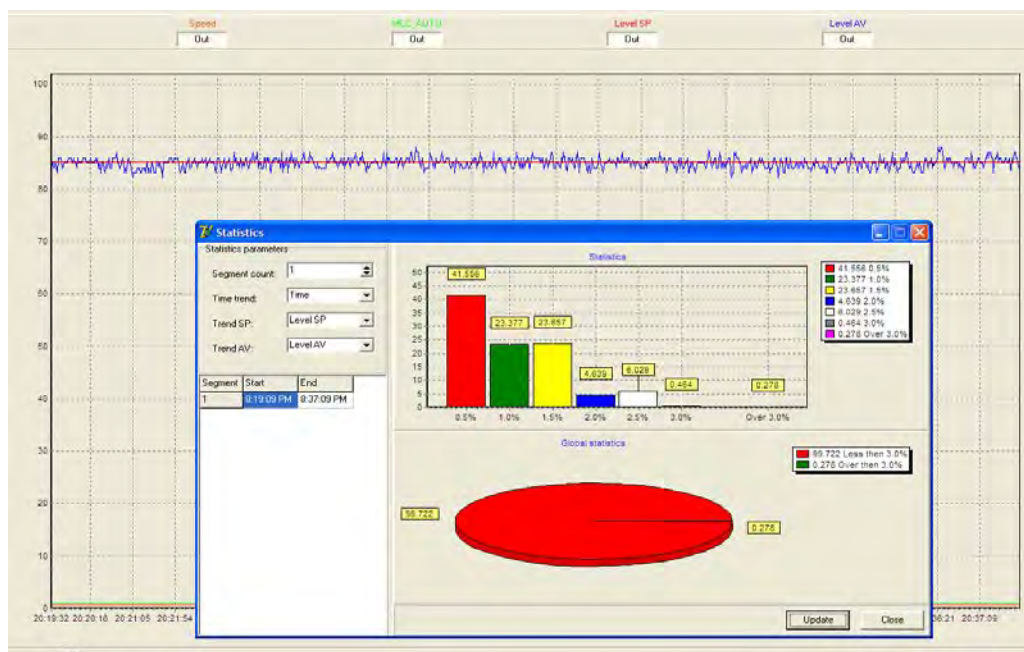


Fig. 10. Automatic casting

The manual castings shows that in 65% of the simulation time, the fluctuations are greater than 3% (6 mm) compared with the automatic one which in 99.72% of the simulation time has fluctuations less than 3% (6mm).

Another remark that can be made is that for automatic casting the variation can be equal to 0.5% in 41.55% of the simulation time.

4. Conclusions

Having a more effective and precise perforation's prediction system and an automatic control of crystallizer's level from the continuous casting machine, the performances of this type of machine can be most seen in the quality of the slabs.

The results are encouraging especially because now it is possible to observe the evolution of the level from the crystallizer during casting. A significant difference which has a noticeable impact on the quality of the slab's surface, can be observed when using the two different ways of casting, the manual one and the automatic one.

References

- [1]. **J. Campbell** – *Castings. The new metallurgy of cast metals*, Butterworth Heinemann, 2003
- [2]. **J. Brown** – *Foseco Ferrous Foundryman's Handbook*, Butterworth Heinemann, 2000
- [3]. **E.N. Budonov** - *Experiențe privind modernizarea producției de piese turnate a firmei Fritz Winter, Germania*, în *Liteinoe Proizvodstvo*, 2005, nr. 5, pag.1-5.
- [4]. **E. N. Budonov** - *Noile tendințe ale dezvoltării tehnologiilor de turnare în 2007* în *Liteinoe Proizvodstvo*, 2006, nr. 12, pag.1-7

INTEGRATED ANALYTICAL STUDY FOR THE SOMES METALIC ARTEFACT DISCOVERY IN IBIDA SITE, ROMANIA

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ABSTRACT

The paper presents the results of the analyses conducted using the SEM-EDX and micro-FTIR co-assisted techniques, on several metallic artefacts unearthed during the excavations at the (L)Ibida archaeological site in Slava Rusă, Tulcea County, Romania, that took place between 2001 and 2008. The data produced is of use in identifying several archaeometrical structural and compositional features which allow for the identification of the origin of the ores, of the alloy type, and of the manufacturing technology. A series of new data is thus produced, that can consolidate the three databases of scientific conservation of metallic artefacts (i-archaeometallurgy/archaeometry/historiography, ii-museum exhibiting, iii-itinerate/transfer/exchange/trade).

KEYWORDS: metal, SEM-EDX, micro-FTIR, archaeology

1. Introduction

The investigation of metallic artefacts requires a close collaboration between specialists from various domains of study: archaeology, history, chemistry, physics, metallurgy, geology, etc. They seek to establish: the nature of the material, the manner of processing the raw material, the manufacturing of the object itself, the subsequent preserving and restoring activities the object underwent.

To these purposes, they most often employ interdisciplinary methods of analysis, such as optical microscopy, scanning electron microscopy (SEM) alongside an EDX detector, micro-FTIR, calorimetry by reflexion, etc. [1].

The present study will provide the results of the SEM-EDX and micro-FTIR analyses performed on several objects discovered

during the excavation conducted between 2001 and 2008 at the (L)Ibida archaeological site from Slava Rusă, Tulcea County, Romania.

As with any valuable cultural heritage asset, metallic artefacts can "travel", from the manufacturer who created them to the museum which exhibits them, by one of the following routes:

- Normal route of artworks, with a range of specific contexts (creation, acquisition, classification, display, preservation/restoration, etc.);

- Abandonment route, with contexts of creation, acquisition, use, loss of use functions, abandonment, archaeological discovery, preservation/restoration, ranking, showdown, etc.;

- Concealment and oblivion route (especially for hoards), with contexts of creation, acquisition, use, loss of use

functions, abandonment, archaeological discovery, preservation/restoration, display etc.;

- Route through theft, with contexts of creation, acquisition, use, loss of use functions, abandonment, archaeological discovery, preservation/restoration, display or reuse etc.;

- Route through falsification, reproduction/copying, destruction, etc. with contexts of creation, acquisition, use, unlawful/illegal activities and their discovery, recovery of heritage functions, reintegration by display setup;

- Route by disaster (earthquake, flood, fire, volcanic eruption, landslide, crash, etc.), with contexts of creation, acquisition, use,

loss of use functions, abandonment, archaeological discovery, preservation/restoration, display;

- Route by plagues (cholera, health disasters etc.), with contexts of creation, acquisition, use, loss of use functions, abandonment, archaeological discovery, preservation/restoration, display;

Some routes may modify a series of heritage elements (patina, share value, conservation status, etc.) as well as the main heritage function, the aesthetic and artistic.

An outline of areas of interest, the purpose of conservation and scientific activities integrated bronze artefacts in accordance with codes of ethics, is shown in Figure 1.

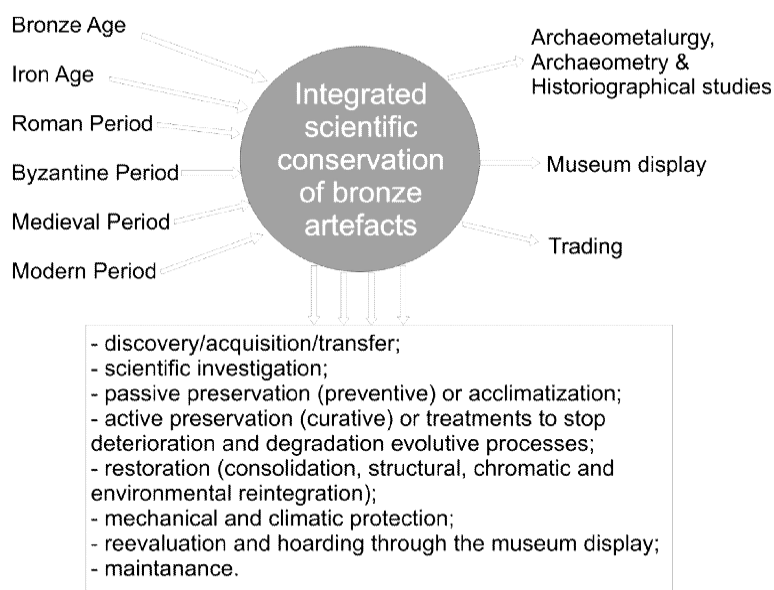


Fig. 1. Scheme of the areas of interest (left), goals (right) and specific integrated scientific conservation activities (bottom) of ancient bronze artefacts.

For the value of a piece of bronze coming from archaeological sites there are some basic steps to be followed, namely [1, 2, 3]:

- Excavation;
- Cleaning;
- Scientific investigation;
- The coherent reconstruction of the shape from fragments;

- Completion of form and ornament;
- Mechanical and climatic protection by coating;
- Display and maintenance.

Depending on the circumstances and purposes, these steps may be detailed or developed with other activities or interventions.

2. Materials and methods

The artefacts selected for investigation have been discovered by the specialists from the Institute of Eco-Museal Research from Tulcea, the Institute of Archaeology from Iasi, and the Institute of Anthropology from Bucharest, during the archaeological diggings of the *Ibida* site from Slava Rusă [4]. They are presented in Figure 2 and consist of:

- *Haft* – P1 (Figure 2a), discovered at *Ibida* in 2006, G Curtain wall, S3, survey C1, inventory no. 48237. The item is 44 mm in length, rectangular, and ends with a pommel with a diameter of 8 mm. At approximately 32.6 mm from the end with the pommel, the handle has two diagonal asymmetrical incisions, and at 5.75 mm from them another two very fine incisions. The weight is 6.47 g. On the side to which the blade was attached, two rivets were preserved; they are positioned at approximately 25 mm from each other, and

most probably were part of the fixing mechanism.

- *Blade of pocket-knife* – P2 (Figure 2b), discovered at *Ibida* (*passim*), Nichifor donation, inv. no. 40344. The length is 51.64 mm and the maximum width is of 10.65 mm. The weight is 5.52 g. Only the blade is preserved, without the handle. Unfortunately, neither the connecting mechanism has been preserved. The piece was dated between the 2nd and 4th century A.D.

- *Fragment of knife* - P3 (Figure 2c), discovered at *Ibida* in 2002, G Curtain wall, S1, square 24, -1.50 m, on the level (north of the wall), inventory no. 45889. The length of the blade is of 48.83 mm, and the width at the base is 24.70 mm. A 19.40 mm fragment of the haft has been preserved. The rivet fixating the blade to the handle can still be observed. The weight is 17.44 g. Given the current shape of the blade, its original length was probably around 130 mm. The artefact was dated between the 4th and 6th century A.D.



Fig. 2. Items discovered during the archaeological diggings from (L)*Ibida* (Tulcea County): a. Haft, inv. no. 48237; b. Blade of pocket-knife, inv. no. 40344; c. Fragment of knife, inv. no. 45889; d. Scissors, inv. no. 31978; e. Pincers, without inventory number; f. Fragment of knife, without inv. number.

- *Scissors – P4* (Figure 2d), inventory no. 31978. The two blades have been preserved almost entirely. The length of the piece is 67.87 mm, the width is 23.84 mm, and the weight is 13.49 g.

- *Pincers – P5* (figure 2e), discovered at Tufani, without an inventory number. The artefact survived entirely, and it is composed of a 6.58 m m-wide metal band, with the arms of 55 mm each, curly, and with a coil with a diameter of 9.87 mm. The piece weights 5.56 g.

- *Fragment of knife – P6* (Figure 2f), discovered at Noviodunum in 2007, without an inventory number. A 31.30 mm fragment of the blade has survived, as well as a 41 mm of the handle. Only one edge was usable, and the maximum width of the blade is of 15.21 mm. The weight of the artefact is 6.12 g.

The SEM-EDX and micro-FTIR methods were employed to investigate the above-mentioned archaeological pieces, in order to identify the materials used in their manufacturing.

a. The SEM-EDX analysis

A SEM (model VEGA II, produced by the Czech TESCANA company) electronic scanning microscope was used co-jointly with an EDX detector (QUANTAX QX2 type, produced by the BRUKER/ROENTEC in Germany).

This method, alongside the visual inspection of the micro-photogram, allows for the mapping (deployment) of the atoms from the investigated area, while alongside the X-ray spectra it allows for the determining of the elemental composition (in gravimetric or molar percentages, of a micro-structure or of a selected area) and the assessment of the compositional variation

along a vector running across the investigated area or section.

b. The micro-FTIR analysis

The spectra were recorded using TENSOR 27 FT-IR spectrophotometer, coupled with a HYPERION 1000 microscope; both pieces of equipment were produced by Bruker Optic, Germany.

The FT-IR spectrophotometer is a TENSOR 27 model that is most appropriate for near-IR (NIR) measurements. The standard detector is the DLaTGS, which covers the spectral range 400–600 cm^{-1} and which works at room temperature. The resolution is in most cases of 4 cm^{-1} , but it can reach up to 1 cm^{-1} .

The equipment used for the investigation was made available by the Laboratory for Scientific Investigation and Conservation of Cultural Heritage Items within the Interdisciplinary Research Platform in the Field of Archaeology – *ARHEOINVEST* from the "Alexandru Ioan Cuza" University of Iasi.

3. Results and discussions

Following the SEM-EDX analysis of the structures from the surface and the cross-section, the elemental composition, in mass percentages, of the objects found during the archaeological excavations, was established (Table 1). On the basis of these results, it was possible to establish the nature of the materials used in manufacturing the objects. Thus, in the P1 haft and in the P5 pincer the main elements are copper and zinc, while in the P2 blade of pocket-knife, alongside copper and zinc, tin is also present. The P3 fragment of knife, the P4 scissors and the P6 fragment of knife, all have iron in their composition.

Table 1. The chemical composition of the investigated items

Index	Item/ Inv. no.	Elemental composition – mass percentages (%)													
		Cu	Sn	Zn	Fe	O	C	S	P	Cl	Na	K	Ca	Al	Si
P1	Haft/ 48237	63.659	-	14.743	0.752	8.463	9.639	-	-	0.299	-	-	-	1.149	1.295
P2	Blade of pocket- knife/ 40344	83.191	2.544	5.317	0.496	6.673	0.900	-	-	0.879	-	-	-	-	-
P3	Fragment of knife/ 45889	-	-	-	54.489	31.730	5.466	-	-	-	3.606	0.559	1.209	1.796	1.144
P4	Scissors/ 31978	-	-	-	67.129	30.478	0.501	0.328	0.327	-	-	-	0.329	0.591	0.317
P5	Pincer/ w/o inv. no.	75.877	-	16.719	-	4.939	2.465	-	-	-	-	-	-	-	-
P6	Fragment of knife/ w/o inv. no.	-	-	-	84.226	13.326	0.696	-	0.442	-	-	-	0.604	0.705	-

Iron, just like copper, is the main metal to be found in processed alloys that is often corroded while lying buried. The processes of chemical alteration, monolithisation, and mineralisation occurring *in situ* means that the following elements should also be present: C, O, Si, Al, Cl, etc. [3, 5, 6]. In our

case, the following contaminants were identified: C, O, Si, Al, Na, K, Ca, S, P and Cl.

Because of the interaction between the soil and the metallic pieces, processes of chemical, electro-chemical, biological, etc. corrosion occur.

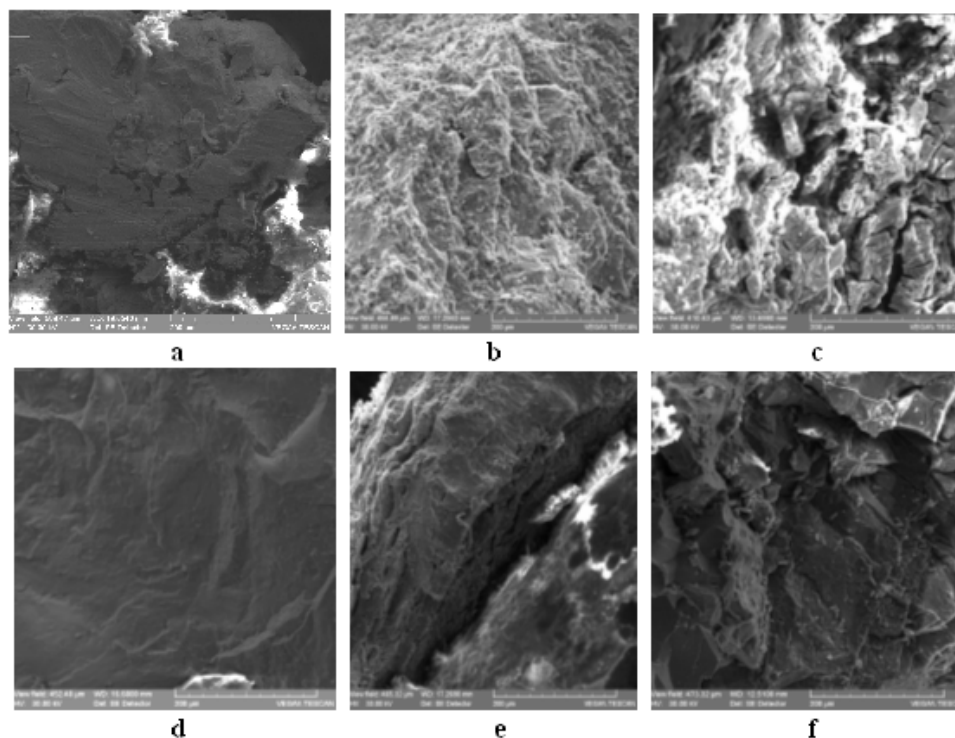


Fig. 3. The SEM images of the investigated objects:

- a. Haft, inv. no. 48237; b. Blade of pocket-knife, inv. no. 40344; c. Fragment of knife, inv. no. 45889; d. Scissors, inv. no. 31978; e. Pincers, without inventory number; f. Fragment of knife, without inv. number.

The altered metal alloy presents on its surface a crust; nonetheless, the mechanism by which this crust is formed cannot be generalised for all types of artefacts. This crust can be thin, smooth and with a homogenous structure, or thick, rugged and with a non-homogenous structure.

Significant similarities or differences can be found on objects of the same type, historical period, manufacturing technology, etc. [5, 6, 7, 8]. In the SEM images (Fig. 3), the internal structure of the analysed samples can be observed. Using the micro-FTIR analysis based on group characteristic vibrations, the nature of the corrosive products from the surface structures has been confirmed. By comparing the obtained spectral bands with the ones from spectra libraries and from the dedicated literature [9, 10], the main components formed on the surface of the objects were identified; they constituted the residual patina which remained after the cleaning operations. Table 2 (Annex 1) presents the main spectral bands, with the representative peaks and their corresponding ions.

4. Conclusions

On the basis of the results obtained by corroborating the results of the SEM-EDX and the micro-FTIR analyses we can conclude that objects P1, P2 and P5 are made from copper-based alloys, while P3, P4 and P6 are made from iron. The objects suffered from prolonged processes of segregation towards the surface of the active metals, and deteriorated, from the surface towards the interior, by redox, acidic-basic and complexing processes assisted by monolithisation by the inclusion of contaminating elements. These features prove the considerable age of these artefacts.

Oxide compounds (CuO , Cu_2O , Fe_2O_3 , Fe_3O_4 , SiO_2 , etc.), hydrated basic carbonates ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_6$, etc.), chlorine compounds

($\text{Cu}_2(\text{OH})_3\text{Cl}$, $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$, etc.) and other compounds were formed by the alteration processes caused by the underground lying environment [5, 6].

Acknowledgement

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References

- [1]. I.G. Sandu, I. Sandu, A. Dima, „Modern Aspects Concerning the Conservation of Cultural Heritage, vol. III, Authentication and Restauration of the Inorganic Material Artefacts”, Ed. Performantica, Iași, 2006.
- [2]. I. Sandu, N. Ursulescu, I.G. Sandu, O. Bounegru, I.C.A. Sandu, A. Alexandru, „The pedological stratification effect of corrosion and contamination products on Byzantine bronze artefacts”, in **Corrosion Engineering Science and Technology**, Maney Publishing, vol. 43, 3, (2008), pp. 256-266.
- [3]. I. Sandu, O. Mircea, A.V. Sandu, I. Sarghie, I.G. Sandu, V. Vasilache, „Non-invasive Techniques in the Analysis of Corrosion Crusts formed on Archaeological Metal Objects”, **Revista de Chimie**, Bucharest, vol. 61, 11, (2010), pp. 1054-1058;
- [4]. D. Aparaschivei, „Cercetările arheologice de la (L?)Ibida (Slava Rusă, jud. Tulcea), Sector X (campania 2008) (I)”, in **Arheologia Moldovei**, XXXII, 2009, pp.167-182;
- [5]. D. A. Scott, „Copper and Bronze in Art: Corrosion, Colourants and Conservation”, Getty Conservation Institute, Los Angeles, 2002.
- [6]. De Ryck, A. Adriaens, E. Pantos, F. Adams, „A comparison of microbeam techniques for the analysis of corroded ancient bronze objects”, **Analyst**, 128, 2003, pp. 1104-1109;
- [7]. I. Sandu, C. Marutoiu, I.G. Sandu, A. Alexandru and A.V. Sandu, „Authentication of Old Bronze Coins I. Study on Archaeological Patina”, **Acta Universitatis Cibiniensis Seria F, Chemia**, 9(2006-1), pp. 39-53;
- [8]. V. Vasilache, D. Aparaschivei, I. Sandu, „Scientific investigation on ancient jewels found in Ibida site, Romania”, **International of Journal Conservation Science**, 2, 2, 2011;
- [9]. K. Nakamoto, „Infrared and Raman Spectra of Inorganic and Coordination Compounds”, Parts A and B, John Wiley & Sons, New York, 1997;
- [10]. John Coates, „Interpretation of Infrared Spectra, A Practical Approach”, **Encyclopedia of Analytical Chemistry**, R.A. Meyers (Ed.), John Wiley & Sons Ltd, Chichester, 2000, pp. 10815-10837.

Annex 1.

Table 2. Representative peaks and spectral bands of the ions identified in the analyzed objects.

Spectral bands (cm ⁻¹)	Functional group	Peak present in analyzed objects (cm ⁻¹)	Analyzed objects
670-745; 800-890; 1040-1100; 1320-1530	Carbonate ion	724. 1378.1465	P1
		1340. 1497	P2
		1413. 1482	P3
		1462. 1515	P4
		723. 1376. 1465	P5
940-1120	Orto-phosphate ion	1001	P3
830-920; 1600-1900; 2150-2500; 2750-2900;	Orto-phosphate dibasic ion	1719. 1896. 2304. 2851	P1
		1675. 2635. 2307. 2862	P2
		1753.	P3
		1613. 1676. 2829	P4
		1743. 2851	P5
570-680; 960-1030	Sulphate ion	618	P3
600-660; 610-630; 900-1150	Chloride ion	965. 1126	P1
		640. 929	P4
600-700	Tin ion	654	P2
		698	P4
860 – 1175	Silicate ion	889	P1
		1130	P2
		1044	P3
		1036. 1123	P4
		887	P5
		888	P6
800 - 920	Aluminate	889	P1
		878	P2
		865	P3
		837	P4
2550-3500	Aquo and hydroxo-compounds. water of coordination	2636. 2920. 3278	P1
		3241	P2
		2999. 2585. 3173	P3
		3318. 3374. 3040. 2950	P4
		3329. 2955. 2922	P5
3500-4000	Waters related physically	3603	P1
		3527	P2
		3651	P3
		3509	P4
		3508	P6

POSSIBILITIES TO INCREASE THE DURABILITY OF THE STEELS OVERLAPPING A MAGNETIC FIELD IN THE CONVENTIONAL HEAT TREATMENT BEFORE THERMO-CHEMICAL TREATMENT

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ABSTRACT

The aim of this work was to study the evolution of two types of steel grades. These materials were subjected to a nitriding thermo-chemical treatment after thermo-magnetic treatments. The structural and diffractometric aspects of the superficial layer of these steels are studied after wear process, using an Amsler machine, taking two sliding degrees at different contact pressures and testing time. The tests were done for determining the durability of these materials, the surface structure evolution under different tests conditions and for establishing the influence of the thermo-magnetic treatments.

KEYWORDS: Thermo-magnetic treatments, nitriding thermo-chemical treatment, wear process, durability

1. Introduction

In this paper, it was made the balance-sheet looking at the advantages/disadvantages between the classic improvement treatment plus ionic nitriding and the improvement treatment in different regimes of magnetic field (continuous or alternative current), the different cooling regimes and the ionic nitriding.

Overlapping a magnetic field in the conventional heat treatments, the energy of the magnetic field interferes in the global energy balance of the solid stage transformation. This magnetic field thermodynamically changes the transformation mechanisms and kinetics, obtaining the thermo-magnetic treatment. In the end, it can be obtained the change of the mechanical properties and the change of the structure configuration for these materials. Overlapping a surface treatment (thermo-chemical treatment) like nitriding with plasma (ionic nitriding), the resistance to

wear increase [1] and the resistance to corrosion, too.

Until 1932, the martensitic steels after the hardening process were considered the principal materials for the magnets [2]. Minkievici, Stark and Zaimovski, Erahtin, Komar and Tarasov röntgenographically studied these alloys. They demonstrated that the optimal magnetic properties are a consequence of their variable structure-that appears in the initials process stages [1, 7].

Because of their variable structure, the materials have individual micro-volumes of different phases. Each of these micro-volumes of ferromagnetic phase has a spontaneous magnetization and a marked magnetic anisotropy. These micro-volumes are isolated magnetic areas, non-magnetic areas or slightly magnetic layers. The result is a big co-ercitive force, which depends on the grain size and the temperature.

The final result must be a stable magnetic texture. In experimental programs, there are preferred two methods: the cooling regime in magnetic field (a thermo-magnetic

treatment) or, thermo-mechanical treatments (based on overlap to unilateral elastic tensions).

The magnetostriction was determined by the influence of the external magnetic field, which generates the orientation of elementary magnetic moments, modifying the balance conditions among the nodes of the crystalline mesh, including variation of the ferrous-magnetic material sample lengths. Under these conditions, the magnetostriction curves evolutions can be a result of having measured the ferrous-magnetic sample lengths along the external magnetic field. In addition to this linear magnetostriction considered above for plotting the magnetostriction curves, with ferrous magnetic materials, it may also be noted a volume magnetostriction, which depends on the shape of the machine element or of the sample concerned as well.

Magnetostriction is defined as a dimensional variation of ferrous-magnetic materials under the action of a magnetic field, also called Joule effect, which depends on the size and direction of the external magnetic field, the material and the heat (thermal) treatment previously applied to this material [3, 4, 5]. The effect of the magnetostriction decreases with higher temperatures and disappears at the Curie temperature. The mechanical oscillations produced by the alternative magnetic fields change the re-crystallization conditions, especially the germination velocity.

The strains generated by magnetostriction, determine elastic deformations which, in turn, produce a magnetic texture, improving the magnetic and mechanical properties in the direction of the externally applied field (characterized by its intensity H_{ext}). From this viewpoint the effect of the thermo-magnetic treatment is maximum in the stages of solid solution decomposition and, especially, during cooling in magnetic alternative field, from temperatures higher than Curie point (when

orientation of ferrous-magnetic phase particles takes place) [1, 2, 3]. Under the influence of an external magnetic field, it is theoretically possible [1, 2] to modify the material state of the structure and the physical and mechanical properties in the material.

2. Experimental researches

It was considered a category of alloy steels, for improvement treatments, useful in metallurgical industry: 42MoCr11 (code V) and 38MoCrAl09 (code R). These materials are presented in table 1. The content of Ni corresponding to 38MoCrAl09 steel grade is 0.26%. The content of Ni corresponding to 42MoCrV11 steel is 0.32%. The steels analyzed reach a max score 4.5 from inclusions and a fine grain (score 8-9).

These materials are subjected to the following heat/magnetic treatments and thermo-chemical treatments:

t1= martensitic hardening process (at 850 °C for code V and 920°C – for code R) and high recovery (at 580°C –for code V and 620°C – for code R), classic treatment (Magnetic field intensity is $H = 0 \text{ A/m}$).

T1= t1 + ionic nitriding (at 530°C).

t2= complete martensitic hardening process in weak alternative magnetic field (cooling in water) and high recovery process (just cooling in water, in strong alternative magnetic field).

T2 = t2 and ionic nitriding (at 530°C).

t3= hardening process (cooling in water, in strong alternative magnetic field) and high recovery process (cooling in water, in strong alternative magnetic field).

T3 = t3 and ionic nitriding (for code V),

T3' = t3 and ionic nitriding (for code R);

t4= hardening process, with cooling in water in strong d.c. magnetic field (Tcc) and high recovery process with cooling in water in strong direct (d.c.) magnetic field (Tcc).

T4 =t4 and ionic (plasma) nitriding.

T5= t1 + laser nitriding (t= 5 seconds);

T6= t1 + laser nitriding (t = 5 seconds);

T7 = t4 + laser nitriding (t = 5 seconds);

T8= t3 + laser nitriding (t = 5 seconds).

The usual methodology for the machinery parts study (roller wheel) useful in the metallurgical industry, presents the theoretic contact like a point (point contact) or, a line (linear contact).

On Amsler machines [3, 10, 11], I tried to determine the durability of the rolls, the structure evolution at different tests. Not must be neglected the other factories, which influence the wear process: the geometric forms in contact of the machinery parts (roll on roll, roll on ring), the technological parameters (the surface quality, the temperature of the treatments) and the exploitation conditions (the solicitation temperature – for example).

It were submissive at wear process on an Amsler machine from “Dunarea de Jos”University of Galati, rolls with different diameters and different materials (code V), which suffered different treatment regimes, like: T1, T2, T3, T4, T5, T6, T7, T8 and for the material noted code R: T1’, T3’, T4’ T5’, T7’, T8’.

2. Experimental results

In figures 1 and 2, t1 represents the classic treatment (with a magnetic field intensity $H=0$ A/m), t3 represents a treatment

(Tca) in a magnetic field–alternative current - a.c. ($H=1300$ A/m) and t4 represents a treatment (Tcc) involving a direct (continuous) magnetic field (d.c.).

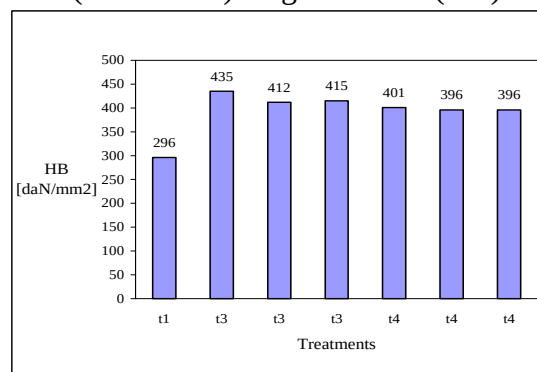


Fig. 1. The influence of the magnetic field on the hardness, for code V samples (42MoCr11) [3]

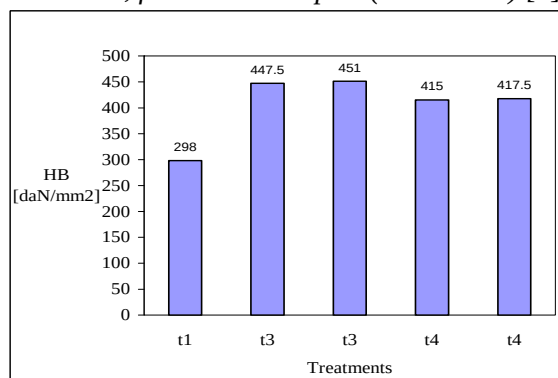


Fig. 2. The influence of the applied magnetic field on the hardness, for code R samples (38MoCrAl09) [3, 11]

Table 1. Chemical composition of the materials, (%)

Steel grade	C	Mn	Si	P	S	Cr	Cu	Mo	Al
42MoCr11 (Code V)	0.42	0.68	0.33	0.030	0.026	1.02	0.220	0.17	0.02
38MoCrAl09 (Code R)	0.38	0.50	0.25	0.026	0.020	1.38	0.058	0.17	1.18

Table 2. Mechanical characteristics of the steels (Standard)

Steel grade	R _{p0.2}	R _m	A ₅	Z	KCU _{300/2}	KCU _{300/5}	HB
	[daN/mm ²]		[%]		[daJ/cm ²]		
42MoCr11 AISI (SAE) 4142	75	95	11	50	8	6	217
38MoCrAl09 AISI(SAE) 4038	85	100	15	50	9	6	229

In table 2 are presented the standard mechanical characteristics of the steels, corresponding to The Society of Automotive Engineers (SAE) and The American Iron and Steel Institute (AISI).

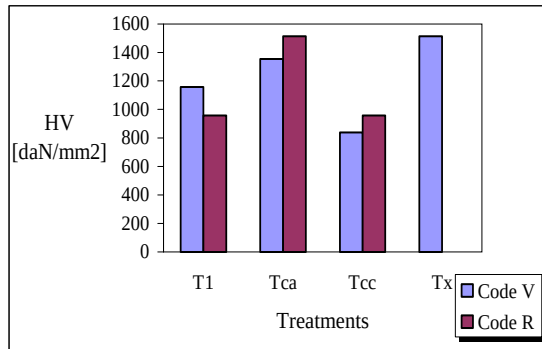


Fig. 3. The micro-hardness values evolution [2, 11]

The magnetic field modifies the grain size. It was obtained a small grain size in the middle of the sample and the orientation of these grains is in the same direction with the lines of the magnetic field.

On Amsler machines [7], the done tests tried to determine the durability of rollers, the surface structure evolution for different parameters of testing regimes. It could not be neglected other factors influencing the wearing process: the contact geometry of the friction couple (roller on roller, roller on ring etc.), the technological parameters (surface quality, heat treatments, etc.) and the exploitation conditions (the thermal sollicitation, for example).

Wear tests were carried out on an Amsler machine, using several couples of rollers, each couple corresponding to a different sliding degree ξ , defined as:

$$\xi = (v_1 - v_2) 100 / v_1 [\%] \quad (1)$$

where v_1 and v_2 are the peripheral velocities of the rollers in contact, each one having their specific peripheral velocity due to a particular combination of angular speeds (n_1 , n_2) and diameter sizes (d_1 , d_2). Index 1 or 2 are added for the roller 1 or 2, respectively, both of the same tested couple. For instance, $\xi=10\%$ is obtained for a pair of

tested rollers having $d_1=40$ mm, $n_1=180$ rev/min and $d_2=40$ mm, $n_2=162$ rev/min. $\xi=18\%$ is obtained for a pair of tested rollers having $d_1=44$ mm, $n_1=180$ rev/min and $d_2=40$ mm, $n_2=162$ rev/min. The level of the stress is corresponding to a specific load of 150 N/mm and a normal load is $Q=1500$ N. The contact between roller is $b=10$ mm.

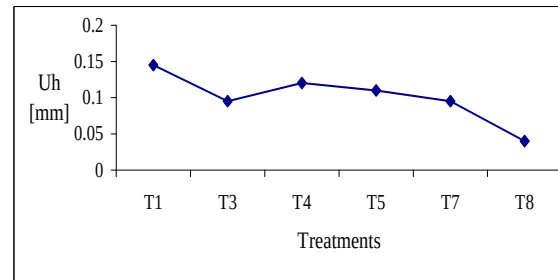


Fig. 4. The magnetic field influence on the worn-out layer depth, after 3 hours of tests, $\xi=20\%$ and $Q=1500$ N, for 42MoCr11 (code V) [3, 11]

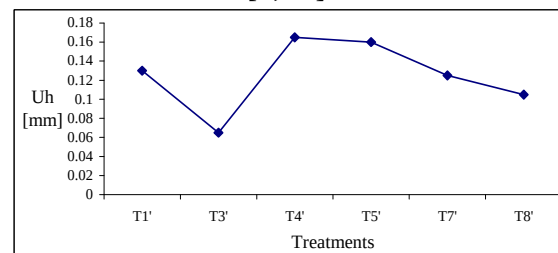


Fig. 5. The magnetic field influence on the worn-out layer depth, after 3 hours of wear tests, $\xi=20\%$ and $Q=1500$ N, for 38MoCrAl09 (code R) (ionic nitrided: T1', T3', T4' or laser nitrided: T5', T7', T8' treatments) [3, 11]

Thus, it was obtained a higher diffusion for thermo-chemical treatments applied after thermo-magnetic treatments regimes. We can see, experimental, the influence of the magnetic field on the worn-out layer depth (thickness) or, on the white superficial layers (superficial layers nitrided). The thickness increase if we apply a magnetic field (applying thermo-magnetic treatments regimes). Each of the stages of the heat treatment in the magnetic field (AC or DC) influences the hardness, the durability of the steels and the thickness of the superficial layers obtained after the thermo-chemical treatment [12].

3. Diffractometry aspects

In figures 6 and 7, are presented the researches possibilities at X-Ray Diffractometry using a Dron 3, from „Dunarea de Jos” University. The angular velocity of the sample is $\omega = 1^\circ/\text{min}$.



Fig.6.



Fig.7

In the analysed superficial layers, the Fe_4N phase has a higher hardness than the Fe_3N phase.

Thus, in the case of thermo-magnetic treatments applied before the thermo-chemical treatments, it was observed a higher quantity of Fe_4N phase as compared to the quantity of the Fe_3N phase.

In this case, the nitrided layer depth increases and the resistance to wear increases, too, with more than 25%.

The resistance to corrosion increases (more than 34%), too. In figures 8 (a, b, c), 9 and 10 (a, b, c, d) there are presented some diffractometry aspects, obtained on the samples, after 1...3 hours of wear tests, using an Amsler machine and a diffractometry equipment Dron 3.

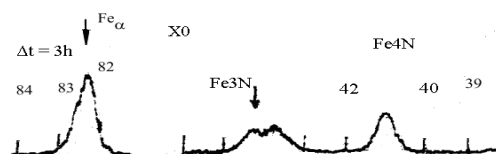


Fig. 8 a. X-Ray analysis corresponding to X_0 samples (T_2 , $Q=75\text{daN}$, $\zeta=10\%$) after three hours of wear tests

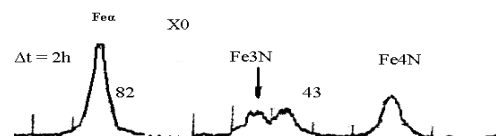


Fig. 8 b. X-Ray analysis corresponding to X_0 samples (T_2 , $Q=75\text{daN}$, $\zeta=10\%$), after two hours of wear tests

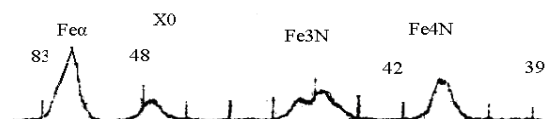


Fig. 8 c. X-Ray analysis corresponding to X_0 samples (T_2 , $Q=75\text{daN}$, $\zeta=10\%$), at the initial moment ($t=0$)

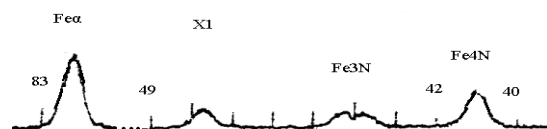


Fig.9. X-Ray analysis corresponding to X_1 samples (T_2 , $Q=150\text{daN}$, $\zeta=10\%$), after three hours of wear tests [11]

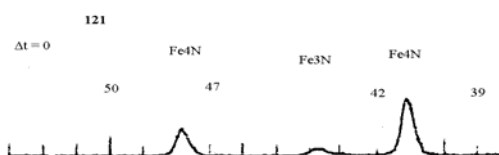


Fig. 10 a. X-Ray analysis corresponding to 121 samples (T_1), at initial time (t_0)

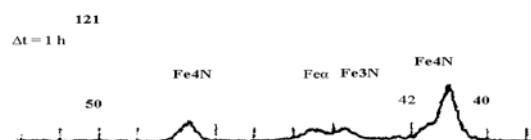


Fig. 10 b. X-Ray analysis corresponding to 121 samples (T_1), after one hour of wear tests

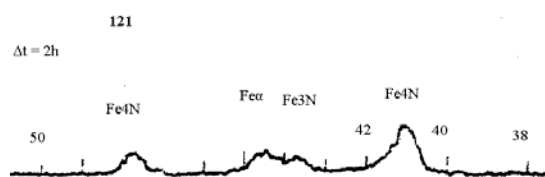


Fig. 10 c. X-Ray analysis corresponding to 121 samples (T1), after two hours of wear tests

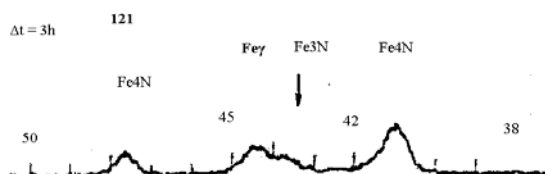


Fig. 10 d. X-Ray analysis corresponding to 121 samples (T1), after three hours of wear tests. Conditions of work: $Q=75\text{daN}$, $\xi=10\%$ [11]

4. Conclusions

The novelty of the present paper involves the application of the diffusion thermo-chemical treatment after the thermo-magnetic one, the temperature of the former being lower than that of the latter, except that the thermo-chemical treatment applied after the thermo-magnetic treatment should not modify (due to the high temperature) the improvements of the mechanical properties by the thermo-magnetic treatment. It was made a balance sheet between classic treatment and unconventional (thermo-magnetic) treatment.

It has been shown that, when applying an alternative current (A.C.) magnetic field treatment (for example, $H=1300\text{ A/m}$), the thickness of the thermo-chemical treated layer increase up to 25% as compared to the conventional (classic) thermal/thermo-chemical treatment ($H=0\text{ A/m}$).

It was observed that for the treatment T1 applied to 42MoCr11 steel grade (classic treatment), the martensite quantity and the nitrides are maintained constants after the friction-wear process. In the case of alternative or continuous magnetic field applied to the steels (Tca, Tcc), it was observed a higher initial quantity of martensite and nitrides. During the wear

process, the martensite quantity increase and the Fe_3N quantity decrease. A good influence of the thermo-magnetic treatment on the surface layer resulted in a higher hardness [4] and a good wear resistance.

References

- [1]. Vonsovschi S.V., 1956, *Teoria modernă a magnetismului* (in Romanian), Editura Tehnica, Bucharest, Romania.
- [2]. Papadatu C.-P., 2006, *The influence of the thermomagnetic treatments on the superficial layers nitrated evolution during friction process (II)*, Proc. of the 14th Intern. Metallurgical and Materials Conf., Metal 2006, 24-26 May 2006, Society for New Materials and Technology, ASM Intern. Czech Chapter, Technical University Ostrava, Czech Republic.
- [3]. Papadatu C.-P., 2005, *Cercetări privind ameliorarea proprietăților și creșterea fiabilității unor oțeluri folosite în construcția utilajelor metalurgice*, PhD Thesis, University "Dunarea de Jos" Galati, Romania.
- [4]. Popescu N. et al., 1990, *Tratamente termice neconvenționale* (in Romanian), Editura Tehnice, Bucharest, pp. 105-117.
- [5]. Berkowitz A.E. et al., 1969, *Magnetism and Metallurgy*, Academic Press, New York and London.
- [6]. Cedighian S., 1974, *Materiale magnetice* (in Romanian), Ed. Tehnică, Bucharest, Romania.
- [7]. Bozorth R.M., 1951, *Ferromagnetism*, New York, Van Nastrand, Co.Inc.
- [8]. Gheorghies C., 1990, *Controlul structurii fine a metalelor curadiatii X* (in Romanian), Ed. Tehnică, Bucharest, Romania.
- [9]. Ștefănescu I., 1984, *Contributii la studiul influentei tratamentului termomagnetic asupra uzurii prin ciupitura (pitting) la otelul de rulmenti RUL1*, (in Romanian), PhD, University "Dunarea de Jos" of Galati, Romania.
- [10]. Ștefănescu I., Spănu C. et al., *Organe de mașini*, Indrumar pentru lucrări de laborator (in Romanian), Editura Fundatiei Universitare "Dunarea de Jos", Galati, 2002.
- [11]. Papadatu C.-P. 2006, *Posibilități de creștere a calității unor oțeluri utilizate în industria metalurgica* (in Romanian), Ed.Fundatiei Universitare "Dunarea de Jos" din Galati.
- [12]. Papadatu C.-P., Bordei M., 2010, *Changes in Tribological Behaviour of Thermo-Chemical Treated Steels after Thermo-Magnetic Treatments*, Metalurgia International Revue, vol. XV (2010), 15, pp. 41-49.

FINITE ELEMENT ANALYSIS OF EQUAL CHANNEL ANGULAR PRESSING OF Al-Mg 5083 ALLOY

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ABSTRACT

Bulk nanostructured materials represent the application of nanotechnology in the engineering material area. Severe Plastic Deformation (SPD) and in particular Equal Channel Angular Pressing (ECAP) are efficient and low cost top-down methods for producing ultrafine or nanostructured bulk materials. Alluminum alloys are very popular materials used for production of ultrafine-grained and nanomaterials by SPD. Understanding both the contact phenomenon at the interface between die and the workpiece in terms of material flow and phenomena associated with strain and forming load in ECAP process becomes important. In this paper, a tridimensional Finite Element Analysis of ECAP was performed for Al-Mg 5083 alloy.

KEYWORDS: severe plastic deformation, equal channel angular pressing, alluminum

1. Introduction

Materials with ultrafine – grains (UFG) or nanometric structures (NS) offer significant advantages in terms of large strength, hardness and ductility or high strain rate superplasticity [1]. They have great impact in biomedical, electronics, military, aerospace, and automotive. Industries and academics have shown great interest in fabrication of NS materials with high performance to weight ratio such Al, Mg, Al-Mg etc.

Wrought non heat-treatable Al-Mg alloys are attractive candidates for different components due to their good weldability, moderate strength, but excellent corrosion resistance. Increasing strength by SPD without any supplementary alloying it's a convenient way to rise up the potential of the material while maintaining all other mechanical properties. At the same time, developing superplasticity needs the material reaches ultrafine structure with reasonable

thermal stability, without presence of secondary phase due to special alloying elements. In these conditions, there is considerable interest in using Al-Mg alloys for structural applications.

Among various techniques developed to obtain UFG materials [2], the Equal Channel Angular Pressing (ECAP) is one of the most effective processes. Fig. 1 shows a schematic principle that outlines the important geometric factors of the ECAP process [3].

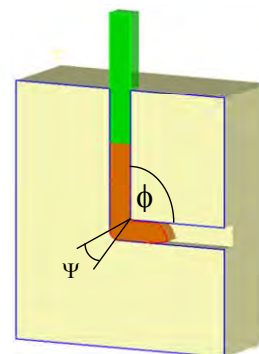


Fig. 1. Principle of ECAP and die geometry components

In ECAP, a billet is pressed through a die that contains two equal cross-sectional channels. In the vertical channel, the billet moves as a rigid body while all deformation is localized in the small area around the channel's meeting line (the bisecting plane). The metal is subjected to a simple shear strain under relative low pressure compared to the traditional extrusion process [3]. Because the cross-section of the billet remains the same during extrusion, the process can be repeated until the accumulated deformation reaches the imposed level. The billet removal involves a new development of ECAP procedure. The introduction of a new sample returns the ECAP process to the initial configuration which permits the next pressing cycle to follow. The new sample is inserted and pressed from the top and the previous sample moves to the right trough horizontal channel of die.

As the microstructures and the mechanical properties of the plastic-deformed materials are directly related to the degree of plastic deformation, the understanding of the strain and stress development is very important in a successful ECAP process design. The theoretical effective strain according to the die geometry is given in Eq. (1), as formulated by Iwahashi et al. [4]:

$$\bar{\epsilon} = \frac{1}{\sqrt{3}} \left[2 \operatorname{ctg} \left(\frac{\phi}{2} + \frac{\psi}{2} \right) + \psi \cos \operatorname{ec} \left(\frac{\phi}{2} + \frac{\psi}{2} \right) \right] \quad (1)$$

where the significance of terms are revealed in fig.1. For $\phi = 90^\circ$ and $\psi = 0$, an equivalent strain of 1.15 is achieved. Note that Eq. (1) was derived for ideal perfect-plastic behavior and frictionless conditions.

From the technological point of view, a successful SPD process requires to surpass two obstacles. First the load level (which directly affects the tool design) and second an adequate formability of the material so that it can withstand high degrees of repeated deformation. Unfortunately there are no criteria which ensure a guaranteed successful

SPD of the material. Only a favorable stress distribution can decide the success of SPD.

Designing both processing and tools needs to take into account the deformation behavior of the billet in combination with effects of strain hardening, friction and die geometry. In this paper, a tridimensional FEA is performed to analyze the ECAP process of Al-Mg 5083 alloy. The purpose of FEA is to evaluate load level, strain and stress distribution during severe plastic deformation in order to successfully pursue the future ECAP processes.

2. Experimental and procedures

2.1. Finite Element Analysis

To carried out the simulation, commercial finite element code DEFORM was used. The workpiece (10x10x60mm) considered a plastic body in whole deformation process was discretized in 8000 tetrahedral elements (this is equivalent to at least 36 elements across the width of the billet). The tolerance, positioning of the workpiece and top/bottom die, convergence criteria, re-meshing conditions, and boundary conditions were specified before the execution of the simulation process. Adaptive meshing was used in the simulation. Poisson's ratio 0.33 and Young's modulus 69Gpa were assumed. The hardening behavior is considered isotropic and independent of strain rate at room temperature. The simulation was performed at room temperature for a stroke of about 50 mm under a constant speed of 8.75 mm/s.

The friction force along contact surfaces was modeled by constant shear friction law $F_r = m \cdot \tau_o$ where τ_o is the yield stress in shear and $m = 0.12$ is the friction coefficient [5].

The die considered for analysis corresponds to high strength hardened steel with the channel angle $\phi = 90^\circ$ and outer corner radius of 2 mm which means $\psi \approx 12^\circ$.

2.2. Processing Al-Mg 5083

A commercial available AA 5083 with a composition in wt.% of 4.5%Mg, 0.7%Mn and aluminum balance was used in this study. Specimens with dimensions of 10x10x60mm were machined from as-received alloy. A subsequently annealing at 723K for 1h was performed before ECAP. The ECAP process was conducted at room temperature (fig. 2) with a constant speed of 8.75 mm/s, using a die with $\phi = 90^\circ$ and $\psi = 12^\circ$. All samples and inner walls of the dies channels were lubricated using zinc stearate.



Fig.2. Experimental device for ECAP

3. Results and discussions

3.1. Working load and model validation

Matching of simulates with experimental load data is important to validate the modeling we have used it. Fig.3 shows load – displacement curve during the ECAP of AA 5083. Four stages can be distinguished on the curve (Fig.3) [5].

In Stage I, the load increases rapidly with the ram displacement, reaching a maximum. This stage begins when the head of the billet first touches the bottom wall of the die channel at the outer corner and ends when the workpiece head bends over the corner. In Stage II the load decreases until the upper surface of the billet begins to touch the upper wall of the outlet channel.

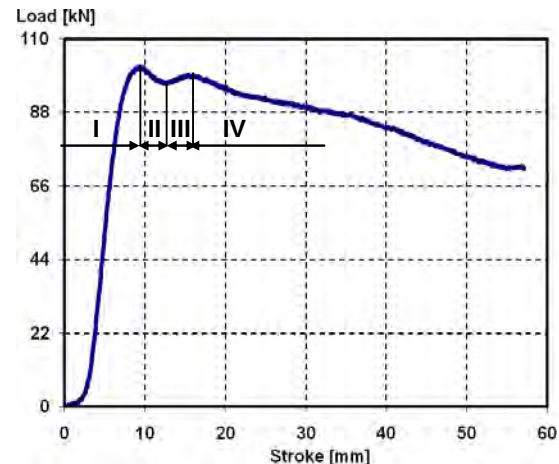


Fig.3. Experimental load – displacement curve for one pass ECAP of AA 5083

In the next stage (Stage III), a slowly increase in load marks the period from the moment the billet head touches the upper wall (end of Stage II) to the moment that sufficient contact is established between the upper surface of the billet head and the upper wall of the outlet channel. Load increases because of deformation in the billet head.

The load decreases gradually with the displacement in Stage IV.

When the billet is pressed from the inlet channel to the outlet channel through the die corner, the contact area in the inlet channel decreases and in the meantime the length of the gap in the outlet channel grows until the head of the billet comes out of the outlet channel. As a result, the total contacting area between the billet and the die wall always decreases with the ram displacement, and so when we have real friction, the response is visible in the load versus displacement curve.

Fig 4 shows the predicted load evolution for the first pass ECAP of investigated alloy. The maximum level of working-load and the general evolution are in good agreement with experimental results, confirming the validity of ECAP modeling.

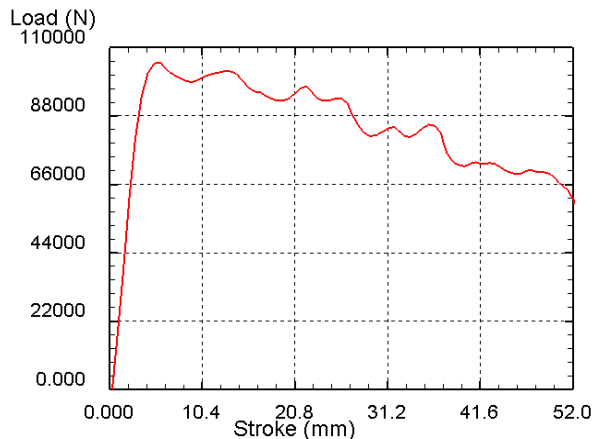


Fig.4. Predicted load evolution for the first pass ECAP of AA 5083 (simulation)

3.2. Strain and stress distribution

Theoretically, uniform strain in the entire sample can be achieved if the deformation follows simple shear perfectly.

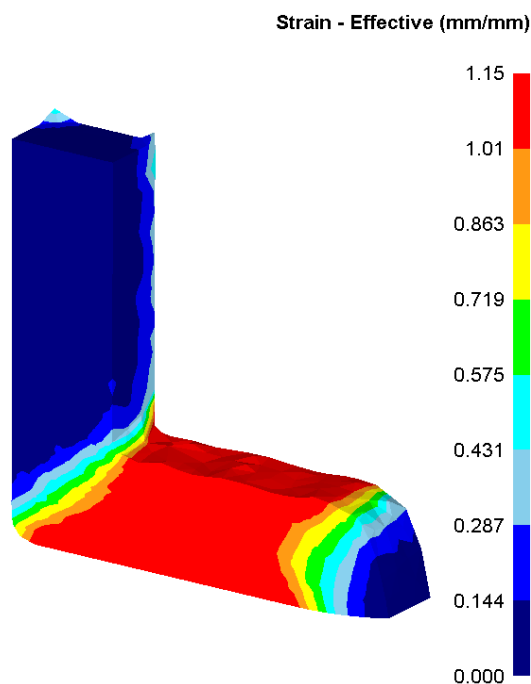


Fig.5. Strain distribution - ECAP of AA 5083 (longitudinal section)

As the workpiece exits from the plastic deformation zone the strain distribution starts to stabilize and is no further variations in the strain. It is shown that at the middle of the total deformation step a steady state

deformation behavior is found. The deformation histories are different for the head part and the tail part. It is obviously that transient regions of the head and tail ends receive smaller amounts of strain. Fig. 5 shows strain distribution as a color map for the first ECAP pass of investigated alloy.

The non-uniform strain achieved in plastic deformation zone (PDZ) and the origin of inhomogeneous behavior is well-known [6].

A few equidistant tracking points ($P_1...P_4$) are defined in longitudinal section of the workpiece across the PDZ in order to estimate strain distribution after the material leaves the main deformation area corresponding to the bisecting plane of the die channels (fig.6).

Naturally and according with Eq. (1), the outer corner radius determine a decrease of the effective strain. Final average strains from the steady-state region are in good agreement with those given by Eq. (1).

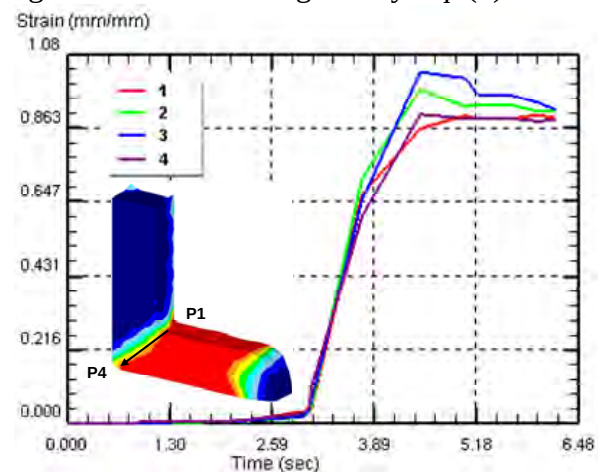


Fig.6. Strain distribution in longitudinal section for the tracking point P_1 - P_4 of PDZ

The effective stress distribution (fig. 7) shows high effective stresses in PDZ and in the region prior to PDZ. This is due to intense compressive action within the inlet channel of the die.

Note that effective stresses are always positive no matter the stress type (compression or tensile stress).

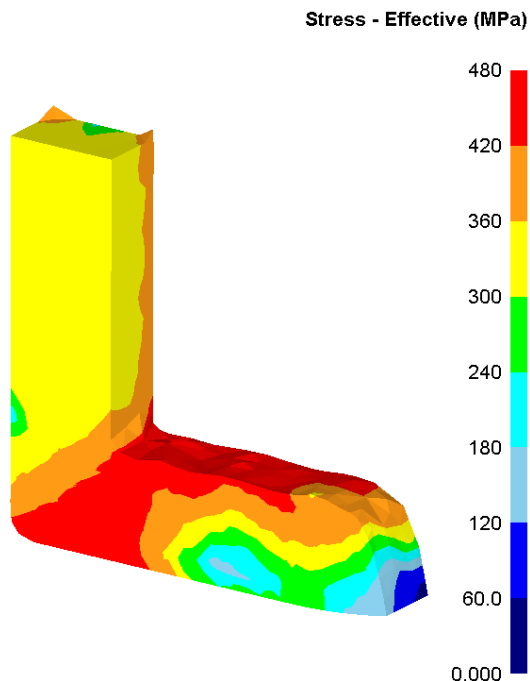


Fig.7. Effective stress distribution - ECAP of AA 5083 (longitudinal section)

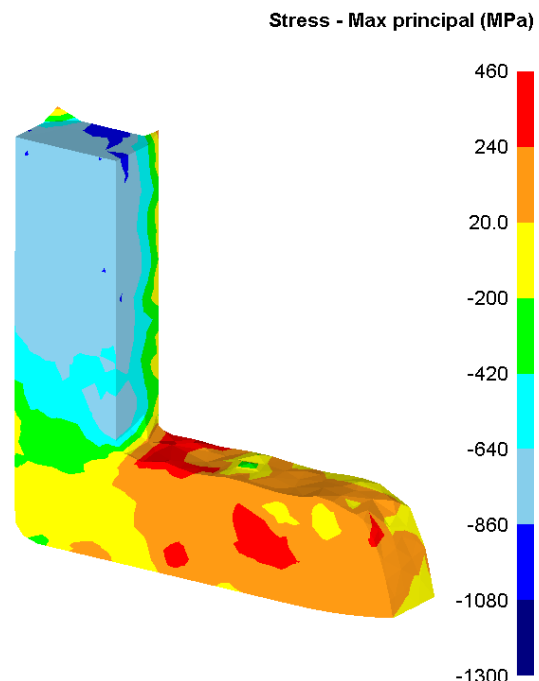


Fig.9. Principal stress distribution - ECAP of AA 5083 (longitudinal section)

But, if principal stresses are revealed as maximum positive stresses in the same area as in effective stress distribution, it means that the region is dominated by tensile tensions which can cause cracks in the workpiece, fig.8. So, the max principal stress distribution becomes relevant.



Fig.8. Cracking during ECAP process. Cracks start from upper surface of the billet

The nature of cracking on upper surfaces of the billet can be depicted from the principal stress distribution (fig.9). High positive maximum principal stresses occur along the top surface of the billet in the exit channel immediately after the plane of channels intersection. This fact is confirmed by other authors [7].

4. Summary and conclusions

Finite Element Analysis was performed to evaluate ECAP process of AA 5083. The analysis shows the maximum estimated load level which it is found in very good agreement with experiments on severe plastic deformation of AA 5083.

At the same time, simulations suggest that the accumulation of high positive maximum stresses on the upper surface of the billets is the main cause of appearance of the cracks on the mentioned area. If the stresses surpass the strength of the material, a technological solution including die geometry and/or processing temperature must be considered for a successful pursue of equal channel angular pressing.

Using the obtained results, tool and process design will become more accurate with all the benefits for research implementation.

References

- [1]. B.Q. Han, E.J. Lavernia, and F.A. Mohamed, *Mechanical Properties of Nanostructured Materials*, Rev. Adv. Mater. Sci. 9 (2005) 1-16
- [2]. A. Azushima, R. Kopp, A. Korhonen, D.Y. Yang, F. Mi cari, G.D. Lahoti, P. Groche, J. Yanagimoto, N. Tsuji, A. Rosochowski, and A. Yanagida, *Severe plastic deformation (SPD) processes for metals*, CIRP Annals - Manufacturing Technology 57 (2008) 716-735
- [3]. V.M. Segal, *Materials processing by simple shear*, Mater. Sci. Eng. A 197 (1995) 157-164
- [4]. Y. Iwahashi, M. Furukawa, Z. Horita, M. Nemoto, and T.G. Lang don, *Microstructural Characteristics of Ultrafine-Grained Aluminum Produced Using Equal-Channel Angular Pressing*, Metall. Mater. Trans. 29(9) (1998) 2245-2252
- [5]. S. Li, M. A.M. Bourke, I.J. Beyerlein, D.J. Alexander, and B. Clausen, *Finite element analysis of the plastic deformation zone and working load in equal channel angular extrusion*, Mater. Sci. Eng. A, 382 (2004) 217-236
- [6]. Wei Wei, A.V. Nagasekhar, G. Chen, Yip Tick-Hon, and Ku n Xia Wei, *Origin of inhomogenous behavior during equal channel angular pressing*, Scripta Mater., 54 (2006) 1865-1869
- [7]. R.B. Figueiredo, P.R. Cetlin, and T.G. Langdon, *The evolution of damage in perfect-plastic and strain hardening materials processed by equal-channel angular pressing*, Mater. Sci. Eng. A 518 (2009) 124-131



SECTION II

**ENVIRONMENTAL ENGINEERING,
SURFACE ENGINEERING,
ADVANCED MATERIALS.**



INTERNATIONAL SCIENTIFIC CONFERENCE
UgalMat 2011
ADVANCED MATERIALS AND TECHNOLOGIES



SURFACE ANALYSIS OF PES FIBRES TEXTILE SUPPORT, BY ZETA POTENTIAL MEASUREMENT

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ABSTRACT

Motivation and objectives. An enhancement of existing features and the creation of new material properties are the most important objectives for the functionalization of textiles. To design these additional materials properties coating and inclusion of particles into fibers can be performed. They represent modification techniques with great potential for synthesis of novel functional materials however these technologies are still inadequately employed in the textile production. The influence of modification on surface properties of PES fiber types has been studied by determination of zeta (ζ) potential as a function of pH. Based on functional dependence $\zeta=f(\text{pH})$ we can conclude about acid – alkaline character of functional groups on fibers' surface and accessibility of these groups. Zeta (ζ) potential of fibers surface is not only a parameter of quantity and type of dissociable species and adsorbed charged molecules or ions; but by measuring ζ -potential the hydrophilic /hydrophobic character of fibers and structural changes on fibers' surface can be valued. Our research deals with colloidal dispersions, subsequently, the measuring of zeta (ζ) potential provides valuable information, data about the stability prediction onto the ZnO particles suspensions onto PES support, or their tendency to agglomerate, as well the system purity.

The main result and characterizing aspect of the research consist of achievement of a multi-functionality that can be evaluated by shifting of some surface properties, especially the surface energy, as well as electro kinetic behavior, quantified by zeta (ζ) potential. The measurement of zeta (ζ) potential onto polyester textile material surface has been performed onto samples with different concentrations of ZnO, each having an approximately weight of 2 g. Before starting the measurements, the samples have been immersed into an electrolyte solution (KCl) for two hours, in order to reach an equilibrium. The solution of electrolyte (KCl 10^{-3}M) was obtained from 20 mL KCl 10^{-1}M and 1800 mL water. Since zeta potential is an analyses related to pH, some different pH-s (4,7,9) have been chosen for comparison. To reach smaller and higher pHs, HCl and KOH solutions have been added. After maintaining the samples into the electrolyte solution for two hours, the measuring of zeta potential by means of a special device connected to the computer, has been performed.

Results and Discussion. By zeta potential measurement, some comparable results have been obtained. For a better dispersion of ZnO particles, methanol has been used, obtaining samples with different concentration of ZnO. The reference sample has been considered a PES fabric treated with a suspension ZnO particles – water.

KEYWORDS: Zeta Potential, ZnO, PES textile fibres

The present research/study presents zeta analysis, meaning surface of PES textile potential measurement through a surface support treated/coated with zinc oxide

powder (emulsions with different concentrations), using various types of dispersion of ZnO.

The value and sign of Zeta potential provide information concerning:

- the solid surface physical-chemical structure (the grouping of molecules on solid surface);
- the composition of electrolytic solution;
- the interaction among the solid surface and liquid components;
- item long term.

1. Introduction

Zeta potential or electro kinetic potential is the result of electric charges accumulations at solid/liquid interface. As interface characteristic, zeta potential is influenced by both solid surface and environmental properties. For instance, zeta potential measurement assures the prediction of particles suspensions or their tendency to agglomerate, in the field of colloidal dispersions [1].

Factors influencing the zeta potential

- pH changes (zeta potential value without a certain nominated pH is otherwise a meaningless number);
- Conductivity (concentration or salt type);
- Modifications in components concentration [2]

Determination of zeta potential

Zeta potential can be quantified by electrophoresis mobility combined with the measurement of particles speed/rate.

The value of zeta potential provides an indication of colloidal system stability. The general value making the separation between the stable and unstable system is ranging between + 30mV and 30mV. The particles with potential values higher than +30 mV or lower than - 30 mV are considered normally established.

Determination of zeta potential also provides information concerning both the emulsions and other structures stability, and the evaluation of system purity etc [1, 4, 5].

Calculus formula for zeta potential

The zeta potential (ζ) was calculated using the Helmholtz-Smoluchwski equation (1):

$$\zeta = \frac{4\pi\eta}{\epsilon} \cdot U \cdot 300 \cdot 300 \cdot 1000 \quad (1)$$

ζ – zeta potential (mV);

η – viscosity of solution;

ϵ – dielectric constant;

$$U = \frac{v}{V/L} \text{ – electrophoretic mobility;}$$

v – speed of particle (cm/sec);

V – voltage (V);

L – the distance of electrode.[3]

The consolidation of functional properties can be explained by means of surface thermodynamic properties modification, in terms of surface energy and surface electric parameters, quantified by Zeta potential [6].

After the Zeta potential measurement (ζ), one of the following results can be obtained:

- $\zeta > 0$; fig 1
- $\zeta = 0$; fig 2
- $\zeta < 0$. fig 3

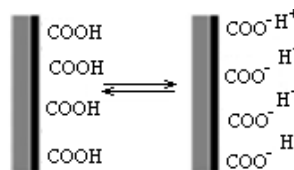


Fig. 1. Origin of surface charge by ionization of acidic groups to give a negatively charged surface

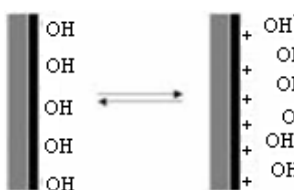


Fig. 2. Origin of surface charge by ionization of basic groups to give a positively charged surface

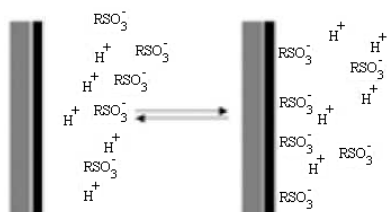


Fig. 3. Origin of surface charge by specific adsorption of an anionic surfactant.
R = hydrocarbon chain [4]

2. Methods of zeta potential measurement

The measurement of Zeta potential onto the PES fibres textile surface has been made on various concentrations of ZnO emulsion, having an approximate weight of 2g each. The sample has been immersed in electrolyte solution (KCl – kalium chloride), for two hours, in order to reach the equilibrium point, before the measuring itself.

The solution has been obtained from 20 mL KCl 10^{-1} M and 1800 mL water, in order to have a KCl 10^{-3} M electrolyte solution. Since zeta potential is an analysis strongly related/ correlated to pH, for comparison various pH-s have been chosen (4, 7, 9). For a lower pH than that of the initial solution, HCl has been used for gaining of equilibrium point; in order to get a higher pH, KOH has been used.

After immersion in electrolyte solution for two hours, the measurement of Zeta potential by means of Keithley device follows, the device being connected to a computer for data processing.

3. Results and discussions

In Fig. 4 plots representing comparable results achieved by Zeta potential measurement are shown.

For a good dispersion of ZnO emulsion, methanol has been used, thus having been obtained different samples with and without methanol, with different concentrations of ZnO emulsion.

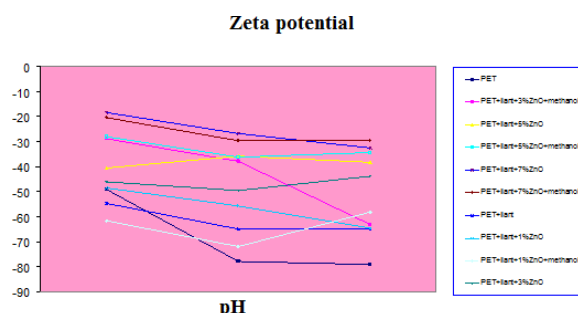


Fig 4. Zeta potential on various probes

4. Conclusion

According to the experimental data performed in the laboratory, it can be concluded that coating with different concentrations of zinc oxide emulsion, at various pH-s, applied onto PES fibres textile support is a stable treatment; there is one exception – both textile compounds made of PES fibres textile substrate with a ligand, 7% ZnO emulsion, at pH = 4 and 7, as well as PES fibres textile substrate with a ligand, 7% ZnO emulsion and methanol, at pH = 4 and 7, which are more stable.

Acknowledgments

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References

- [1]. http://www.icmpp.ro/grants/Aurica%20Chiriac/MIMTECA_ro.pdf;
- [2]. Loredana Elena Niță - „Analiza distribuției dimensionale și mărimii nano- și micro-particulelor prin tehnici de difracție și difuzie laser. Metode și aplicații“
- [3]. http://niton.com/en/products/zeecom_s.htm
- [4]. <http://www.malvern.com/>
- [5]. http://www.icechim-pd.ro/syst_heter/sisteme_heterogene_dls.html
- [6]. Christine Campagne, Anne Perwuelz and F. Leroux - “Zeta Potential and Surface Physico-chemical Properties of Atmospheric Air-plasma-treated Polyester Fabrics” - Textile Research Journal vol. 79 (15) 2009

TWO STEPS FOR AN ENVIRONMENTAL FRIENDLY PROPULSION ENGINE

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ABSTRACT

A logical way to preserve the natural resources and lowering the pollution level is the improving of the thermal engine efficiency in order to reduce the fuel consumption. Considering the weight factor of the spark ignition engine in automotive market, the authors propose a combined solution to improve the performances of this thermal engine.

First, in order to improving the combustion efficiency, we are trying to obtain a closer approach to the ideal constant volume combustion cycle, specific to the spark ignition engine, by developing a variable sequential ratio engine.

Secondarily, by modifying the architecture of the compression ring, the theoretical model developed allows the determination of a new transversal profile of the compression ring in order to obtain better lubrication conditions, to lower friction ware and increase the mechanical efficiency.

This theoretical and experimental study regards the both modification of these parameters in various situations, aiming at the optimization of this environmental friendly propulsion engine.

KEYWORDS: combustion and mechanical efficiencies, environmental friendly propulsion engine

1. Introduction

The spark ignition engines for automotive propulsion still represent about 65%-70% of the world market, and about 85%-90% of the American market. On the other side, although the alternative (also called hybrid) propulsion solutions are becoming more and more popular, they are not widely spread. The American market, one of the largest fuel consumers in the world, is dominated by medium-large sized spark ignition engines with high fuel consumption. These types of engine have been improved step by step. The fueling systems have been optimized; improved solutions for gases distribution have been used, the compression ratio has been

modified, etc. This is an old area of interest and specialists proposed several solutions. Currently, the most popular solution [1], introduced in small production numbers, is the one developed by SAAB.

On the other hand, in the purpose of improving the spark ignition engines efficiency, the actual researches taken into account the amelioration of constructive and technological solutions.

2. Proposed Engine Solutions

2.1. Improving the operating cycle basis efficiency

The study developed by the authors has the goal of improving the efficiency of the spark ignition engine, in the first step, by

improving the basis efficiency of its operating cycle. Moreover, one of the ways consists in obtaining a higher relative efficiency, i.e. a closer match to the ideal thermodynamic cycle (constant volume combustion). This goal can be achieved by assuring an almost constant volume during the combustion process. An engine functioning in this manner will lead to a higher compression ratio close to the TDC, during the burning process (when the lowest heat quantity is developed). The compression ratio varies only in certain moments of the cycle, remaining unchanged for the rest of the cycle.

The solution proposed by the authors achieves the variation of the compression ratio by moving a small piston in the opposite direction to the main piston, during a 90 degree angular interval after the TDC, thus achieving an almost constant volume for the main part of the burning process. In the Fig. 1 this solution are shown for a position near the TDC.

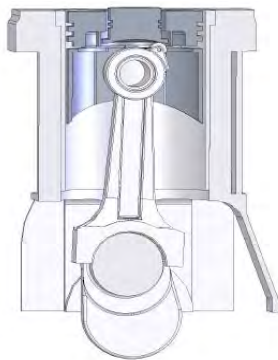


Fig.1. Position near the TDC

2.2. Increase of the mechanical efficiency

The second step of the researches consist in the increase of the mechanical efficiency by improving the lubrication condition for the compression ring; this is the consequences of increased values for the minimum film thickness and reduced friction forces inside the cylinder liner-piston ring couple.

The modified compression rings developed by the authors are based upon the rectangular ring (ISO 6621-1); the rings are modified as their peripheral surface has a bi-conical shape.

3. Analysis and Modeling

Aiming to obtain results that would allow a comparison between real conditions and the proposed solution (in terms of differences between efficiencies), we developed a detailed analysis of this engine solution. For improving the basis efficiency of operating cycle, two separate cases were taken into account: the first one presumes a constant bore of the small piston, while displacing it between 1 and 10 mm. The second case preserves the stroke of the same small piston, while its bore varies between 44 and 97 mm. An analysis of the obtained efficiencies led us to the optimization of the mechanical parameters.

3.1. The basis efficiency of operating cycle analysis

First case modeling

The momentary stroke of the main piston is:

$$s(\alpha) = r \cdot \left[1 - \cos(\alpha) + \frac{1}{\lambda} \left[1 - \left(1 - \lambda^2 \sin^2(\alpha) \right)^{\frac{1}{2}} \right] \right] \quad (1)$$

and the momentary volume generated by the main piston is:

$$Vp(\alpha) = \frac{V_s}{S} \cdot s(\alpha) \quad (2)$$

The momentary volume of the cylinder is:

$$Vp(\alpha) = V_c + Vp(\alpha) \quad (3)$$

The momentary volume occupied by the small piston is:

$$Vm(\alpha_m, Sm) = \frac{Vsm(Sm)}{Sm} \cdot s(\alpha_m, Sm) \quad (4)$$

The momentary volume of the cylinder, as affected by the movement of the small

piston during the angular interval of its stroke, becomes:

$$V2(\alpha m, Sm) = V(\alpha m) - Vm(\alpha m, Sm) \quad (5)$$

and is shown in Fig. 2, in comparison with the one of standard (unmodified) engine. Further on this engine solution will be named shortly **VSCR** (Variable Sequential Compression Ratio).

The momentary compression ratio, for the standard engine is given by the expression:

$$\varepsilon1(\alpha m) = 1 + \frac{Vs}{V(\alpha m)} \quad (6)$$

while, for the **VSCR** engine, we get:

$$\varepsilon2(\alpha m, Sm) = 1 + \frac{Vs}{V2(\alpha m, Sm)} \quad (7)$$

Overlapping the two compression ratios, for the small piston working domain, results in the curves shown in Fig. 3.

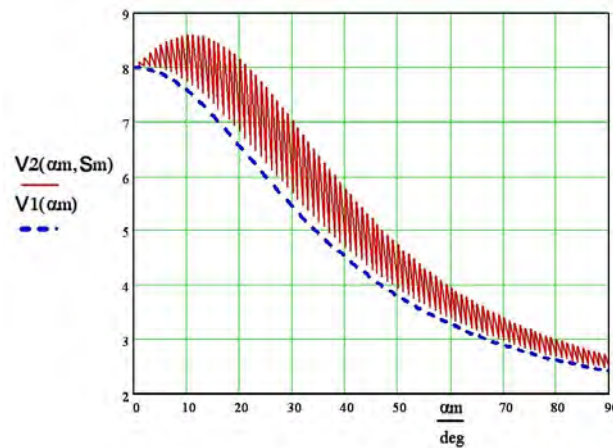


Fig. 2. Variation of the cylinder volume as affected by the movement of the small piston, for different strokes

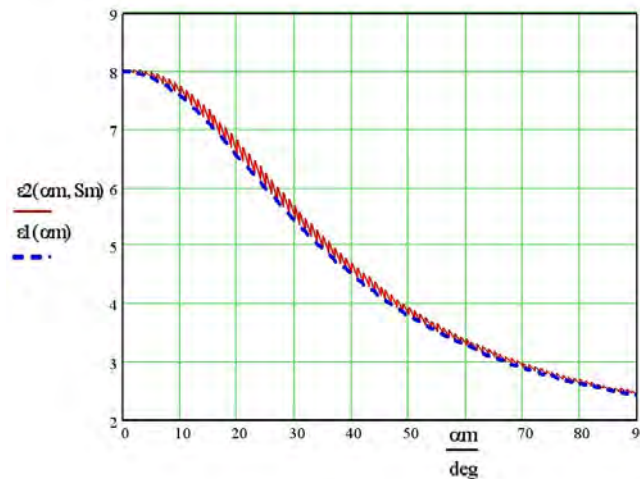


Fig. 3. Overlapped variation of the compression ratios

Considering an adiabatic coefficient $k=1.3$ the efficiencies for the two studied cases become:

$$\eta_{tv1}(\alpha m) = \left(1 - \frac{1}{\varepsilon1(\alpha m)^{k-1}} \right) \cdot 100 \quad (8)$$

For the working range of the small

piston we get the thermal efficiency gain of the **VSCR** solution as:

$$A\eta_{tv}(\alpha m, Sm) = |\eta_{tv2}(\alpha m, Sm) - \eta_{tv1}(\alpha m, Sm)|\% \quad (10)$$

The efficiency gain variation range for

different strokes or diameter of the small piston is shown in Fig. 4 and Fig. 5.

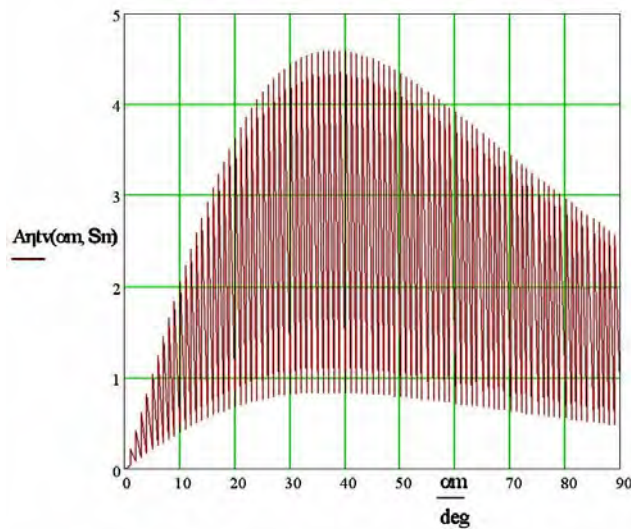


Fig. 4. Efficiency gain variation for different strokes of the small piston

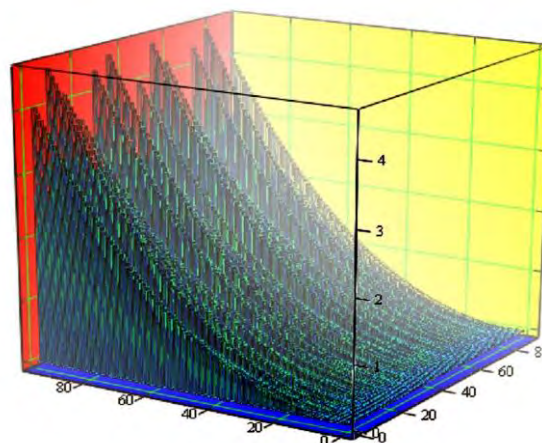


Fig. 5. Efficiency gain by modifying the diameter of the small piston

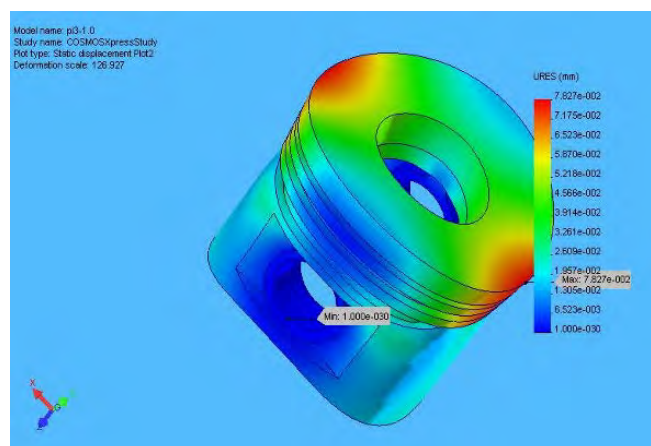


Fig. 6. Strain for the main piston of the VSCR engine obtained using FEM

Second case modeling

In this case the highest value for the small piston stroke (10 mm) is used, which leads to the most significant efficiency increase, while the diameter of the small piston is modified, starting with the lowest value, $D_m=44$ mm, and ending when the diameter of main piston is reached ($D_m=D=97$ mm). The previous formulae are modified accordingly, only the intermediate and final results being presented.

For the both cases, stresses and strains of the main piston of the **VSCR** engine were evaluated, using the **Finite Element Method (FEM)**; some results are shown in Fig. 6.

3.2. Compression rings profile optimization

When the peripheral surface of the piston ring is correctly aligned with the cylinder liner surface, the piston – piston rings-cylinder assembly acts as a labyrinth, insuring an efficient seals [2].

Starting from the p_0 pressure inside the combustion chamber, the pressure decreases to p_{s1} behind the first compression ring, to p_1 after the first ring, to p_{s2} and p_2 behind and after the second ring etc.

Due to the high value of the chamfer angles h_1 , only the surface with the length $h_r = h - 2h_1$ [m] is considered as the hydrodynamic active surface of the piston ring-cylinder liner couple.

Thus, for the downward piston stroke,

the length of the wedge shaped interstice, marked $h_{\text{eff}(d)}$, is:

$$h_{\text{eff}(d)} = (1 - X)(h - 2h_1) \text{ [m]} \quad (11)$$

and accordingly for the upward stroke we have $h_{\text{eff}(u)}$

$$h_{\text{eff}(u)} = X(h - 2h_1) \text{ [m]} \quad (12)$$

The specific relations for the hydrodynamic lubrication regime, correlated with the combustion chamber pressure, are used in order to establish the conditions for the oil intake and exhaust inside the piston ring-cylinder liner couple, thus leading to the best values for the angles of the conical surfaces that insure a preponderant hydrodynamic lubrication regime.

The oil flow through the cylinder liner-piston ring is calculated using the flow equation for the hydrodynamic reciprocating couples [3].

The equations are:

- for the downward stroke:

$$Q_{L(d)} = \pi \cdot D \cdot \left[\frac{h_1 h_2}{h_1 + h_2} v_p + \frac{1}{6} \frac{(h_1 h_2)^2 (p_1 - p_0)}{\eta (h_2^2 - h_1^2)} \right] \text{ [m}^3/\text{s]} \quad (13)$$

- for the upward stroke:

$$Q_{L(u)} = \pi \cdot D \cdot \left[\frac{h_1 h_2}{h_1 + h_2} v_p + \frac{1}{6} \frac{(h_1 h_2)^2 (p_0 - p_1)}{\eta (h_2^2 - h_1^2)} \right] \text{ [m}^3/\text{s]} \quad (14)$$

In order to evaluate the overall oil flow during one engine cycle we define the overall oil circulation Q_{Lt} [m³/s], calculated by graphical integration of the oil flow according to Fig. 7.

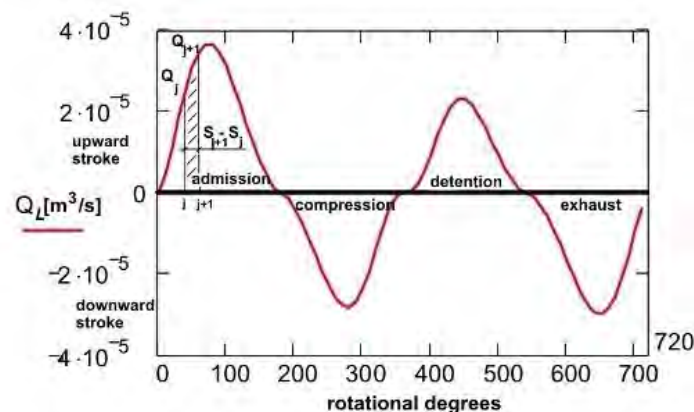


Fig. 7. The oil flow through the cylinder liner-piston ring and the overall oil circulation Q_{Lt} calculated by graphical integration

The relation for the overall oil circulation is:

$$Q_{Lt} = \sum_{j=0}^{71} \frac{Q_{Li+1} + Q_{Li}}{2S} |S_{i+1} - S_i| [\text{m}^3/\text{s}] \quad (15)$$

A positive value of the overall oil circulation means that the oil flow is directed towards the combustion chamber.

Starting from the shear forces in the reciprocating couple [4], for the hydrodynamic lubrication regime, we evaluate the friction forces inside the cylinder liner-piston ring couple using the equations:

- for the downward stroke:

$$F_{f(d)} = \frac{2 \cdot \pi \cdot D \cdot \eta \cdot v_p}{k_d} \cdot \left[3 \cdot \frac{h_2 - h_1}{h_1 + h_2} - 2 \cdot \ln \frac{h_2}{h_1} \right] + \dots$$

$$\dots + \pi \cdot D \cdot k_d \cdot \frac{h_1 \cdot h_2}{h_1 + h_2} \cdot (p_1 - p_0) [\text{N}] \quad (16)$$

- for the upward stroke:

$$F_{f(u)} = \frac{2 \cdot \pi \cdot D \cdot \eta \cdot v_p}{k_u} \cdot \left[3 \cdot \frac{h_2 - h_1}{h_1 + h_2} - 2 \cdot \ln \frac{h_2}{h_1} \right] + \dots$$

$$\dots + \pi \cdot D \cdot k_u \cdot \frac{h_1 \cdot h_2}{h_1 + h_2} \cdot (p_0 - p_1) [\text{N}] \quad (17)$$

Defining the piston ring mechanical work of the friction forces $L_{fr}[\text{J}]$ we may evaluate the mechanical losses, using a graphical integration method for the variation shown in Fig. 8.

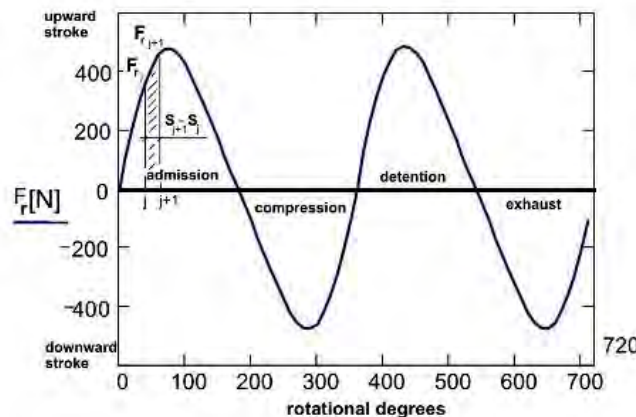


Fig. 8. The friction forces inside the cylinder liner-piston ring couple and piston ring mechanical work of the friction forces $L_{fr}[\text{J}]$ calculated by graphical integration

Using the general expression of the mechanical work, we get the relation:

$$L_{fr} = \sum_{j=0}^{71} \frac{|F_{ri+1} + F_{ri}|}{2} |S_{i+1} - S_i| [\text{J}]. \quad (18)$$

A high value of this mechanical work means high friction forces inside the couple and diminishes the engine's mechanical efficiency.

Computational procedure

The theoretical model we have developed allows the determination of the transversal profile of the first and the second compression ring in order to obtain a

different profile but similar lubrication conditions, to reduce oil consumption, to obtain a lower friction forces and to increase the mechanical efficiency of the piston ring – cylinder line coupling.

So, the slope repartition will be optimized in order to reduce oil flow towards the combustion chamber. Using the relation (13), (14) and (15) and giving values comprised between 0 and 1 for the slope repartition X , the calculus are made in order to obtain a zero value for the overall oil circulation Q_{Lt} . In that case, the oil flow towards the combustion chamber and the oil consumption is reduced to the minimum

values. The upper and bottom slope angle of the peripheral surface of the rings will be optimized in order to insure a preponderant hydrodynamic lubrication regime and diminish the friction forces and piston rings and cylinder liner wear. Calculus, using the relation (16), (17) and (18), are made starting at 0 value for the upper and bottom slope angle and is considered ended when we obtain a maximum percentage from entire engine cycle with the hydrodynamic

lubrication regime for the piston ring and the minimum value for the piston ring mechanical work of the friction forces L_{fr} [J].

In Fig. 9 we will expose the oil flow through the cylinder liner-piston ring and, in Fig. 10, the friction forces inside the cylinder liner-piston ring couple variation for the entire engine cycle for the both compression piston ring.

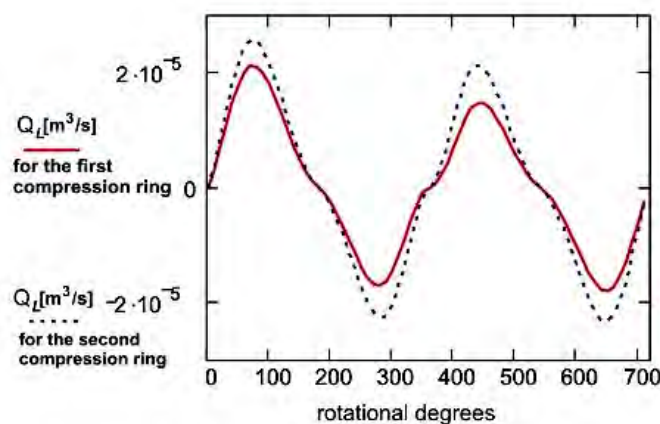


Fig. 9. The oil flow through the cylinder liner-piston ring for the first and the second modified compression ring of a four-stroke S.I. engine

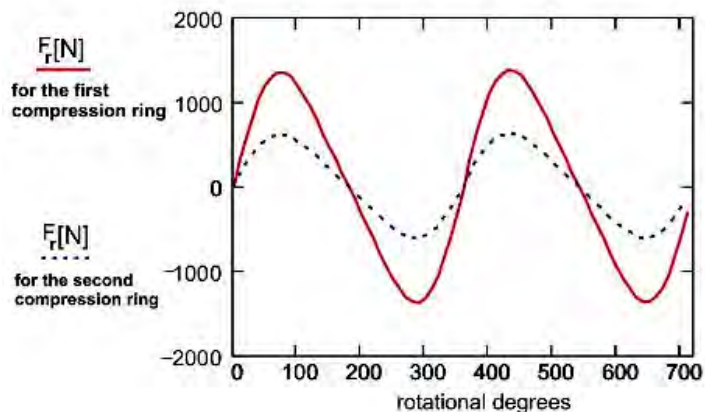


Fig. 10. The friction forces inside the cylinder liner-piston ring couple for the first and the second modified compression ring of a four-stroke S.I. engine

4. Conclusion

- For all the studied cases, the models have revealed a smoother drop in the thermal efficiency of the **VSCR** engine, during the combustion process.
- In the meantime, higher values of the thermal efficiency were recorded during the

main phase of the combustion process and towards its end.

- The maximum thermal efficiency increase (up to 4%) was obtained when the small piston's stroke is 10 mm and when its diameter equals the one of the engine's main piston (the "fake piston head" case).
- A study of the efficiency increase

shows that, in the first case, its maximum value is obtained at 35 degrees CA after the TDC, while for the second case, the maximum value is attained at 37-38 degrees CA after the TDC, thus showing the

advantage of this method in terms of a fuel consumption decrease.

- The lubrication conditions for the second compression ring are better to the first piston ring.

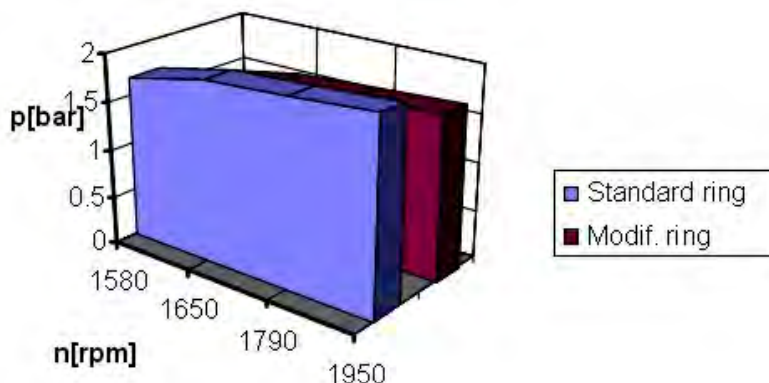


Fig. 11. Crankcase pressure variation at 85% partial load

- Several new notions were defined (*overall oil circulation and mechanical work of the piston ring friction forces*), in order to improve the profile of the compression rings of an internal combustion engine, to reduce oil consumption, insure a preponderant hydrodynamic lubrication regime and diminish piston rings and cylinder liner wear.

- The tests carried out with modified rings showed a decrease in gas pressure escaped in the crankcase, the situation exposed in Fig. 11, and lower consumption of lubrication oil.

- In conclusion, the modification of those parameters leads to an optimized engine solution for lowering the fuel

consumption and the pollution level, an environmental friendly propulsion engine

References

- [1]. **Gray Jr.:** *Piston in Piston Variable Compression Ratio Engine*, U S Patent, No. 6,752,105 B2, 2004
- [2]. **Heisler H:** *Advanced Engine Technology*, SAE International, 1995
- [3]. **Taylor C.M:** *Engine Tribology*, Tribology Series, 26, Elsevier Science Publisher B.V., Amsterdam, 1993
- [4]. **Zhu D., Cheng H.S.:** *An Analysis and Computational Procedure for EHL Film Thickness, Friction and Flash Temperature in Line and Point Contacts*, STLE Tribology Transactions, v32, n3, p364-370, Park Ridge, IL, USA, 1989

STUDY CONCERNING THE INORGANIC FUELS MIXTURES INFLUENCES IN ORDER TO REDUCE VEHICLES PROPULSION ENGINES EMISSIONS

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ABSTRACT

The objective of this study is the evaluation of the opportunity to use an inorganic oxygenated compound as ammonium nitrate or urea, to reduce fossil fuels pollution.

The research done by us, consider the ammonium nitrate water solution, mixed with diesel fuel, in various proportion, as fuel for a diesel engine. The results are very promising, the reduction of the consumption is near 20% and the reduction of particulate mater emission is near 75%, without particulate filter on the exhaust pipeline.

The paper intends to explain the ammonium nitrate influence in this process. It is to consider the role of the oxygen which is released in the process of ammonite decomposition in the engine cylinder and the role of the atomic nitrogen, which results in the same process, as fuel with a great energetic value. The energy released at the formation of a nitrogen molecule, N_2 , with his triple chemical bound $N \equiv N$, is almost the same as the carbon burning but without CO_2 as reaction product.

KEYWORDS: combustion and mechanical efficiencies, binary fuel, chemical supercharging

1. Introduction

The automotive propulsion, means today for 95% of the vehicles, internal combustion engine. Statistics show that half the CO_2 quantity released in the air by burning fissile fuels has his origin in the automotive engine [1]. The reduction of the CO_2 emission in this case can be done by reducing the fuel composition. The threshold of 140g CO_2 /km emission for vehicles is the equivalent of consumption less then 5 liter / 100 km.

The main way to reduce fuel consumption for the propulsion system of the automotive are:

a) Increasing the performance of the propulsion system, regarding the fuel efficiency of the engine and the reduction of fuel consumption trough the optimization of

the management of integrated propulsion system, engine – gearbox – transmission – wheel. Each component of this system is able to contribute to the reduction of mechanical losses which are covered by the mechanical work done by the engine.

b) Reduction of the carbon content of the engine fuel, the carbon been the one which, by burning, creates the carbon dioxide (CO_2). Theoretically speaking the reduction of the carbon content of fuel is done by using fuels with less carbon in the molecule, like the alcohols, which has a smaller calorific power compared with gasoline or diesel fuel, less 40% for the ethylic alcohol and less 57 % for the methyl alcohol $CH_2 OH$.

In the frame of the same theory, it will be very efficient to add to the oxygenated

fuel (alcohols) molecular hydrogen (H_2 gas).

This solution is apparently very elegant but inefficient because the poor solubility of the H_2 in liquid alcohols, less than 1% in normal condition, and a minim economically attractive concentration is around 5% in volume, additional H_2 .

c) The use of a new type of fuels with a very low concentration of molecular carbon and a big quantity of H_2 in the molecule. We do not discuss here the use of pure hydrogen as fuel for piston engine because of his poor heat efficient of the engine do to his poor resistance to compression and also do to the economic issue regarding the price of his fabrication, transportation and storage.

2. Actual situation of the fuel inventory used for the automotive propulsion

The conventional fuels for thermal engine, gasoline, diesel fuel, kerosene, diesel marine and the heavy fuel all originated from crud oil. It is a fact the slow but inevitable reduction of crud oil reserve and known deposits [1]. The advantage of this type of fuel is that they are easy to use, they have a big energetic density, 41500 kJ/kg, and they have dedicated thermal engine, Otto engine, Diesel engine, naval engine, or turbo engine. Also the transportation of crud, the production plants, and the distribution

network are already in place and very dens.

From this perspective the nearest unconventional fuel are the vegetable oil for Diesel engine and the alcohols for Otto engine. The advantage of this “fuels” is that they use “regenerative” primary sources like sugar cane, or potatoes. If the decision will be to use intensively this alternative, the problem is what to do, eat or drive a car?

It is another energy sources wide spread, easy to extract and burn – the methane gas. This one is used in big power plants and for domestic use. The use of CH_4 as fuel for piston engine, especially in road transportation is very punctual for very different reasons, like the gas explosion psychosis, to economic reasons. The use of CH_4 on a large scale for transportation means new engines adapted to this fuel and a new distribution network (tank station). Actually the CH_4 dedicated engine are used in co-generative or regenerative installation where the piston engine run an electric generator, and the heat of the exhaust gases and cooling system are used to heat water for domestic purposes.

An example of a hydrogenated compound without any carbon in the molecule is the ammonia, NH_3 . This chemical compound can be used as fuel for piston engine as show in Table 1.

Table 1

	Hydrogen	Diesel Fuel	Gasoline	Ammonia	Methanol
Calorific Power [kJ/kg]	117.040	42.636	43.054	18.684	21.318
Max. burning temperature [$^{\circ}C$]	2750	2400	2600	2500	2700
Boiling temperature [$^{\circ}C$]	-252	73	110-120	-33	65
Auto ignition temp. [$^{\circ}C$]	570-650	260	440	660	500
Vaporization heat [kJ/kg]	451	292	292	1358	1086
Minim ignition energy [mJ]	0.18	0.30	0.30	9	0.27
Flame speed [cm/s]	300	100	37-100	10-33	50
Octane number (Research)	130	55-70	91-100	10-35	50
Cethane number	-	35-60	0-5	7	3-10
Density at 16 $^{\circ}C$ [kg/mc]	0.0889	0.84	0.73	0.61	0.8
Air /Fuel Ratio (stoechiometric)	0.029	0.068	0.068	0.165	0.160

In the same category we can put the ammonium nitrate NH_4NO_3 (AN), the hydrate of hydrazine $N_2H_4H_2O$ - know as a racket fuel and urea $(NH_2)_2CO$. As you can

see all three compound are very rich in nitrogen and hydrogen.

Regarding the latest fuel category, with a powerful inorganic character, this one can be considered like **energetic accumulators**.

3. Researches regarding the use of energetic accumulators to the vehicles propulsion

The ammonia, the ammonia nitrate and urea are compounds with very special proprieties characterized by big synthesis energy. This synthesis energy is coming from classical energy sources like fissile fuels, atomic power or hydropower. The synthesis energy is accumulated in the chemical bounds of the compound. Notice that all the compound contain nitrogen and hydrogen. These two substances have the most energetic bond in the class of diatomic molecules. In Table 2 it is shown the value of these bonds. The ammonia and the ammonium nitrate can be synthesized from the H_2 obtained from water in hydrolysis or thermolyses process and the N_2 from the distillation of liquid air at $197^\circ C$.

These compounds accumulate energy in the synthesis process and later this energy is released in the burning chamber of the engine to be transformed in mechanical work, this is why these compounds can be considered as energetic accumulators, they transfer the primer energy in the burning chamber of the engine through the chemical bounds energy [2].

The use of these substances as fuels raises very delicate problems compared with classical fuels. The ammonia is a very common chemical compound in chemical industry in developed economies, but its use in the engine is only an experimental faze because of its toxicity and transportation problems. The NH_3 liquid faze is at 170 kPa at normal temperature [3].

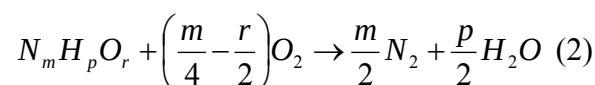
The ammonium nitrate is classified along with other compound, as cellulose nitrate, fulmicoton, trinitro glycerin, as

explosives. If the intention is to reduce the reaction speed from "explosive", supersonic speed, to normal burning process, meter per second, it must be done an addition of disperser or neutral compound to reduce the concentration of the active substance and as result the reaction speed. The kinetic equation of first degree chemical reaction shows that the speed is proportional with the concentration, C :

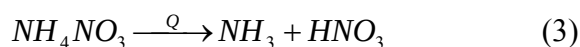
$$-\frac{dC_a}{dt} = k_1 C_a; v = k C^n \quad (1)$$

where k , k_1 is proportionality constant, v is reaction speed, C_a is the reactant concentration and C^n is the concentration of the final compound of the reaction.

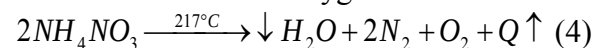
Thermodynamically, for chemical accumulator it's preferable to use compound of hydrogen, nitrogen and carbon dioxide. If we considered the general formula of this virtual fuel been $N_m H_p O_r$, the decomposition reaction will be:



In our specific case the ammonium nitrate decomposition reaction has two stages. If heated with a moderated speed, first the ammonium nitrate is melting. The melting point is at $169^\circ C$. After this temperature, if heated, the liquid AN decompose nonviolent after the reaction [3]:



At $217^\circ C$ or more, the AN decompose violent with heat and oxygen release:



Because of the release of a big quantity of molecular oxygen the decomposition process in a burning chamber of an engine is like a chemical supercharging of the engine.

The chemical supercharging with nitrogen compound it's known as "NO_x buster" for racecars. In this case the chemical supercharging is done with penta nitrogen oxide $N_2 O_5$ injected in the burning chamber or in admission.

In our facilities we mix pure ammonium nitrate water saturated solution, to the normal temperature, with diesel fuel in the following proportion [4]:

Diesel fuel-----55%
Pure ammonium nitrate -----32.2%
Water-----10.8%
Emulsifier -----2%

This binary fuel (BF) is injected in the burning chamber of a diesel engine. The physic-chemical process is the following:

- the fuel jet spread in the cylinder is heated, the water from the BF evaporate releasing the ammonium nitrate from the solution;
- the ammonium nitrate as very small particulate reach 217°C and decompose with heat release, oxygen and atomic nitrogen;
- the oxygen is oxidizing the diesel fuel

particulate from the interior of the fuel jet, producing the supercharging effect;

- the heat release increase the general thermal efficiency of the burning process;
- the atomic nitrogen N^* produces by the decomposition of the AN reacts with an other N^* following the chemical law that stipulate that, always the most probable reaction will be the one which consume or release the greater chemical energy.

Table 2 show the energy of this chemical bound, the triple bound of the nitrogen molecule N_2 been the greatest. The energy releases in this process of nitrogen atom "fusion", in a nitrogen molecule, increase the total amount of energy release in the oxidation process of binary fuel.

Table 3 show a summary of the effect of the burning of binary fuel, on engine performances.

Table 2

Biatomic Molecules	Bound energy	Double Covalent Bound	Bound energy
	[kJ/mol]		[kJ/mol]
H--H	435	C= =C	610
O= =O	497	C= =N	615
N≡ ≡N	944	C= =O	748
Covalent Bound	Bound energy [kj/mol]	N= = N	418
H--C	413	N= =O	606
H--N	388	Triple Covalent Bound	Bound energy [kj/mol]
H--O	463	C≡ ≡C	836
N--N	163	C≡ ≡N	890

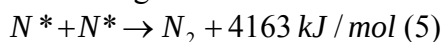
Table 3

	Engine speed	Power	Specific diesel fuel cons.	Specific binary fuel cons.	Smog emission	Diesel fuel economy
	(rev/min)	(kW)	(g/kWh)	(g/kWh)	%	(kg/h)
DIESEL FUEL	1200	43	272	-	75	-
	1800	48	307	-	87	-
	2300	65	299	-	95	-
BINARY FUEL	1200	43	239	435	14	1.30
	1800	48	217	397	26	4.25
	2300	65	207	370	38	6.10

Previously a thermodynamic calculus for the engine fueled with binary fuel has been done. Comparing this data whit the experimental data obtained on the research

facilities, the results show that the experimental data are superior to the calculus. A second round of calculus has been done considering also the thermal

energy released by the “fusion” reaction of the atomic nitrogen:



In this case, the calculus data coincides almost perfectly with the experimental data, under 3% difference. This experiment proves the energetic contribution of the atomic nitrogen bound energy release in the combustion period of the thermodynamic cycle of an engine fueled with binary fuel. The binary fuel considered as energetic accumulator and is the one which done a chemical supercharging of the engine.

4. Conclusion

The use of binary fuel to realize the chemical supercharging has salutary influences the engine performances. The fuel consumption of classic diesel fuel reduces with 25-30% without a reduction of engine power. The use of binary fuel drastically reduces the smog and the particulate emission, especially of high speed and load of the engine. This phenomenon is do to a better atomization of

the fuel jet in the burning chamber, a complete burning process do to the extra oxygen resulted from the decomposition of the ammonium nitrate.

The real power of the engine it increased with a factor between 15 – 25% and contributes to increase of the maximum speed of the engine possible do to a better burning process.

For the future the researches will continue in this mater, to obtain a better understanding of the energetic contribution of the nitrogen.

References

- [1]. **Sher E.** *Handbook of Air Pollution from Internal Combustion Engine*, Academic Press, 1998.
- [2]. **Feuillade. G.** *Le Stockage Chimique de L'Energie*, Revue Entropie, no.118.1984.
- [3]. **Garabedian C., s.a.** *The Theory of operation of a NH₃ Burning Internal Combustion Engine*, Army Science conf., West Point, 1966.
- [4]. **E.Golgotiu.** *Procedeu de obtinere a u nui combustibil binar pentru motoare cu ardere interna*, Brevet RO. 103534, 1991

PRODUCT LIFE CYCLE ASSESSMENT, A SELECTION TOOL IN ENVIRONMENT MANAGEMENT AND PERFORMANCES MEASUREMENT

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ABSTRACT

Risks will always be a challenge. Companies acknowledgement that it is advantageous and in the same time responsible that Product Life Cycle Assessment Methodology is well exploited, led to eco-management development. Modeling the life cycle will require optimizing the environmental performances, and environmental auditing tends to be almost unavoidable in the desire to obtain real performances.

KEYWORDS: product life cycle assessment, eco management, environmental auditing, strategic priorities

1. Introduction

„Green Movement” of Europe our years, requires as necessity and obligation a new methodology for products analyzing, called life cycle analysis [4]. More relevant than other analysis (for ex. the risk assessment), this method treats product’s environmental impact through his life from manufacture, use, distribution and elimination and therefore can be considered a „birth to death” analysis. The evaluation of energy and resources and also the overall effect on the environment and human health has become a priority in the manufacturing of a new product.

Products life cycle assessment, in the globalization context, is one of the major influences in higher sales. In ISO 14040-2002 standard, life cycle assessment represent: “consecutive and interlinked stages of one product- system, from raw materials acquisition or the natural resources generation to post-use.” Life cycle assessment became a new marketing concept, and therefore an extremely useful tool for decision makers. Encyclopedic

Dictionary of Environment (2005) explains: „Evaluation of a product life cycle, is to assess and analyze the environmental consequences of product action: evaluation following the product from raw materials extraction and processing, passing through all productions stages, transporting and distribution, use, reuse, maintenance and recycling, till the final disposal or reintegration into the environment.”

Environmental total impact of a product is a factor which is often simplified. Companies which take account of LCA (Life Cycle Assessment), consider the environment products performances, the evolution key. This led to eco management development which promotes product design in reducing environmental impact and also a new approach of linear programming and life cycle modeling. The main actors that define environmental strategies and lay the foundations strategic methodologies for life cycle assessment are: SETAC – Society of Environmental Toxicology and Chemistry and UNEP – United Nations Environmental Program. This analysis identifies all particular aspects of the product that

influence the environment, and also all the ways for reducing the product impact in all its phases:

- preproduction
- production
- distribution
- use
- elimination

The components of environmental products impact are technical: - LCA (life cycle assessment) and economic: - LCC (life cycle cost) and will be analyzed in terms of *ecological health* (alteration of habitat, global warming), of *human health* (toxicological impact, awareness, allergies) and of *resources depletion* (of energy, materials, water, ozone)

LCA Methodology provides:

1. Time limiting of product's life;
2. Limiting of possible pollution effect;
3. Identifying relevant impact types ;
4. Establishing of a functional and well defined unit, measurable and relevant to entry and exit data system.

The recent globalization has brought an increase in competitiveness. Evaluation methods are:

- *Environmental Themes Method*- Netherlands, Guinee 1993;
- *Eco-Scarcity Method* -Switzerland- based on relation between the critical polluted load in the environment and anthropogenic emissions;
- *Environmental Priority Strategy* - Sweden Volvo, according to human health, biodiversity, production, resources and aesthetic values.

COMPA SA Sibiu Company is strongly committed to pay particular attention protecting and conserving environment. In the following we study the case of a pinion gear for the steering mechanism that is processed in the above company. We chose this item because of the wide range of ecological and economic involvement in the environment.



Fig. 1. Pinion gear

Thus, we can consider the following:

- Vehicle and transmission mechanism design;
- Materials management, from producers to recycler;
- Recycling and management of resources related to eco management perspectives;
- Responsibility of development authorities on health and safety related to the future development policies.

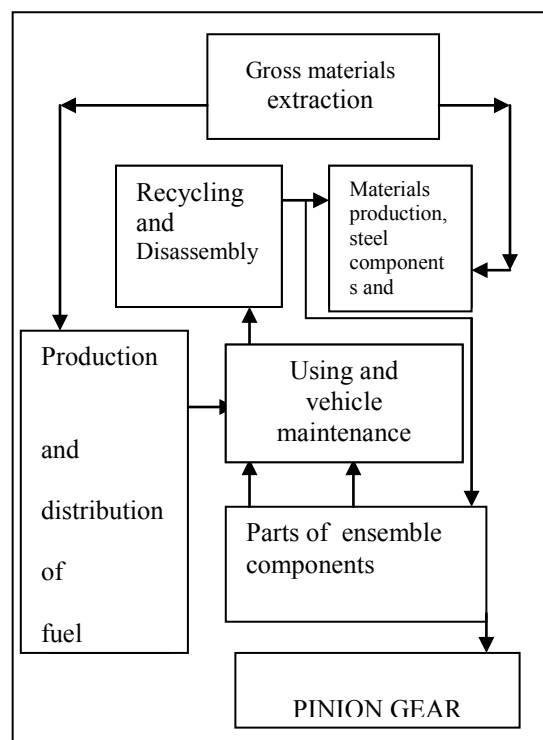


Fig. 2. Life cycle of pinion gear

Environmental tasks are related to the use of energy and materials, from the first performer that uses them till their environmental impact [3]. A key role in this context, are having the costs, which can be:

- Direct related to raw materials;
- Indirect related to waste management;
- Contingent and external.

2. Design perspectives

The design is reviewed at each stage by designers using CAD or SIGMA programs as help during the eco functional process viewing customer requirements as good as costs improvements[1]. It was observed that at higher purchase prices of cars there is the benefit of a cheaper maintenance during the car lifetime, so there are chances of obtaining a better price on resale. The initiatives of life cycle reduction will include also specifications based on fuel economy, and maintenance.

The use of hierarchical maps and accounting sheets will lead to higher the Baldrige index of performance score. Hierarchical process maps, promotes the understanding that combined sub-processes can be analyzed as a system. For building a hierarchical map, we need information's about the manufacturing processes of raw materials suppliers. Future action plans will be elaborated on running up evidence sheets through hierarchy, so as to clearly distinguish the purpose, delivery terms and the responsible persons. It can also be used the Malcom Baldrige quality assessment plan in seven stages, that include: leadership, planning, strategy, focusing on customer and market, information's and analysis, human resources development, management processes and results.

3. Managerial perspectives

Management decisions are taken in the context of internal (business objectives and resource limitations) and external (market niche and financial expectations) interests and combinations between factors that define each organization. These factors aren't necessary independent and they can

promote interfaces for business decisions on the environment, as for example:

- o Dioxide emissions will be related to fuel efficiency technologies.
- o Heavy metals wear, can be related to recycling and water decontamination.

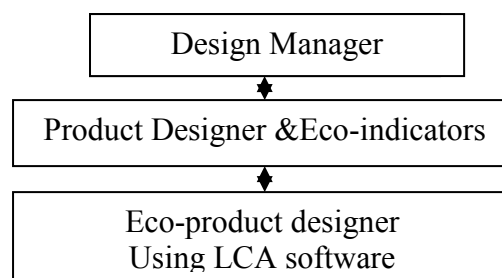


Fig. 3. LCA tools used in products design

3.1. Design process and perspective decisions

In the design decisions which must be improved, an essential role will be taking account of LCA, whose implementation is different at each organization level.

LCA is implicitly part of the design process and helps connecting different parts of manufacturing chain from an organization leading to the creation of a common designers language related to the environmental attributes. As noted, development policy is based only on parts of LCA process and not on the entire process. Changes aren't perceptible at the surface. Not even the most careful managers will notice the signals announcing them. It is necessary to anticipate the industry areas from which they are part of. Many managers are aware of external factors like changes, innovation of new products and new partners entry on the market. Emerging industries tend to have short horizons and to exist in a state of uncertainty. An industry that has reached maturity can have a completely different set of requirements.

Whether it is a private organization or a government agency, the products or services attributes create the impact on customers. Only if somebody on the market makes the

product bigger, faster, more mobile, it is not a sign of change. It is more significant when customers requirement are moving to change the price, easy of use, etc.[6].

This changes can affect the bases on which the business is build on.

Together with the change in customers desires and requirements, products and services suffer. Very close to customer changes are the changes in competition industry structure where as harder the competition is, stability become more rigorous.

The time as long a product stay in the market before being replaced, is the best measure of the change time.

The shortening of a product life cycle, signalize the beginning of major changes in industry[6].

Some of the basic fundamentals in running a company are:

- The concept of fixed pricing(must be covered even if the business structure is changing), and those variables(increase or decrease in the same time with the business volume);
- The ability to establish an economic scale in product development;
- Fixed costs managing;
- Retention of consulting staff ;
- Developing intelligent network to knew the customer's needs ;
- Publication of expertise;
- New government policies. ISO 14001 requirements say that to maintain and stabilize the programs and procedures for audit, we must note:
 1. If the environmental management system is according to the plan of environment arrangement ;
 2. If the organization has implemented and maintain EMS (Environmental Management System);
 3. If the environmental audit results were correctly announced.

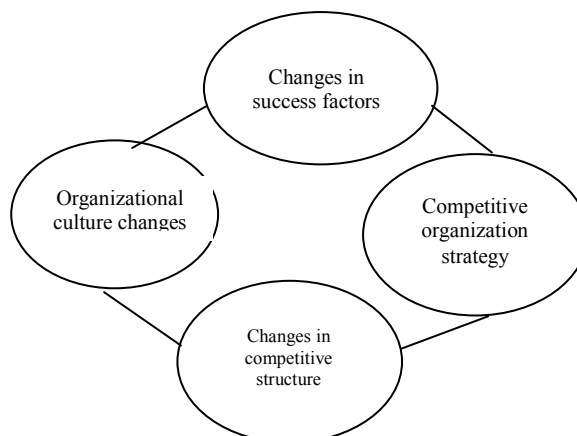


Fig. 4. *The change cycle in an organization*

4. Environmental audit

The audit programs are based on the importance of environmental activities. In ISO 14011 audit is defined as: „a systematic process for obtaining and objective assessment of organization's safety determinations, regarding the environmental activities, events and conditions about how the measurements were made to establish criteria and to communicate the results to customers.” Protocol, practices and procedures for an environment audit are similar to those of a quality. The best team will be formed between traditional auditors in quality and environmental specialists[6].

Schlumberger[11] extended audit procedures, based on quality management procedures and developed the environmental audit methodology integrating in it also quality, health, safety and environment.

The audit procedure has seven factors:

1. Specific activities and areas of interest including: organizational structure, roles, responsibilities, environmental performances
2. The schedule of audit activities, will be based on previous audits results;
3. Defining audit activities responsible for each area;
4. Defining choosing criteria for auditing staff;

5. Management audit protocol for data collecting and recording;
6. The reporting results procedure is including: conformities and EMS nonconformities, conclusions and recommendations;
7. Typing results procedures.

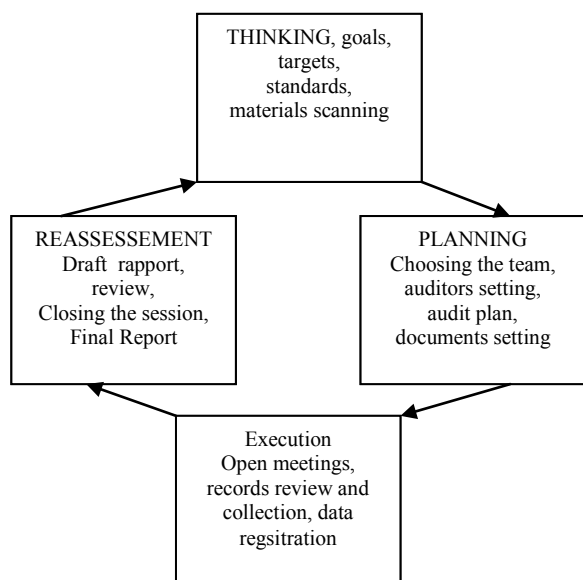


Fig. 5. Key steps in environmental audit management

4.1. System development life cycle

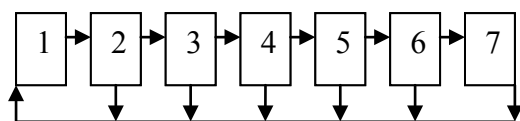


Fig. 6. Spiral way

1. Problems and opportunities identify-action;
2. Documentation on existing system;
3. Informational requirements determination;
4. Staff and design requirements;
5. Testing development;
6. System implementation;
7. System maintenance evaluation.

Development cycle is an iterative and evolutionary one, each steps having his own

importance in identifying new problems and opportunities. Making a minor shift in a system without taking account what was stated above, may cause unanticipated and unwanted effects that may seriously harm the whole system working. As we can see, all cycle steps are permitting the returning to the point of origin at any time. This feature makes lifecycle to present a spiral characteristic and not a sequential one.

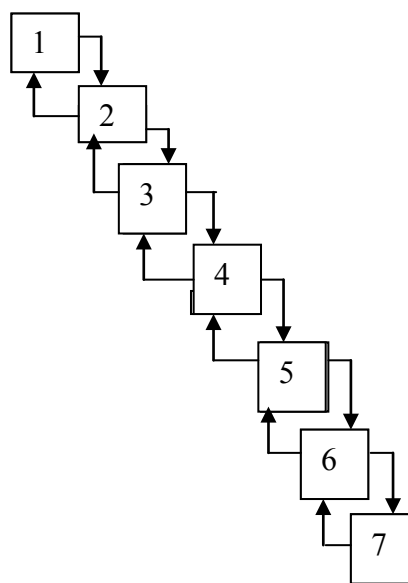


Fig. 7. Waterfall way

The traditional waterfall life cycle is inflexible to the business climate changing. It's natural down moving, involves that up returning to previous steps is unnatural, undesirable and to avoid.

The rapid business changes suggest a model that facilitates previous steps review to reduce future downstream changes.

5. Conclusions

The concept of sustainable development has become one of the highest importances in industry and therefore further developments will be alert to the maximum level of aggression on the environment.

In the case of processes which get our item ready to use, the energy and materials consumption become important design

components. Obviously will become the choice decision on how we produce them, which will also determine the ecological process impact.

Economic attributes as manufacturing time and costs, will be brought to optimum, which requires decisions on profit share.

5.1. Feasibility Study

Project profitability analysis provides an inside view of the problem, offering real solutions to the problem before allocating important resources. The aim is the:

○ Technique feasibility – can be solution applied with the existing technology?

○ Economic feasibility – regarding costs, is technology efficient?

○ Functional feasibility – if implemented, the solution will work within the organization?

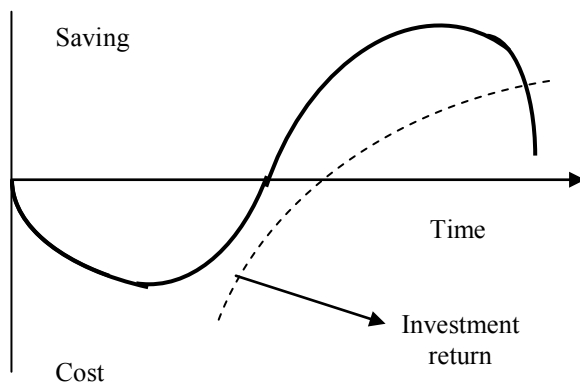


Fig. 8. Profitability analysis and investment return

The final feasibility study product will be a project proposal for the management with well-documented arguments and justifications in terms of costs (saving/effect generated by the new system exceed the cost of its development).

Here of course there is a talk about investment return and a rentability/profitability analysis.

This indicates the moment when initial investment is recovered by additional income. One essential is to understand things before the change and analysis, once completed should be understood too.

The research team advantage is exploring the whole interoperable system. Thus, business reengineering involves radical changes in business plan for substantially improving of organization performances[2]. These improvements are made by a competition between the old ways of doing things and the need to find new and better ones. This means that organization's and process restoring involves redrawing the organizational boundaries, rethinking of jobs, duties and skills through the three R:

- Redrawing
- Renewal of equipment
- Reorchestrating

References

- [1]. **Bondrea, I., Avrigeon, E.** *Optimizarea produselor si proceselor tehnologice de prelucrare*. Editura Universitatii 'Lucian Blaga' din Sibiu. Sibiu. 2001.
- [2]. **Bondrea, I.** *Reingineria prin CATIA V5 – Intre teorie si aplicatie*. Editura Universitatii Lucian Blaga, Sibiu 2010.
- [3]. **Le Roy Thompson, Jr.** *Mastering the Challenges of Change. Strategies for Each Stage in Your Organization's Life Cycle*. Amacon, New York 1994
- [4]. **Gilbert, M., Gould, R.,** *Achieving Environmental Standards*. BSI Financial Times Pitman Publishing, second edition, London 1998.
- [5]. **Brissaud, D., Tichkiewitch, S. and Zwolinski, P.** *Innovation in Life Cycle Engineering and Sustainable Development*. Springer. Dordrecht, Olanda. 2006.
- [6]. **Buse, Fl.,** *Manual de inginerie economica*. Editura Dacia, Cluj Napoca 2002.
- [7]. **Draghici, A., Draghici, G.** *Product and Product Life-Cycle Typology from the Marketing Perspective*. C2I International Conference on Integrated Engineering. Timisoara. 2005.
- [8]. **Lupulescu, N., B., Parv, A., L.** *Product Life-Cycle (PLC) Costs Management*. C2I International Conference on Integrated Engineering. Timisoara. 2005



- [9]. **Niemann, J., Westkamper, E.** *The Paradigm of Product Life Cycle Management – Continuous Planning, Operation and Evaluation of Manufacturing Systems*. C2I International Conference on Integrated Engineering. Timisoara. 2005
- [10]. http://www.ngo.ro/img_upload/b247143d65c7290473692bc6171e3654/ manual_final.pfd. *Manual*

de practice europene in managementul mediului. Consultat 1-9 sept. 2011

- [11]. **Schlumberger, E.**, *Auswirkungen des Steuersenkungsgesetzes auf die Unternehmensbewertung*, Finanz-Betrieb, München, 2000.

- [12]. **Voicu-Vedea, V., Drăgulescu, C-tin.**, *Îndrumător pentru cercetare și elaborarea lucrărilor științifice*. Editura Mira Design, Sibiu, 2000.

MICROWAVE SINTERING OF METAL-CERAMIC HYBRID COMPOSITES

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ABSTRACT

Electrical contact materials are used in a variety of applications such as electrical switches, circuit breakers, voltage regulators, switch gears and relays. Materials used as electrical contacts for these applications must have not only high electrical and thermal conductivity, enhanced antifriction and antiwear characteristics, but also high resistance to environmental reaction as well as high arc erosion to maintain the contact integrity. Mechanical alloying is a solid-state powder processing technique involving welding, fracturing and rewelding of powder particles in a high-energy ball mill. Mechanical alloying is a complex process and type of mill, milling time, type, size and size distribution of the grinding medium, ball-to-powder weight ratio, temperature of milling are some of the important process variables. In microwave sintering, heat is generated internally, due to microwave – material molecular interaction and the sample becomes the source of heat. The direct delivery of energy to the material through the molecular interaction determines the volumetric heating. This results in improved quality of the product with time and energy savings. This paper aims to be a comparative analysis between two metal matrix hybrid composites sintered using microwave heating.

KEYWORDS: microwave sintering, hybrid composites, mechanical alloying.

1. Introduction

Metal matrix composites are used for tribological applications due to their improved wear resistance and better properties. Among the available metal matrices, copper received more attention recently due to its inherent properties. Copper and its alloys are used widely where high electrical and thermal conductivity are necessitated along with corrosion and wear resistance [1]. Mechanical attrition of copper powders with ceramic particles has allowed the uniform introduction of small strengthening phases and also promotes a microstructural grain refinement [2]. As a way to improve the mechanical properties at low temperatures, the matrix must be strengthened with very low solubility particles, which have a low diffusivity in

copper by means of mechanical alloying equilibrium with the electrical properties obtained [3].

Hybrid composites show enhanced properties compared with single reinforced composites as it combines the advantages of its constituent reinforcements [4,5]. Copper hybrid metal matrix composites reinforced with ceramic and soft lubricant materials are suitable for an electrical sliding contact material [6,7]. Self lubricant reinforcment like graphite improves antifriction properties due to its lamellar structure, and TiC particles have higher hardness, higher melting point and abrasion resistance with reasonable electrical conductivity [8]. There are other available reinforcments like alumina and SiC that have improved the strength of the

composites, but they sacrificed the electrical conductivity of the material. Rajkuman and Aravindan [9] have studied the microwave sintering of copper-graphite composites with a proposed microwave heating model. The same authors have studied the tribological performance of microwave sintered copper-TiC-graphite composites. The conclusion was that these composites with the newer addition of TiC can serve as a more potential material.

2. Experimental procedures

2.1 Materials

Composites used were manufactured through the powder metallurgy route. For the first experiment, electrolytic copper powder with the average grain size of $12\mu\text{m}$ and graphite powder of $50\mu\text{m}$ were used. Copper powder was mixed with different volume fractions of graphite powder 5, 10, 15, 20, 25 and 30% in an electric agate pestle mortar with the speed of 20rpm for 2h for the uniform mixing. For the second

experiment electrolytic copper powder with the average grain size of $12\mu\text{m}$ was used as matrix material and TiC and graphite powders were used as reinforcing materials. Copper powder has a mean particle size of $50\mu\text{m}$ and TiC particles of $11\mu\text{m}$. Mixed powders were preheated at 150°C and uniaxially compacted in a hydraulic press at 630MPa to obtain disc shaped green specimens with a 14mm diameter and 10mm height.

2.2 Microwave sintering and characterisation

Sintering was carried out in a 3.2 kW microwave furnace with 2.45 G Hz multimode cavity. Hybrid sintering setup consisted of two envelopes, inner envelope was SiC susceptors which absorbs microwaves and dissipates the heat uniformly to the specimen. Outer envelope was alumina wool which allows microwaves to pass through and insulates the heat generated. The microwave sintering device used in these experiments is shown in fig. 1.

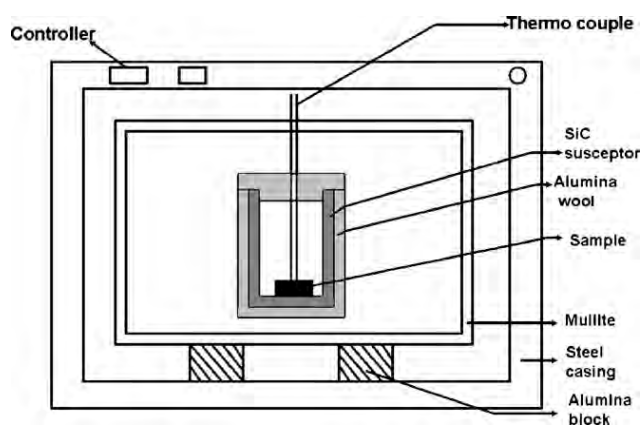


Fig. 1. Hybrid microwave sintering setup

The green samples were sintered at a sintering temperature of $700-900^\circ\text{C}$ and the isothermal holding time was about 10-30 min. The microwave interact with the green body sample and generates the heat internally due to the penetrating property of microwave in powder compacted samples.

Heating rate was set within $12^\circ\text{C}/\text{min}$. After the isothermal holding time, the samples were kept inside the furnace to cool.

Sintered density of the samples was determined using the Archimede principle. Porosity was calculated according to C1309-85 standard. The hardness of the composites

was evaluated using a Vicker's hardness tester with 10kg indenting load. The results are shown in tabel 1 for the copper-graphite

samples and in tabel 2 for the copper-TiC-graphite samples.

Table 1. Properties of the copper-graphite samples

No	Sample	Sintered density	Porosity	Hardness
		(g/cm ³)	(%)	(HV)
1	Cu-5%Gr	7.6	11.5	85
2	Cu-10%Gr	7.45	9	90
3	Cu-15%Gr	7.3	7.5	80
4	Cu-20%Gr	7.1	6.5	65
5	Cu-25%Gr	6.8	6	59
6	Cu-30%Gr	6.4	7	55

Table 2. Properties of copper-TiC-graphite samples

No	Hybride composites	Sintered density	Porosity	Hardness
		(g/cm ³)	(%)	(HV)
1	Unreinforced copper	8.71	2.4	65
2	Cu-TiC(5%)-Gr(5%)	7.80	5.71	88.5
3	Cu-TiC(10%)-Gr(5%)	7.72	5.73	94.5
4	Cu-TiC(15%)-Gr(5%)	7.53	6.98	98.8
5	Cu-TiC(5%)-Gr(10%)	7.39	7.2	67.2
6	Cu-TiC(10%)-Gr(10%)	7.29	7.7	79.2
7	Cu-TiC(15%)-Gr(10%)	7.11	8.3	89.2

3. Results and discussion

Hardness of hybrid composites is higher than the unreinforced copper. Addition of graphite to copper matrix leads to reduction in hardness due to the softer nature of graphite and it results in increased porosity. Addition of TiC in copper matrix increases the hardness of the composites not only due to its higher hardness but also due to the resulting finer microstructure. The wear rate of the composites is increased with the decrease in hardness and the hardness of the composites decreases as the amount of graphite volume fraction increases.

Due to the inherent self lubricity of smeared out graphite film, the composites with higher graphite exhibited lower rates. Increase in TiC volume fraction increases the wear resistance of hybrid composites. The improved wear resistance is attributed to the presence of hard TiC particles in the copper matrix. The microwave sintering of the metallic powders is successfully extended to metal matrix composites. Copper-graphite composites and copper-TiC-graphite composites were effectively sintered using microwave hybrid heating without any crack.

Acknowledgement

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References

- [1]. Rajkumar, K., Aravindan, S., *Microwave sintering of copper-graphite composites*, Journal of materials processing technology, 209, 2009, pg. 5601-5605;
- [2]. Lopez, M., Jimenez, J.A., Corredor, D., *Precipitation strengthened high strength-conductivity copper alloys containing ZrC ceramics*, Composites, pg. 272-279;
- [3]. Lopez, M., Corredor, D., Camurri, C., Vergara, V., Jimenez, J.A., *Performance and characterization of dispersion strengthened Cu-TiB₂ composite for electrical use*, Material Characterisation, pg.252-262;
- [4]. Ramesh, C.S., Noor Ahmed, R., Mujeebu, M.A., Abdullah, M.Z., *Development and performance analysis of novel cast copper-SiC-Gr hybrid composites*, Material Description, 2009, pg. 1957-1965;
- [5]. Riaz, A.A., Asokan, P., Aravindan, S., *EDM of hybrid Al-SiC_p-B₄C_p and Al-SiC_p-Glass*, Advanced Manufacturing Technology, 2009, pg.520-528;
- [6]. Zhan, Y., Zhang, G., *Friction and wear behavior of copper matrix composites reinforced with SiC and graphite particles*, Tribology International, 2004, pg.91-98;
- [7]. Uecker, A., *Lead free carbon brushes for automotive starters*, Wear, 2003, pg. 1286-1290;
- [8]. Kestursatya, M., Kim, J.K., Rohatgi P.K., *Wear performance of copper-graphite composite and a leaded copper alloy*, Materials Science and Engineering, 2003, pg. 150-158;
- [9]. Rajkumar, K., Aravindan, S., *Tribological performance of microwave sintered copper-TiC-graphite hybrid composites*, Tribology International, 2011, pg. 347-358.

REGENERATION OF USED ENGINE LUBRICATION OIL BY SOLVENT EXTRACTION. THE INFLUENCE OF THE SOLVENT TO OIL RATIO

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ABSTRACT

Huge amounts of used lubricating oils from automotive sources are disposed of as a harmful waste into the environment. For this reason, means to recover and reuse these wastes need to be found. Problems arising from acid treatment include environmental problems associated with the disposal of acid sludge and spent earth, low product yield (45–65%) and incomplete removal of metals.

The processes of re-refining of used lubricating oils depend greatly on the nature of the oil base stock and on the nature and amount of contaminants in the lubricant resulting from operations. The study was carried out on a sample of 15W40 type used oil collected from one automobile. The re-refining process of used oil consists of dehydration, solvent extraction, solvent stripping and vacuum distillation. This study aims to investigate a process of solvent extraction of an alcohol–ketone mixture as a pre-treatment step followed by vacuum distillation at 5 mmHg. The primary step was conducted before the solvent extraction that involves dehydration to remove the water and fuel contaminants from the used oil by vacuum distillation. The solvent extraction and vacuum distillation steps were used to remove higher molecular weight contaminants. The investigated solvent to oil ratios was 2, 3, 4, 5 and 6. The solvent composition is 25% 2-propanol, 50% 1-butanol and 25% butanone or methyl ethyl ketone (MEK). The percentage of oil recovery for the solvent to oil ratio of 6:1 is further improved, but for the ratio values higher than 6:1, operation was considered economically not feasible. Finally, the re-refined oil properties were compared with the commercial virgin lubricating oil properties.

KEYWORDS: regeneration used oil, solvent extraction, vacuum distillation, ash content

1. Introduction

Large and increasing amounts of lubricating oil are produced each year that, after use, are considered a hazardous waste because of their high content of pollutants (thermal degradation products from the base oil and additives and combustion products from the fuel and lubricant). Nevertheless, the used oil still contains a large proportion of valuable base oil that may be used to formulate new lubricants if undesirable pollutants are separated from the oil by an

appropriate recycling procedure [1]. Thus, not only environmental but also economical reasons justify the waste oil regeneration process.

The principal obstacle of regeneration process is that cleaning used motor oil by filtering or centrifuging does not ensure that the products of aging, contained in fine particles (0.5–5.0 μm), are not totally removed. Those contaminants can form sludge and promote the formation of varnish, carbon deposits, and other deposits on engine parts, thus shortening their service life.

Clarification of oil during cleaning to remove mechanical impurities and water is a necessary operation in the technology of reprocessing collected oil, although this does require special conditions and materials and improved equipment. [2].

Used Oil Recovery Processes

There are a large number of physical and chemical processes for reclamation, re-refining and reprocessing of used lubricating oil [3-5]. The earliest process known was the acid-clay treatment process. This treatment involves mixing the used oil with 93 to 98% sulfuric acid. The sulfuric acid acts as an extraction medium for the removal of asphaltenes, unsaturates, dirt, additives, color bodies and other impurities from the used oil. The acid treated oil will be then mixed with clay and filtered to remove mercaptans and other contaminants and to improve oil color. 30-42% of acid sludge can be combusted, whereas the remaining portion is called combustion residual.

Problems arising from acid treatment include environmental problems associated with the disposal of acid sludge and spent earth, low product yield (45–65%) and incomplete removal of metals, especially lead.

An alternate process using dehydration, distillation and hydro finishing consists in passing of feed oil through a flash furnace and a tower to separate water and gasoline fractions. The oil is then heated up to 360–370°C and passed to vacuum fractionators operating at 400°C and 34 m Bar. The column separates the oil into light and heavy oil products [6].

The main problems encountered in vacuum distillation processes are plugging of the lines, fractionators and furnace tubes due to formation of a resinous material that fouls the equipment. All modern technologies have included a physical or chemical pre-treatment step in order to avoid or eliminate these problems.

Some authors [3,7] describe a method of treating the dehydrated used oil with a mixture of one part 2-propanol, two parts of 1-butanol and one part of MEK. The solvent to oil ratio was 3 to 1 by volume. By this treatment the alcohol–ketone mixture will reduce coking and fouling problems during distillation.

2. Experimental results

The experimental procedure of solvent extraction process is presented schematically in Fig.1.

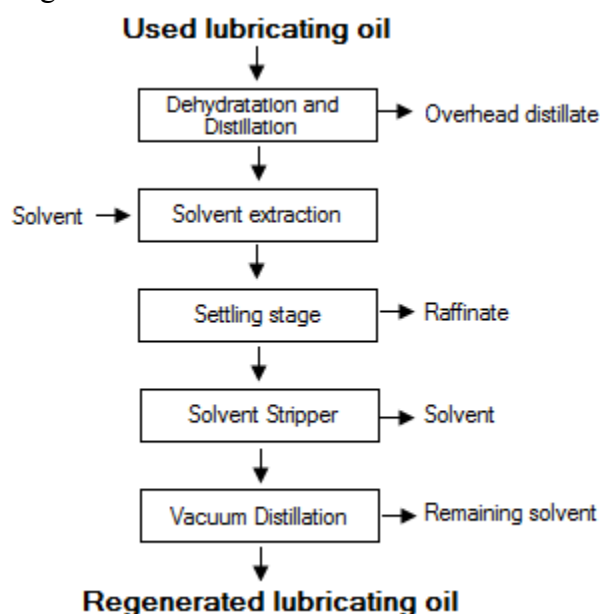


Fig.1. Detail of the solvent extraction process

2.1. Dehydration

The dehydration of used lubricating oil was performed in a simple batch vacuum distillation (Fig. 2) to eliminate water and light hydrocarbons (gasoline). In this process used lubricating oil is firstly filtrated to remove debris and other solid particles.

Water and gasoline fractions were separated under vacuum at 5 m mHg and 210°C (atmospheric equivalent temperature). Distillation was carried out until no further distillate was produced.

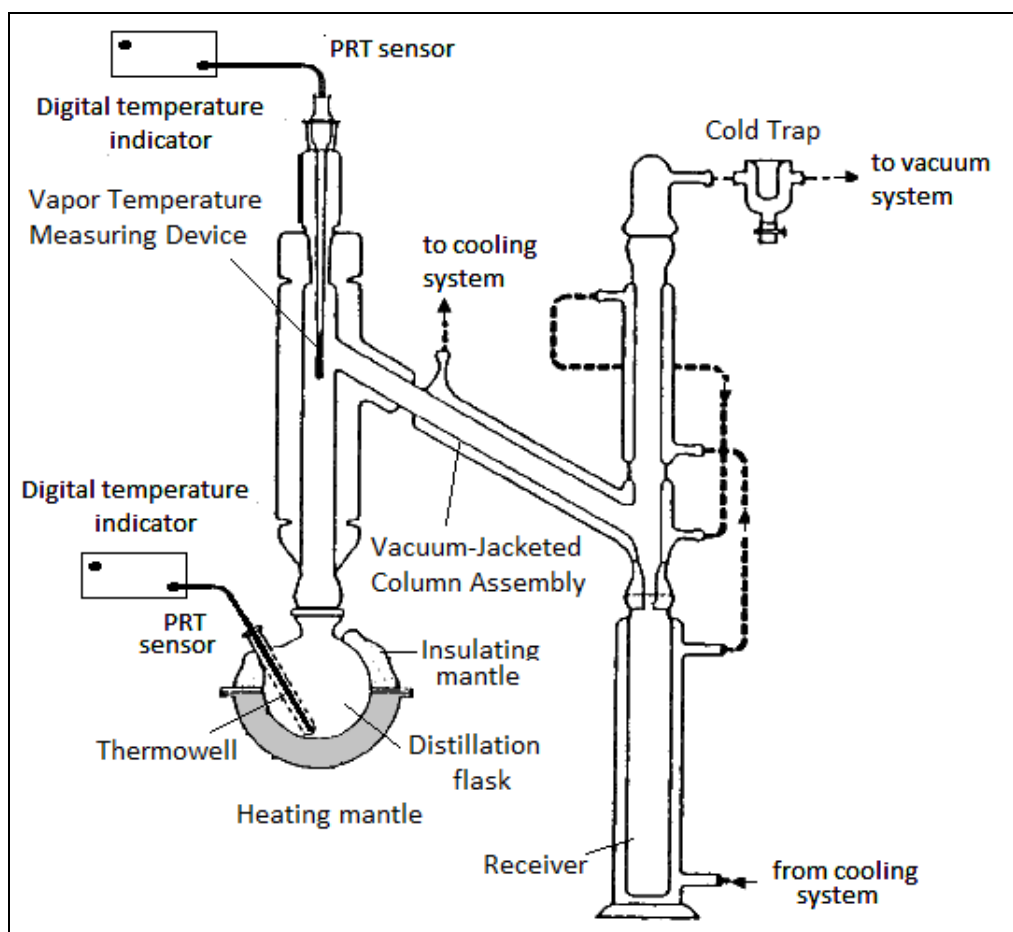


Fig.2. Vacuum distillation apparatus

The dehydrated used oil was collected and then used for the next step of solvent extraction.

2.2. Solvent Extraction

The dehydrated used oil was prepared in amount of 100 ml for each experiment.

The solvent composition was fixed to one part 2-propanol, two parts 1-butanol and one part MEK (25% 2-propanol, 50% 1-butanol and 25% MEK) as reported by some authors [7]. The main solvent properties are presented in Table.1.

Table 1. The main solvent properties

Test	2-propanol	1-butanol	MEK
Formula	C_3H_7OH	C_4H_9OH	C_4H_8O
Molecular weight, g/mol	60.1	74.12	72.11
Density, g/cm ³ , at 20°C	0.786	0.81	0.8050
Viscosity, cP at 20°C	2.46	3	0.43
Refractive index, n_d^{20}	1.3776	1.399	1.3788
Boiling point, °C	82	118	80
Pour point, °C	-89	-90	-86
Solubility in water g/l	miscible	63.2	275

According to Table 1 there are three boiling point temperature of two of the solvents in the oil with large differences in solvents, i.e., 2-propanol (82 °C) and MEK

(80 °C), compared with the third solvent 1-butanol (118 °C). Thus, all atmospheric distillation experiments failed to recover all the solvent amounts at temperature below 250 °C, which is the degradation temperature of the oil, while 2-propanol and MEK were successfully recovered at 200 °C.

The investigated solvent to oil ratios were (2, 3, 4, 5 and 6). Solvent to oil ratio less than 2 produced viscous mixture during separation. For a solvent to oil ratio higher than 6 to 1, operation is considered economically not feasible. According to these considerations the solvent amounts added were (200, 300, 400, 500 and 600 ml).

Adequate mixing of the solvent-oil mixture was obtained by stirring for 30 minutes at 2.5 rot/s. The mixture was allowed to settle for 24 hours in order to separate the extract phase (solvents and base oil components dissolved) from the raffinate phase (contaminants or sludge). Separation of the two phases was carried out in 1 liter separating funnels. The extract phase was red to brown in color and of low viscosity, while the raffinate phase was black and semisolid.

This procedure was repeated in all experiments for every solvent to oil ratio. The extract phase was subjected to simple batch atmospheric distillation to recover the solvent from the oil by heating up to 200°C.

2.3. Vacuum distillation

The vacuum distillation operation is done to recover the remaining 1-butanol from the amount of used oil after the solvent extraction process.

The vacuum distillation experiments were carried out according to ASTM D 1160 - 03 by the vacuum distillation apparatus described in Fig.2. The operation conditions of the vacuum distillation process of the treated oil were at 5 mm Hg and 190°C to minimize cracking and to maximize yield.

After each experiment, the vacuum distillation apparatus was washed with *n*-

hexane solvent in order to remove any contaminants that accumulated in the column, condenser and vacuum lines. The *n*-hexane washed the contaminants and accumulated them at the bottom of the still pot where they can be removed. After washing, all connections and joints were re-lubricated, and prepared for the next experiment.

Vacuum distillation apparatus

The vacuum distillation apparatus, shown schematically in Fig. 2, consists in part of the components described below:

- *Distillation Flask*, of 500 ml capacity, made of borosilicate glass and having a heating mantle with insulating top.
- *Vacuum-Jacketed Column Assembly*, of borosilicate glass, consisting of a distilling head and an associated condenser section. The head shall be enclosed in a completely silvered glass vacuum jacket with a permanent vacuum of less than 10^{-7} mm Hg. A vertical glass slide window along the column is available to observe the liquid and vapor behavior in the column. The attached condenser section shall be enclosed in water jackets as illustrated in Fig. 2.
- *Vapor Temperature Measuring Device* and associated signal conditioning and processing instruments for the measurement of the vapor temperature. The system must produce readings with an accuracy of $\pm 0.5^{\circ}\text{C}$ over the range 0 to 400°C. The location of the vapor temperature sensor is extremely critical. The vapor temperature measuring device shall be centered in the upper portion of the distillation column with the top of the sensing tip 3 ± 1 mm below the spillover point. The vapor temperature measuring device shall be mounted through a compression ring type seal mounted on the top of the glass temperature sensor/vacuum adapter or fused into a ground taper joint matched to the distillation column. The boiler temperature measuring device may be either a thermocouple or PRT.

- Receiver of borosilicate glass
- Vacuum Gage, capable of measuring absolute pressures with an accuracy of 0.01 kPa in the range below 1 kPa absolute and with an accuracy of 1 % above this pressure.
- Cold trap mounted between the top of the condenser and the vacuum source to recover the light boiling components in the distillate that are not condensed in the condenser section.

3. Results and discussions

Used lubricating oil was analyzed to investigate density, cinematic viscosity, flash point and ash content.

The analysis and tests used for analyzing the oil samples to evaluate their properties were done according to the standard methods as shown in Table 2.

Table 2. Used lubricating oil properties

Test	Method	Apparatus	Value
Density, (g/cm ³) at 20°C	ASTM D 7042	Anton Paar SVM 3000	0.896
Viscosity, (cSt) at 20°C	ASTM D 7042	Anton Paar SVM 3000	89
Ash content % wt.	ASTM D 482-03	-	2.39
Flash point, °C	ISO 2592	Marcusson open cup	184

Flash point of the used oil showed evidence of gasoline dilution, which has to be removed by distillation during the dehydration process.

The best dehydration results are obtained at lower vacuum pressure and even though there is a wide range in boiling point between water, gasoline and the base oil cut. Also lower vacuum pressure is preferred to ensure that the temperature will not rise above 250 °C, which is the oil degradation temperature. The final dehydration temperature depends on the amount of water and gasoline fractions in the used oil. The concentration of light hydrocarbons after this treatment was expected to be negligible. Both types of compounds are undesirable for

the formulation of new lubricants. Elimination of water was also necessary because it may modify the solubility parameter of base oil components in solvent.

The amounts of water and gasoline separated in all dehydration experiments were small due to low fuel dilution.

The results for mass balance for the optimum solvent to oil ratio experiments are tabulated in Table 3 while the tests percent of oil recovery and of ash content are presented in Table 4. The properties of produced solvent treated oil, i.e., oil recovery, solvent recovery and ash reduction in relation to solvent to oil ratio are shown in Fig. 3.

Table 3. Measurements of mass balance for optimum solvent to oil ratio experiments

Solvent to oil ratio	Oil feed	Solvent	Extract	Raffinate	Extract		
					Oil	Solvent	Loss
				(ml)			
2:1	100	200	265.4	34.6	78.3	185.2	2
3:1	100	300	373.9	26.1	86.4	285.7	1.8
4:1	100	400	478.8	21.2	92.3	384.9	1.6
5:1	100	500	587.8	12.2	95.5	490.8	1.5
6:1	100	600	690.7	9.3	96.1	593	1.6

Table 4. Test analysis of the optimum solvents to oil ratio experiments

Solvent to oil ratio	2:1	3:1	4:1	5:1	6:1
Oil recovery (vol %)	78.3	86.4	92.3	95.5	96.1
Ash content (wt%)	1.91	1.45	1.23	1.42	1.87

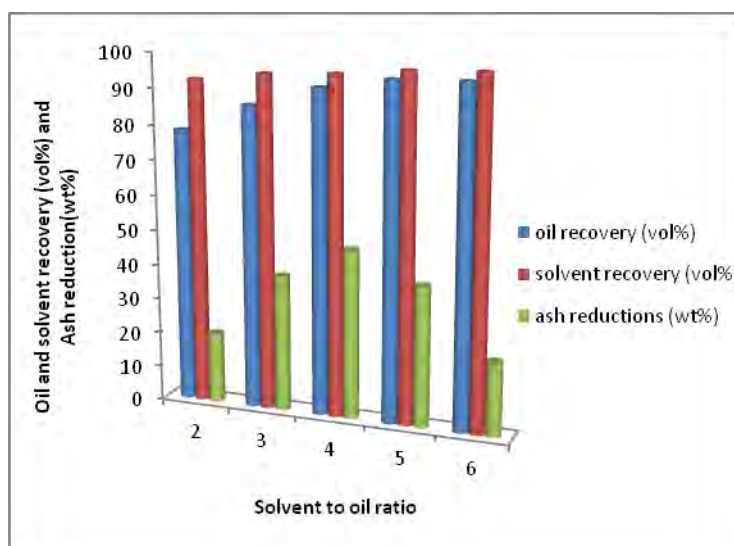


Fig. 3. The percentage of oil recovery, solvent recovery and ash reduction vs. solvent to oil ratio

The results of the investigation, Table 4 and Fig. 3 indicate that the maximum ash reduction is achieved for solvent to oil ratio of 4:1. The oil recovery and ash reduction for the some ratio are better than that obtained for solvent to oil ratio of 3:1 and 2:1. This indicates that by increasing the solvent amount, the solvency power is improved. The percentage of oil recovery for the solvent to oil ratio of 6:1 is further improved, but this solvent to oil ratio produces an ash reduction lower than that obtained for the solvent to oil ratio of 4:1 and 5:1 as shown in

Fig. 3.

Ratios above 3:1 were not considered economically feasible by industry, but considering that the solvent can be recovered and reused, the ratio of 4:1 was considered to be the better solvent to oil ratio for treatment of used lubricating oil.

A comparison between virgin oil and solvent treated oil (at solvent to oil ratio of 4:1) is presented in Table 5 which shows that the solvent treated oil is more pure than virgin oil as indicated by the lower ash content and the same density value.

Table 5. Comparison between virgin oil and solvent treated oil properties

Test	Method	Virgin oil	Solvent treated oil
Density, (g/cm ³) at 20°C	ASTM D 7042	0.890	0.890
Viscosity, (cSt) at 20°C	ASTM D 7042	117.5	98.4
Ash content % wt.	ASTM D 482-03	1.3	1.23
Flash point, °C	ISO 2592	225	212

The solvent extraction process can be followed by clay treatment or hydrotreatment to improve color and odor of regenerated oil.

4. Conclusion

Four process stages were studied, namely: dehydration, solvent extraction, solvent stripping, and vacuum distillation. The study was carried out on a sample of 15W40 type used oil collected from one automobile.

All gasoline and water fractions were separated using vacuum distillation at 5 mm Hg and 210 °C for the dehydration process.

Solvent to oil ratio of 4 to 1 with solvent composition of 25% 2-propanol, 50% 1-butanol and 25% MEK were found to be the optimum composition for solvent extraction. Solvent stripping was conducted by two stages: atmospheric distillation to recover 2-propanol and MEK solvents and vacuum distillation at 5 mm Hg to remove the remaining 1-butanol.

Extraction reduces the contaminants (inorganic materials) to low level, i.e. 49% ash reduction, such that no further operational problems were encountered on vacuum distillation.

The best oil recovery and ash reduction by extraction were obtained using optimum evaluated solvent to oil ratio of 4 to 1 with solvent composition of 25% 2-propanol, 50% 1-butanol and 25% MEK were 49% ash reduction and 92% oil recovery. That means that solvent to oil ratio larger than 4:1 will lead to dissolution of some contaminants in the solvent phase especially the ash forming material, which was considered to be

undesirable.

As a result of the above mentioned facts, the solvent to oil ratio of 4:1 was considered to be the better solvent to oil ratio used for treatment of used lubricating oil

Finally, it should be pointed out that these results can be very useful for the design of the continuous extraction process to recycle waste oil at industrial scale.

References

- [1]. Rincon J., Canizares P., Garcia M.T., *Regeneration of used lubricant oil by ethane extraction*, Journal of Supercritical Fluids, v39, p315-322, 2007
- [2]. Ostrikov V.V., Prokhorenkov V. D., Nagornov S. A., *Industrial Ecology. Waste-Free Technology For Processing Used Lubricating Oil*, Chemical and Petroleum Engineering, v.39,n 5–6, p292-297, 2003
- [3]. Whisman M.L., Reynolds J.W., Goetzinger J.E. and Cotton F.O., *Re-refining makes quality oils*, Hydrocarbon Processing October, p141–145, 1978
- [4]. Ostrikov V.V., Prokhorenkov V.D., *Waste-free technology for processing used lubricating oil*, Chemical and Petroleum Engineering v39, p5–6, 2003
- [5]. Bhaskar T., Azhar Uddin M., Muto A., Sakata Y., Omura Y., Kimura K., Kawakami Y. *Recycling of waste lubricant oil into chemical feedstock or fuel oil over supported iron oxide catalysts*, Fuel v83, p9–15, 2004
- [6]. Snow R.J., Delaney S.F., *Vacuum distillation of used lubricating oil*, Chemeca ,v77, p14–16, 1977
- [7]. Awaja F., Pavel D., *Design Aspects Of Used Lubricating Oil Re-Refining*, Elsevier Science Publisher B.V., Amsterdam, 2006

SYNTHESIS AND CHARACTERISATION OF Ag/SnO₂/CLAY NANOCOMPOSITES WITH POTENTIAL APPLICATION AS PHOTOCATALYSTS

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ABSTRACT

This work reported a novel synthesis and characterization of Ag/SnO₂/clay nanocomposites. The obtained materials were characterized using techniques such as X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy, particles size distribution, BET analyses and Scanning Electron Microscopy. The Ag/SnO₂/clay nanocomposites have been used as efficient and environmentally benign photocatalysts. The protocols developed using this kind of material is advantageous in terms of simple experimentation, reusable catalyst, excellent yields of the products, short reaction time and preclusion of toxic solvents. The synthesized nanosized Ag/SnO₂/clay nanocomposites have been used as photocatalysts for degradation and discoloration of synthetic wastewater containing Eosin Y dye, xanthene fluorescent dye, under solar radiation.

KEYWORDS: clay, nanocomposite, dye, wastewater

1. Introduction

A great variety of methods have been used in recent years to synthesize nano powders of oxide materials and especially semiconducting powders like TiO₂, MgO, Fe₂O₃, SnO₂ and ZnO. Nano-sized tin oxide (SnO₂) is an interesting semiconducting material with a wide band gap ($E_g = 3.6$ eV, at 25°C) [1]. Nanoparticles of tin oxide have found a wide range of applications in gas sensors, lithium batteries, optoelectronic devices, transparent electrodes and photocatalysts [2-8]. It is general known that by changing the method of preparation it is possible to change the structural, morphological and textural properties of metal oxide particles. A very promising candidate for such an application is represented by the system silver tin oxide [9]. The noble metals deposited on the surface of nano oxide powders can improve its photo-catalytic properties.

There has been very limited study in this direction. The researches about the preparation of silver nanoparticles have been an extraordinary active region due to its potential applications in nanoelectronics, magnetics, biosensor, data storage, catalysis, surface enhanced Raman scattering and excellent antibacterial activity [10-15]. Most of these applications require nanoparticles with a small particle size and a narrow size distribution [16, 17].

To the best of our knowledge, there has been no publication on the synthesis of the Ag/SnO₂/clay nanocomposites. The present method for silver nanoparticles preparation is not only the formation rate of silver nanoparticles much quicker, particle size distribution more uniform, but also offers numerous benefits of eco-friendliness and compatibility for pharmaceutical and biomedical applications due to all the materials used in the experiments are environmentally benign and renewable [18].

Metals or semiconductor nanoparticles synthesized by various techniques have found potential application in many fields such as catalysis, sensors, etc. [19 -22]. In most of the applications, nanoparticles are used as building blocks toward functional nanostructures. The coinage metal nanoparticles such as silver, gold, and copper are mostly exploited for such purposes as they have surface plasmon resonance absorption in the UV visible region[23]. The surface plasmon band arises from the coherent existence of free electrons in the conduction band due to the small particles size effect, which is dependent on the particle sizes, chemical surrounding, adsorbed species on the surface, and dielectric constant. [23-26] The unique feature of the coinage metal nanoparticles is that a change in the absorbance or wavelength provides a measure of the particle size, shape, and interparticle properties. For small particles (2 nm), the surface plasmon band is strongly damped due to low electron density in the conduction band. However, as particle size increases, the intensity of the surface plasmon band increases. It has been suggested that, although both absorbance and scattering contribute to the optical property, the contribution of the latter is relatively insignificant as compared to that of the former for very small nanoparticles (≤ 15 nm). [19-33]

2. Experimental Methods

2.1. The starting material

As raw material, we used clay of montmorillonite bentonite type, provided by firma Riedel-de Haen Chemicals Company. Given the compositional complexity of clay materials, we considered useful to perform an ion exchange process, as a first step, for their cleansing, their transition to sodium cation form, respectively. The clay exchange in Na^+ form has been performed by treating

with a 1M NaCl solution, having a solid/liquid ratio of 1:10 [34, 35].

2.2. Preparation of Ag/SnO₂/clay nanocomposites

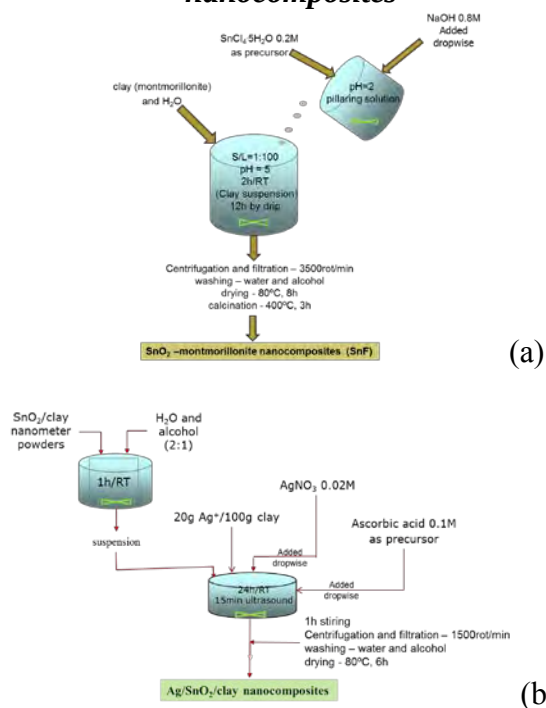


Fig. 1. Schematic illustration for preparation of nanosized Ag/SnO₂/clay compounds (AgSnF)

Bentonite montmorillonitic-clay, provided by firma Riedel-de Haen Chemicals Company, was used as starting material. The nanosized SnO₂ particles were prepared by pillaring method (dispersing the tin oxide particles). Preparation of Ag/SnO₂/clay nanocomposites takes place in two steps preparation of SnO₂/clay nanometer powders (Fig. 1, a) and obtaining of Ag/SnO₂/clay nanocomposites is shown in Fig. 1, b.

2.3. Studies of photocatalysis

Investigations of photocatalytic oxidation have been performed, having as objective degradation and discoloration of synthetic solution containing Eosin Y dye, by varying the concentration of catalyst (0,5-2g/l). Photocatalysis occurs in two stages: first step consists in adsorption in the dark

conditions, for 30 minutes and the second step relies to photometric measurement the dye concentration, by exposure to UV light running at wavelength of 254 nm at equal time intervals based on the calibration curve.

The study was conducted in an initial concentration of pollutant (Eosin Y dye) in water of 20 mg/L, using nanometer SnO_2 as photocatalyst. Other working conditions are as follows: for photocatalysis 1g catalyst/L, 2g catalyst/L respectively, have been used, at an initial $\text{pH}=5.5\pm0.2$, temperature $25^\circ\text{C}\pm2^\circ\text{C}$. Photocatalytic test was done using a type UV lamp UVP, 254 nm surface. Photocatalyst sample was stirred for 30 min to reach equilibrium and then coupled to the UV lamp and start the timer.

2.4. Characterization methods

The structure and properties of the obtained materials were studied by X Ray Diffraction (XRD), FTIR spectroscopy, N_2 adsorption-desorption isotherms and UV-Vis diffuse reflectance spectroscopy. The structures of pure and modified clay were investigated using Shimadzu LabX XRD 6000 diffractometer. The diffraction angle was scanned from 10 to 80 degrees, an usual interval for complex clays and SnO_2 . Measurement conditions were: X-ray tube, Cu target Cu, voltage = 40.0 (kV), current 30.0 (mA) and scanning: scan mode-Continuous Scan, scan speed 2.0000 (deg/min). FTIR spectra were recorded on a FTIR JASCO 660+ spectrometer. UV-vis diffuse reflectance spectra recording were performed by a Shimadzu UV-2401 PC Recording Spectrophotometer ranging between 200–600 nm. The adsorption isotherms of N_2 , specific surface areas and porosities were determined with a Nova 2200e (Quantachrome Instruments) automated sorptometer at 77 K. Particles size distribution and mean particle size diameter (D_p , nm) measurements were recorded using an optic measurement device

SALD-7001 type Laser Diffraction Particle Size Analyzer (Shimadzu, Japan).

3. Results and Discussion

Changes occurring in the structure of lamellar supports can be monitored on the basis of Bragg reflections determined from the X-ray diffractograms of the $\text{Ag}/\text{SnO}_2/\text{layer}$ silicate samples.

Identification of peaks was performed using the diffractometer software. The pure clay presents all specific peaks for complex clays: quartz, bentonite, feldspar, aluminum silicate and mica. Reference diffractogram for thin oxide shows a nanocrystalline powder with tetragonal structure of elementary cell. These elementary cell dimensions are well fitted in SiO_2 sites of clay, as identification image show. Thus, the stable monodisperse, uniform particle size distribution of silver nanoparticles are formed.

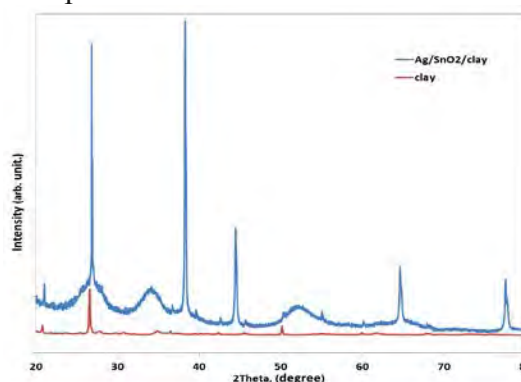


Fig. 2. X-ray diffraction (XRD) patterns of the studied samples

X-ray diffraction patterns of clay and $\text{Ag}/\text{SnO}_2/\text{clay}$ nanocomposites have been given in Fig. 2. The crystallite sizes of these samples were obtained by using Scherrer's equation. $D = k\lambda / b \cos \theta$ where D is crystallite size, k is the radiation wavelength (1.5406 Å), b is the peak full width at half maximum (FWHM), θ is the diffracting angle and $k = 0.94$ for spherical shape particle. The average crystallite size was found to be 18.17 Å and 11.75 Å (± 1) nm, respectively for clay and $\text{Ag}/\text{SnO}_2/\text{clay}$ nanocomposites mode powder. As shown in Fig. 2 the original d-spacing of clay, 3.32 Å and 2.34 Å

of Ag/SnO₂/clay nanocomposites 2θ angles (2θ = 26.82° and 38.29° respectively). This value is a direct proof of the fact that, in the path of Ag⁺ ions are bound not only on the external surfaces and edges of MMT but also in the interlamellar space. Since the ionic radius of Ag⁺ is 1.22 Å it is expected that silver occupies interstitial position which in turn can lead to expansion of lattice parameters. We presume that some of the Ag⁺ rests go to surface of the clay.

The IR spectra of the clay and Ag/SnO₂/clay nanocomposites are shown in Figure 3. The band situated at 3614 cm⁻¹ is specific to montmorillonite by its elongation vibrations belonging to OH groups from octahedral layer coordinated, the 1014 cm⁻¹ and 1025 cm⁻¹ wavelength specific to Si-OH silanolic groups from the material surface and the 784 cm⁻¹ wavelength specific to the deformation vibration of O-H group, bound by a Al-Al-OH cation.

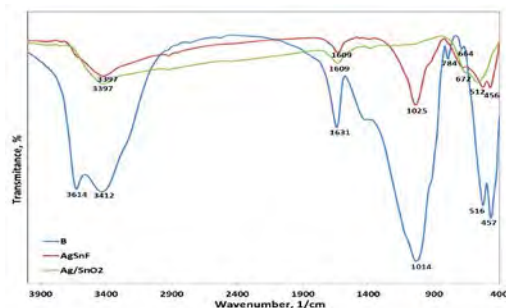


Fig. 3. FTIR Spectra: B – clay; AgSnF – Ag/SnO₂/clay nanocomposites; Ag/SnO₂ – Ag/SnO₂ nanoparticles

At the O–H stretching frequency region, all the impregnation and pillared clay materials show two intense IR 3412 cm⁻¹ (Fig. 3). These two bands have been assigned to the stretching vibration of the structural OH groups in the clay sheet and to the water molecules present in the interlayer, respectively [36, 37]. If one compares the intensity of these bands for the clay samples, note that the pillaring has a positive impact on the water retention capacity of the clay minerals and the intensity of the band decreases with the process of pillaring. [38]

The IR band observed at 1631 cm⁻¹ is due to the bending vibration mode of OH groups. Montmorillonite clay is known to contain two types of hydroxyl groups. One of them is more labile, with an IR absorption pattern similar to that of liquid water and has been ascribed to the water molecules present in the outer coordination spheres of the interlayer cations. The other type is more firmly held and is associated with the water molecules directly coordinated to the exchangeable cations. The latter directly coordinated to the exchangeable cations. The latter type also contributes significantly to the this absorption band [36]. The hydrated aluminum species present in the clay interlayer contain significantly larger amounts of water molecules in the first coordination sphere. The intense band observed for the impregnation and pillared clay suggests the possibility of increasing the acidity due to pillaring since the water molecules in the first coordination sphere dissociate in the clay interlayer producing protons. The structural OH-bending mode in montmorillonite shows a series of discrete IR absorption bands between 784 cm⁻¹ depending upon the cation composition in the octahedral sheet [39]. Fig. 4 shows bands around 3397 cm⁻¹ and 1609 cm⁻¹ for Ag/SnO₂ nanoparticles and Ag/SnO₂/clay nanocomposites.

Micromorphology and textural characteristics of clay and Ag/SnO₂/clay nanocomposites described by the results of nitrogen adsorption/desorption isotherms. The specific surface area has been calculated using BET method at a relative pressure ranging between 0.05-0. The pore volume has been calculated at a relative pressure of 0.95. The distribution of pore size has been determined from the nitrogen adsorption isotherm using Barrett-Joyner-Halenda model (BJH model). Subsequently, isotherms and distributions corresponding to the pore sizes has been performed (Fig. 4).

The general aspect of the samples isotherm reveals an IUPAC IV type

isotherm, characteristic to the porous adsorbers, presenting the so-called capilar condensation phenomenon. The results of pore distribution calculus (Fig. 4) indicate the occurrence of some mesoporous with 4.18 nm and 3.73 nm radius, respectively.

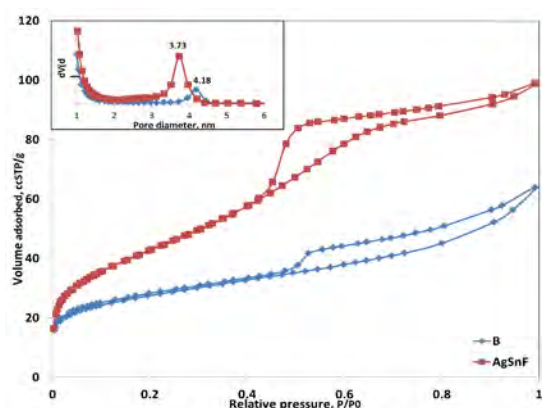


Fig. 4. The N_2 adsorption/desorption isotherms of the clay (B) and Ag/SnO_2 /clay nanocomposites (AgSnF)

In the domain of partial pressures values higher than $p/p_0 > 0,5$ the isotherm unveils the appearance of an H3 type hysteresis, indicating the existence of pores with a relative even distribution [40]. The amounts of adsorbed nitrogen measured at identical relative pressures are considerably higher in Ag/SnO_2 /clay nanocomposites than in the bare clay support. In the Ag/SnO_2 /clay nanocomposites samples, N_2 molecules have access to a much larger surface (the nanoparticles own surface also contributes to the overall increase in surface area) than is the case in the unmodified support. [41]

Sample	Surface area, α_{BET} (m ² /g)	Pore volume, cc/g	Pore diameter, nm
B	97.206	0.127	4.18
AgSnF	153.471	0.267	3.73

Table 1. Textural properties of the materials

From Table 1 data, it is noteworthy that after the intercalation of silver/tin oxide

between the clay's interlayers the BET specific surface area, pore size and total volume increase, which confirm the fact that silver/tin oxide has been intercalated between the clay's interlayers.

The particle size distribution for clay and Ag/SnO_2 /clay nanocomposites is shown in fig. 5 and fig. 6. For a sample two consecutive measurements were made. The particle size distribution of clay appeared to be bimodal, with particles averaging about 0.1 μm .

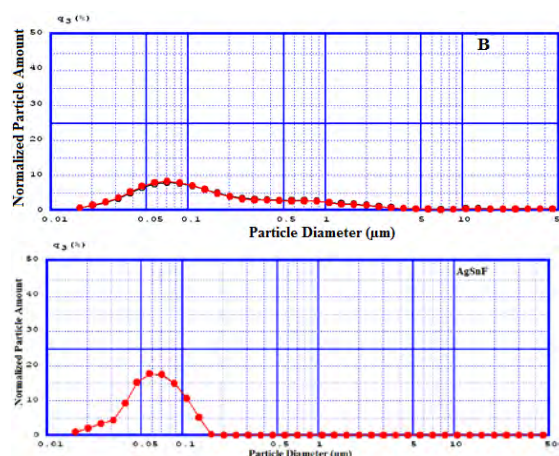


Fig. 5. Volume histogram of the particle size distribution in clay (B) and Ag/SnO_2 /clay nanocomposites (AgSnF)

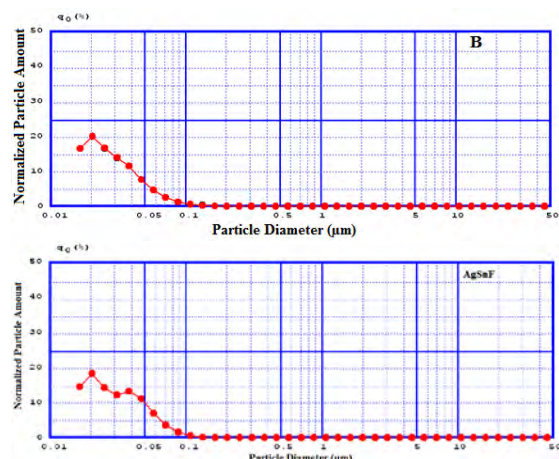


Fig. 6. Numerical histogram of the particle size distribution in clay (B) and Ag/SnO_2 /clay nanocomposites (AgSnF)

Representing the numerical histogram we could say that the particle size

distribution is unimodal with the particle diameter of 0.06 μm .

We firstly checked the photocatalytic performance of the Ag/SnO₂/clay nanocomposites for degradation of Eosin Y dye. The results are shown in fig. 7. Samples investigations of photocatalytic oxidation having as objective degradation and discoloration of synthetic solution containing Eosin Y dye, by varying the concentration of catalyst: 1g/L and 2g/L respectively. Some blank experiments (without UV irradiation or catalysts) in order to check if the Eosin Y dye removal is really due to a photocatalytic process. The experiments conducted in the absence of photocatalyst but with the assistance of UV irradiation showed the fact the Eosin Y cannot be degraded. The absorption spectra of the obtained Ag/SnO₂/clay nanocomposites are shown in Fig. 7. Eosin Y shows a mean absorption peak in visible region at 516 nm and the rate of decolorization was recorded with respect to the change in intensity of this absorption peak. The main absorption peak has diminished and finally disappeared during photoirradiation process, which indicated that the Eosin Y has been degraded.

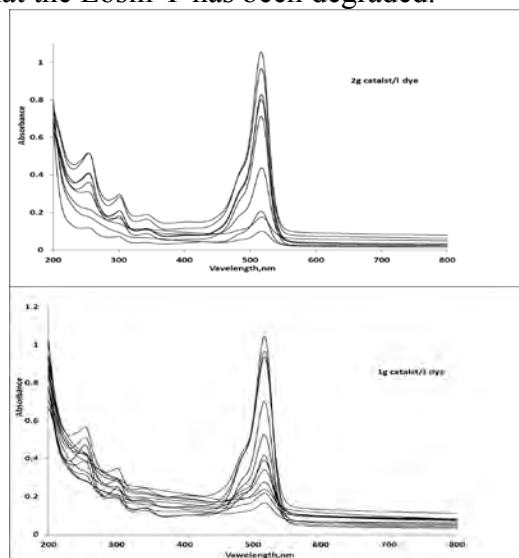


Fig. 7. UV-vis spectra of the studied samples: 1-2g Ag/SnO₂/clay nanocomposites/L Eosin Y dye

It is known that the photocatalysed decolourization of a dye in solution is initiated by the photoexcitation of the SnO₂, followed by the formation of electron-hole pair on the surface of catalyst. The high oxidative potential of the hole in the catalyst permits the direct oxidation of the dye to reactive intermediates. Another reactive intermediate which is responsible for the degradation is hydroxyl radical (OH•). It is either formed by the decomposition of water or by reaction of the hole with OH⁻. The hydroxyl radical is an extremely strong, non-selective oxidant ($E_0 = +3.06\text{V}$) which leads to the partial or complete mineralization of several organic chemicals [42, 43]. It can be seen that the loading of silver can significantly enhance the photocatalytic efficiency of SnO₂ in degradation of Eosin Y. The positive effect of noble metal deposits is commonly due to the fact that Ag nanoparticles on the semiconductor surface behave like electron sinks, which provide sites for accumulation of the photogenerated electrons, and then improve the separation of electrons and holes. This can be understood based on the proposed charge separation of Ag/SnO₂ under UV illumination. [44, 45]

An efficient photocatalytic process needs very crystalline semiconductors, in order to reduce the recombination electrons/positive holes pairs. Thus, for an increasing of catalyst quantity up to an optimal dose, a higher quantity leads to an augmentation of the efficiency of Eosin Y removal, due to the generation of a higher number of active species. The more the quantity of catalyst is, the more HO• radicals. The last one will be considered as main oxidant species responsible for the photocatalytic process [46].

An increasing of photocatalyst quantity over the optimal limit leads to an augmentation of suspension turbidity, thus decreasing the intensity of UV radiation at its passing by the specimen, consequently resulting a decreasing of HO• radicals number generation.

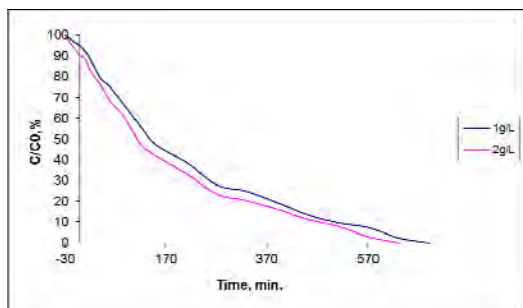


Fig. 8. Efficiency photocatalytic degradation of Eosin Y dye in the presence of Ag/SnO₂/clay nanocomposites catalysts samples

4. Conclusions

We reported the synthesis and characterization of some new Ag/SnO₂/clay nanocomposites. Intercalation of argint/tin dioxide nanoparticles into clay was unambiguously proven by X-ray diffraction. The presence of nanoparticles in the samples was verified by monitoring the specific surface area of the samples and the particle size distribution. It was established that this parameter increases because the crystallinity of nanocomposites increases. The ability of the nanocomposites to degrade Eosin Y dye under UV light was studied. It is observed that nanosized Ag/SnO₂/clay photocatalysts are an efficient photocatalyst, both in respect of decolorization as well as mineralization of Eosin Y. The synthesized Ag/SnO₂/clay nanocomposites are potential photocatalysts for treatment of organic wastewaters by converting the residual dyes to harmless compounds.

Acknowledgments

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References

[1]. Sikhvivilu L.M., Pil lai S.K., Hillie T.K., Influence of Citric Acid on SnO₂ Nanoparticles

Synthesized by Wet Chemical Processes Submitted to Journal of Nanoscience and Nanotechnology (Revised version)

- [2]. Chappel S., Zaban A., Sol. Energ. Mat. Sol. Cells. 71:141 (2002)
- [3]. Schlamp M.C., Peng X., Alivisatos A.P. J. Appl. Phys. 82:5837 (1997)
- [4]. Cirera A., Vila A., Dieguez A., Cabot A., Cornet A., Morante J.R., Sens. Actuat. B 64:65 (2000)
- [5]. Miyauchi M., Nakajima A., Watanabe T., Hashimoto K., Chem. Mater. 14:2812 (2002)
- [6]. Morales J., Perez V.C., Santos S., Tirado L.J., J. Electrochem. Soc. 143:284 (1996)
- [7]. Aurbach D., Nimberger A., Markovsky B., Levi E., Sominski E., Gedanken A., Chem. Mater. 14:4155 (2002)
- [8]. Artemyev M.V., Sperling V., Woggon U., J. Appl. Phys. 81:6975 (1997)
- [9]. Patent no. 2644284, 14/09/90 CLAL, Nouveaux matériaux à base d'argent et d'oxide d'étain pour la réalisation de contacts électriques.
- [10]. Kameo A., Yoshimura T., Esumi K., Colloids Surf. A: Physicochem. Eng. Aspects 215 (2003) 181–189.
- [11]. Ullah M.H., Kim Il, Ha C.S., Mater. Lett. 60 (2006) 1496–1501.
- [12]. Zou X.Q., Ying E.B., Dong S.J., J. Colloid Interf. Sci. 306 (2007) 307–315.
- [13]. Tian X.L., Wang W.H., Cao G.Y., Mater. Lett. 61 (2007) 130–133.
- [14]. Mohan Y.M., Lee K., Premkumar T., Geckeler K.E., Polymer 48 (2007) 158–164.
- [15]. Courrol L.C., Silva F.R., Gomes L., Colloids Surf. A: Physicochem. Eng. Aspects 305 (2007) 54–57.
- [16]. Chen Z.T., Gao L., Mater. Res. Bull. 42 (2007) 1657–1661.
- [17]. Khanna P.K., Singh N., Charan S., Viswanath A.K., Mater. Chem. Phys. 92 (2005) 214–219.
- [18]. Xu Guang-nian, Qiao Xue-liang, Qiu Xiaolin, Chen Jian-guo, Colloids and Surfaces A: Physicochem. Eng. Aspects 320 (2008) 222–226
- [19]. Templeton A. C., Wuelfing W. P., Murray R. W., Acc. Chem. Res. 33, 27 (2000).
- [20]. Storhoff J. J., Mirkin C. A., Chem. Rev., 100, 409 (2000).
- [21]. Shipway A. N., Katz E., Willner I., Chem.Phys.Chem. (2000) 1, 18.
- [22]. Zhong, C. J.; Maye, M. M. Adv. Mater. (2001) 13, 1507.
- [23]. Kamat P. V., Chem. Rev. (1993), 93, 267.
- [24]. Belloni J., Radiat. Res. (1998), 150, 39.
- [25]. Henglein A., Meisel D. J., Phys. Chem. B (1998), 102, 8386.



- [26]. Dimitrijevic N. M., Bartels D. M., Jonah C. D., Takahashi K., Rajh T. J., Phys. Chem. B (2001), 105, 954.
- [27]. Henglien A. Isr., J. Chem. (1993), 33, 77.
- [28]. Bruchez M., Moronne M., Gin P., Weiss S., Alivisatos, A. P. Science (1998), 281, 2013.
- [29]. Brust M., Bethell D., Keily C. J., Shiffrin D. J., Langmuir (1998), 14, 5425.
- [30]. Geirsig M., Pastoriza-Santos I., Liz-Marzan L. M., J. Mater. Chem. (2004), 14, 607.
- [31]. Link S., El-Sayed M. A., J. Phys. Chem. B (1999) 103, 8410.
- [32]. Musick M. D., Pena D. J., Botsko S. L., McEvoy T. M., Richardson T. N., Natan M. J., Langmuir (1999), 15, 844.
- [33]. Anjana Sarkar, Sudhir Kapoor, Tulsi Mukherjee, J. Phys. Chem. B (2005), 109, 7698 7704
- [34]. Popovici E., Hristodor C.M., Alexandroaei M., Hanu A.M. (2006) Rev. Chem. 57: 8-11
- [35]. Popovici E., Humelnicu D., Hristodor C.M. Rev. Chem. (2006) 57: 675-678
- [36]. Trillo J.M., Alba M.D., Castro M.A., Munoz A., Poyato J., Tobias M. (1992) Clay Miner. 27, 423
- [37]. Miller S.E., Heath G.R., Gonzalez R.D. (1982) Clays Clay Miner. 30:111
- [38]. Sowmiya M., Sharma A., Parsodkar S., Mishra B.G., Dubey A. (2007) Applied Catalysis A: General 333:272–280
- [39]. Sposito G., Prost R., Gaultier J.P., (1983) Clays Clay Miner. 31:9.
- [40]. Rouquerol J., Rouquerol F., Sing K., Adsorption by powders and porous solids, ISBN 10: 0-12-598920-2, Published: OCT-1998
- [41]. Németh J., Dékány I., Süvegh K., Marek T., Klencsár Z., Vértés A., Fendler J. H. (2003) Langmuir 19 (9):3762-3769
- [42]. Daneshvar N., Salari D., Khataee A.R., (2003) J. Photochem. Photobiol. A: Chem. 157:111
- [43]. Kansal S.K., Singh M., Sud D., (2007) Journal of Hazardous Materials 141:581–590
- [44]. Linsebigler A. L., Lu G. Q., Yates J. T., Photocatalysis on TiO₂ Surfaces: Principles, Mechanisms, and Selected Results Chem. Rev. 95 735–58, (1995)
- [45]. Weiwei L., Guosheng L., Shuyan G., Shantao X., Jianji W., Nanotechnology 19 (2008) 445711
- [46]. Nishio J., Tokumura M., Znad H.T., Kawase Y. (2006) J. Hazard. Mater. B138:106-115

A COMPARATIVE APPROACH TOWARDS THE DEGRADATIVE POTENTIAL OF TWO DIFFERENT NANOPHOTOCATALYSTS ONTO A MODEL TEXTILE DYE

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ABSTRACT

Motivations and objectives. It is quite a difficult issue to treat, decolorize and mineralize textile dye waste containing dyes by conventional chemical methods (primary: adsorption, flocculation and secondary: chlorination, ozonization). It has been demonstrated that semiconductor photocatalytic oxidation of organic substances can be an alternative to conventional methods of removal of organic pollutants from water [1]. Advanced oxidation processes (AOPs) employing heterogeneous catalysis have emerged as potential destructive technology leading to the total mineralization of most of organic pollutants. An additional advantage of the photocatalytic process is its mild operating conditions and the fact the semiconductor can be activated by sunlight (near UV), thus reducing significantly the electric power requirement and hence the operating cost [2].

The main result and characterizing aspect of the research consist of the effectiveness of a semiconductor photocatalytic treatment of synthetic wastewater. Nanophotocatalysts ZnO have been successfully grown by hydrothermal method, onto some fibrous supports previously functionalized (grafted with MCT (monochlorotriazinyl- β -cyclodextrin, MCT- β -CD). The synthesis is reported elsewhere. The hydrothermal synthesis was performed using two types of surfactants widely used in nanoparticles preparation: Pluronic P123 (triblock copolymer) and CTAB (cetyltrimethylammonium bromide). The novelty of the study consists in using these two different surfactants in the growth of ZnO onto the fibrous supports. For degradation of Erionyl Roth dye, batch experiments were performed by irradiating the aqueous solution of model textile dye, containing ZnO nano-coated fibrous supports as semiconductor, in the presence of UV light. The photocatalytic process occurs under the illumination of an UV lamp, emitting light at wavelength 365 nm. The rate of decolorization was estimated from residual concentration spectrophotometrically.

Results and discussion. The enhancement of the photocatalytic activity is attributed to the CTAB. The performance of the photocatalytic system indicated that the photodegradation of the Erionyl Roth, in the presence of CTAB, occurred with a 20 % reduction of time, compared to P123. The study has demonstrated that using the semiconductor performed by CTAB using on the ZnO nano-oxides synthesized onto previously MCT grafted fibrous supports is effective in degradation of dyes as well as in the treatment of textile dye waste.

KEYWORDS: fibrous linen nanocomposites, photodegradation, nanophotocatalyst, zinc oxide

1. Introduction

Generally present in the effluents of the textile, cosmetics, paper, leather, pharmaceutical, food and other industries, dyes are among the most important water pollutants. There are many methods (coagulating sedimentation, filtration, electro-coagulation, and adsorption by activated carbon) having been investigated to remove the dyes; the main disadvantage of these methods consists in only transferring the dyes from one medium to another. Consequently, the developing of environmentally benign routes combining effective adsorption with enhanced photocatalytic efficiency, which completely mineralizes the organic pollutants became crucial[1,2]. Due to advances in its synthesis and unique optoelectronic, catalytic, and photochemical properties, ZnO, a compound semiconductor with a band gap of 3.37 eV, has attracted substantial attention in recent years. Although TiO₂ has been widely used as the most active photocatalyst[3,4], ZnO could be a suitable alternative because of its lower cost, larger quantum yields, and better antibacterial effect. ZnO has been successfully used in photocatalytic degradation of pollutants[5,6] and is more efficient in the decomposition of several organic contaminants than TiO₂ [2,7,8]. However, ZnO nanoparticles are prone to aggregation especially after calcination above 400°C. This results in a remarkably reduced surface area and much larger crystallite size. In addition, ZnO has a relatively low adsorptive capacity, and its photocatalytic efficiency is not high in very dilute solutions of organic pollutants. Consequently, enrichment of reactants by adsorption is required for a highly efficient photocatalytic performance [9-11].

Recently green chemistry and chemical processes have been emphasized on the preparation of nanoparticles to eliminate or minimize generated waste and implement

sustainable processes [12]. Nanoparticles of metal oxide and sulfides are prepared with polysaccharides as the stabilizer. Zinc oxide nanoparticles can be synthesized using water as a solvent and MCT-β-CD(MonoChlorotriazinyl-β-Cyclodextrin) as a stabilizer [13,14,15].

2. Experimental approach

2.1 Synthesis of nano-ZnO particles

In our research ZnO nanoparticles were synthesized *in-situ* on linen fibrous supports having a certain concentration of MCT-β-CD (monochlorotriazinyl-β-cyclodextrin) by using the hydrothermal method. The linen samples with sizes of 30 x 30 cm² were immersed in the solution prepared as follows: zinc acetate Zn(CH₃COO)₂·2H₂O, purity – 99%) (0,005 mol) as precursor was solved in de ionized water to form a clear solution by stirring and then 0,1 mol of urea solution was added drop-wise with constant stirring. Second, the pH value of the mixed solution was adjusted to 5 by adding acetic acid, added drop wise. The final reaction mixture was then magnetic stirred for two hours at room temperature and poured into into a stainless-steel autoclaves with a 100-ml Teflon (poly[tetrafluoroethylene]), followed by immersion of the fibrous supports. Then the autoclaves were placed in the oven for the hydrothermal treatment at 90°C overnight.

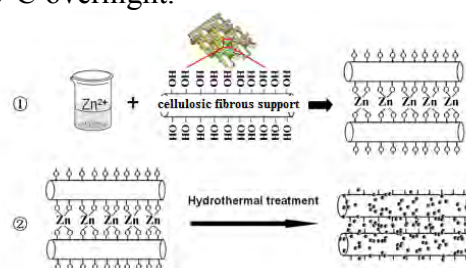


Fig. 1. Flow chart for the preparation of nanoparticles-coated linen support

The autoclaves had been cooled down to room temperature naturally. The textile samples are then extracted from the autoclaves. The obtained products were

washed several times with distilled water. After complete washing nanocomposites were dried at 60°C overnight for 3 h for complete conversion of the remaining zinc hydroxide to zinc oxide.

2.2. Photocatalytic activity of the the synthesized catalysts

The photocatalytic experiments were conducted in a 400 ml beaker under the illumination of a single UV light lamp produced by Vilber Lourmat France, which predominantly emits at 365nm with intensity of 350 $\mu\text{W}/\text{cm}^2$. Erionyl Roth was provided by a certain textile enterprise. All aqueous solutions were prepared using deionised water. For each experiment, the reaction suspension was prepared by adding 0.3 mg catalyst into 150 mL Erionyl Roth solution with an initial concentration of 30 mg/L. The suspension was magnetically stirred for 30 minutes in the dark to ensure the absorption/desorption equilibrium between dye molecules and the photocatalyst surface. Afterwards, the suspension was irradiated by the UV lamp. During the photodegradation process, the UV lamp was positioned horizontally above the surface of the suspension. In all experiments, the reaction temperature was kept at $25 \pm 2^\circ\text{C}$.

Samples were taken out for measurement after various reaction times. The upper clear liquid obtained after centrifugal separation was analyzed by UV-Vis spectroscopy, on a Shimadzu UV-2401 UV-Vis spectrophotometer. The maximum absorbance of the Erionyl Roth was found at 516 nm, and the concentration of the solutions has been determined using the calibration curve.

2.3. Instrumentation for characterization of ZnO–MCT-B-CD (Monochlorotriazinyl– β -Cyclodextrin) grafted linen fibrous nanocomposites

The phase and the microstructure of the samples were characterized by using X-ray diffraction and scanning electron

microscopy-EDX, humidity (water vapors) sorption measurement/ humidity sorption/desorption.

2.3.1. Scanning electron microscopy (SEM)

Scanning Electron Microscope (SEM) images of the samples were obtained from a Quanta 200 3D Dual Beam type microscope from FEI Holland.

2.3.2. X-ray diffractometry

The ZnO–MCT- β -CD Monochlorotriazinyl- β -Cyclodextrin) powders were tightly packed into the sample holder. X-ray Diffraction (XRD) data for structural characterization of the various prepared samples of ZnO were collected on an X-ray diffractometer (PW1710) using Cu- $K\alpha$ radiation ($k = 1.54 \text{ \AA}$) source (applied voltage 40 kV, current 40 mA). About 0.5 g of the dried particles were deposited as a randomly oriented powder onto a Plexiglass sample container, and the XRD patterns were recorded at angles between 20° and 80° , with a scan rate of $1.5^\circ/\text{min}$. Radiation was detected with a proportional detector.

2.3.3. FTIR spectroscopy

FTIR was used to examine changes in the molecular structures of the samples. Analysis has been recorded on a FTIR JASCO 660+ spectrometer. The analysis of studied samples was performed at 2 cm^{-1} resolution in transmission mode. Typically, 64 scans were signal averaged to reduce spectral noise.

3. Results and discussion

3.1. Characterization of ZnO–linen fibrous supports nanocomposites

SEM images below belong to linen support, non-functionalized (non-grafted), without hydrothermal treatment under different magnifications.

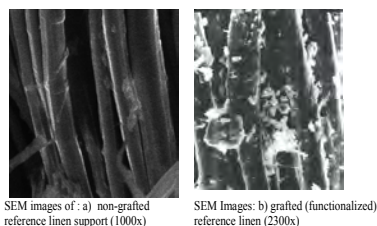


Fig. 2. SEM images of: non-grafted reference linen support; grafted (functionalized) linen support

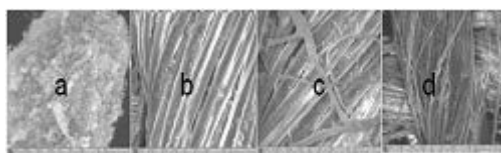


Fig. 3. SEM images of: a- ZnO powder hydrothermally synthesized; b- ZnO powder hydrothermally synthesized on grafted linen support (4_ZnO (1200x)); c- ZnO powder hydrothermally synthesized on grafted linen support with assistance of Pluronic P123 (poly(ethylene glycol) (4_P123(1200x)); d- ZnO powder hydrothermally synthesized on grafted linen support with assistance of CTAB (Cetyltrimethylammoniumbromide) (4_CTAB (1200x))

As shown in Fig.4, the surfaces of the linen supports are very clear, with diameters of about 10-20 μm . This implies that the large particles may be formed via precipitation followed by a step-like aggregation process.

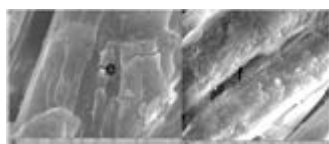


Fig. 4. SEM images of: e) ZnO powder hydrothermally synthesized on grafted linen support with assistance of CTAB (Cetyl trimethylammonium bromide) (4_CTAB (5000x)); f) ZnO powder hydrothermally synthesized on grafted linen support with assistance of Pluronic P123 (poly (ethylene glycol) (5000x) (4_P123)

Due to its high number of coordinating functional groups (hydroxyl and glucoside groups) as polysaccharide, MCT- β -CD (monochlorotriazinyl- β -cyclodextrin) could form complexes with divalent metal ions [15]. It might be possible that the majority of the zinc ions was closely associated with the MCT- β -CD (monochlorotriazinyl- β -cyclodextrin) molecules. Based on the previous research, it can be claimed that nucleation and initial crystal growth of ZnO may preferentially occur on MCT- β -CD (monochlorotriazinyl- β -cyclodextrin).

Moreover, as polysaccharide, MCT- β -CD (monochlorotriazinyl- β -Cyclodextrin) showed interesting dynamic supramolecular associations facilitated by inter- and intra-molecular hydrogen bonding, which could act as matrices for nanoparticle growth in size of about 30–40 nm. They aggregated to irregular ZnO-CMC nanoparticles in a further step.

Figures 4e) and 4f) show SEM images of linen supports coated with ZnO with assistance of the two surfactants. As shown in the figures above, the nanoparticles exhibited an approximately lamellar morphology and the particles can be seen to be coated on the fibrous support surface. The fibrous supports surface became coarser after the treatment.

In addition, according to the SEM images of the coated fabric, the uniformity of the fabric coated with ZnO powder hydrothermally synthesized with assistance of CTAB (Cetyl Trimethylammonium Bromide) is better than that of ZnO powder hydrothermally synthesized in the presence of Pluronic P123 and possesses good washing fastness. The coating particles fell off easily for the ZnO powder hydrothermally synthesized without any surfactant assistance after washing, which might have been caused by the weak attaching force (covalent bonding between ZnO and linen) induced by the deteriorated crystallinity.

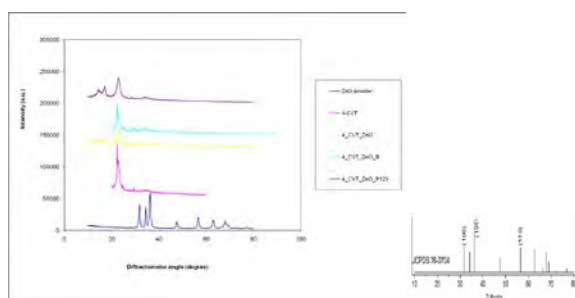


Fig. 5. (Color online) XRD patterns of: ZnO-powder (ZnO non-calcinated powder hydrothermally synthesized); MCT- β -CD (Monochlorotriazinyl- β -cyclodextrin)₄ grafted (functionalized) linen fibrous support (4-CVT); ZnO powder hydrothermally synthesized on MCT- β -CD (Monochlorotriazinyl- β -Cyclodextrin)₄ grafted linen fibrous support (4_ZnO); ZnO powder hydrothermally synthesized on MCT- β -CD (Monochlorotriazinyl- β -Cyclodextrin)₄ grafted linen fibrous support in presence of Cetyl trimethylammonium bromide (4_CVT_ZnO_B); ZnO powder hydrothermally synthesized on MCT- β -CD (Monochlorotriazinyl- β -Cyclodextrin)₄ grafted linen fibrous support in presence of P123 (4_CVT_ZnO_P123)

The standard XRD pattern of ZnO - non-calcinated powder hydrothermally synthesized with hexagonal phase structure corresponds to JCPDS card No 76-0704 [16]. All peak positions and relative very small, decreased peak intensities of ZnO-linen supports nanocomposites matched well with those of the standard XRD pattern, which confirms that the samples consist of ZnO on linen matrix without any other impurity phase. As can be seen from Fig. 5, the intensities of the diffraction peaks weaken as the FWHM of the peaks decrease with the assistance of the two surfactants. In the case of ZnO nanoparticles synthesized with the assistance of those two surfactants, the result is suppressed ZnO grain growth and deteriorated crystallinity; it can be noted that the width of the peaks for nano-ZnO fibrous composites has decreased in a more relevant manner, in case of the presence of P123, compared with the sample synthesis assisted by CTAB.

The diffraction peaks of ZnO-linen nanocomposites showed a broadening at the base due to the nano-size effect.

In Fig. 6, the FTIR spectrum of hydrothermally synthesized, non-calcinated ZnO powder exhibited a high intensity broad band at about 3400 cm⁻¹ due to the stretching of the zinc and oxygen bond.

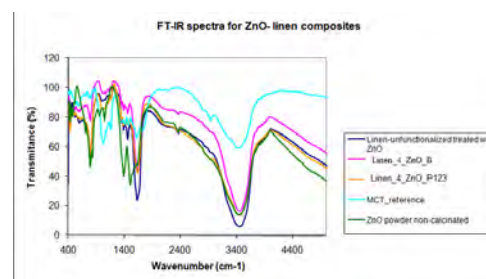


Fig. 6. (a) FTIR of spectra of: linen fibrous – unfunctionalized and hydrothermally treated with ZnO (Linen unfunctionalized, hydrothermally treated with ZnO); the linen fibrous support grafted with MCT- β -CD (Monochlorotriazinyl- β -Cyclodextrin)₄ and hydrothermally treated with ZnO in presence of Cetyl trimethylammonium bromide (Linen_4_ZnO_B); the linen fibrous support grafted with MCT- β -CD (Monochlorotriazinyl- β -Cyclodextrin)₄ and hydrothermally treated with ZnO in presence of P123 (Linen_4_ZnO_P123), MCT- β -CD (Monochlorotriazinyl- β -Cyclodextrin) powder (MCT- β -CD (Monochlorotriazinyl- β -Cyclodextrin) _reference), ZnO powder non-calcinated

A similar band was also observed in synthesized nano-ZnO composites. As shown in the FTIR spectrum of MCT- β -CD (Monochlorotriazinyl- β -Cyclodextrin), the absorption bands between 1000 and 1200 cm⁻¹ were characteristic of the –C–O– stretching on polysaccharide skeleton. And two peaks appeared at 1420 and 1610 cm⁻¹

corresponding to the symmetrical and asymmetrical stretching vibrations of the carboxylate groups. And the peak at 2920 cm⁻¹ was ascribed to C–H stretching associated with the ring methane hydrogen atoms. A broad band centered at 3450 cm⁻¹

was attributed to a wide distribution of hydrogen-bonded hydroxyl groups. The FTIR spectra indicated that in ZnO–MCT- β -CD (Monochlorotriazinyl- β -Cyclodextrin) nanoparticles, there was the strong interaction, but no obvious formation of covalent bonds between MCT- β -CD (Monochlorotriazinyl- β -Cyclodextrin) and ZnO.

The degradation efficiency, as a function of reaction time, was calculated considering the concentration ratio of the original solution and the ones of the analyzed samples (Eq.1) [17,18].

$$\eta = (C_0 - C) \cdot 100 / C_0 = (A_0 - A) \cdot 100 / A_0 \quad (1),$$

where C_0 and A_0 are the initial concentration and absorbance of Erionyl Roth in solution at fixed wavelength, corresponding to the maximum absorption wavelength; C and A are the concentration and absorbance of the Erionyl Roth solution after UV light irradiation at different moments of time.

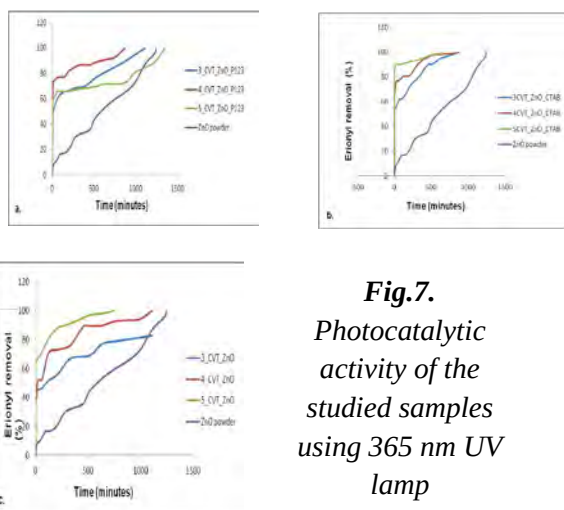


Fig.7.
Photocatalytic
activity of the
studied samples
using 365 nm UV
lamp

Based on the photocatalytic experiments (Fig.7) using irradiation lamp at 365 nm, the following conclusions were drawn:

- 5_CVT_ZnO_CTAB > 4_CVT_ZnO_CTAB > 3_CVT_ZnO_CTAB > ZnO powder;
- 5_CVT_ZnO > 4_CVT_ZnO > ZnO powder > 3_CVT_ZnO;
- 4_CVT_ZnO_P123 > 3_CVT_ZnO_P123 > 5_CVT_ZnO_P123 > ZnO powder.

4. Conclusions

The ZnO nanoparticles were hydrothermally synthesized on linen fibrous supports having a different concentration of MCT- β -CD. The samples were characterized using a co-assisted characterizing methods (RDX, SEM, FTIR). Comparing the two photocatalysts (with CTAB and P123) adsorption potential, it was found that the photocatalyst containing CTAB retained more than the one possessing P123. Among the probes containing CTAB as surfactant, the 5_CVT_ZnO_CTAB indexed sample is the best, in terms of photocatalytic activity.

Acknowledgments

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References

- [1]. Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. Chem. Rev. 1995, 95, 69–96.
- [2]. Tryba, B.; Morawski, A. W.; Tsumura, T.; Toyoda, M.; Inagaki, M. J. Photochem. Photobiol., A 2004, 167, 127–135.
- [3]. Li, Y. Z.; Song, J. S.; Lee, N.; Kim, S. Langmuir 2004, 20, 10838–10844.
- [4]. Sun, B.; Smirniotis, P. G.; Boolchand, P. Langmuir 2005, 21, 11397–11403.
- [5]. Sakthivel, S.; Neppolian, B.; Shankar, M. V.; Arabindoo, B.; Palanichamy, M.; Murugesan, V. Sol. Energy Mater. Sol. Cells 2003, 77, 65–82.
- [6]. Khodja, A. A.; Sehili, T.; Pilichowski, J. F.; Boule, P. J. Photochem. Photobiol., A 2001, 141, 231–239.
- [7]. Sun, J. H.; Dong, S. Y.; Wang, Y. K.; Sun, S. P. J. Hazard. Mater. 2009, 172, 1520–1526.
- [8]. Yu, J. G.; Yu, X. X. Environ. Sci. Technol. 2008, 42, 4902–4907.
- [9]. Ooka, C.; Yoshida, H.; Suzuki, K.; Hattori, T. Microporous Mesoporous Mater. 2004, 67, 143–150.
- [10]. Fukahori, S.; Ichiura, H.; Kitaoka, T.; Tanaka, H. Environ. Sci. Technol. 2003, 37, 1048–1051.

- [11]. Zhang, G. K.; Ding, X. M.; He, F. S.; Yu, X. Y.; Zhou, J.; Hu, Y. J.; Xie, J. W. *Langmuir* 2008, 24, 1026–1030.
- [12]. Raveendran, P., Fu, J., Wallen, S.L., Completely “green” synthesis and stabilization of metal nanoparticles, *J. Am. Chem. Soc.* 125, 13940–13941 (2003)
- [13]. Vigneshwaran, N., Kumar, S., Kathe, A.A., Varadarajan, P.V., Prasad, V., *Functional finishing of cotton fabrics using zinc oxide–soluble starch nanocomposites*, *Nanotechnology* 17, 5087–5095 (2006)
- [14]. Ma, X.F., Chang, P.R., Yang, J.W., Yu, J.G., *Preparation and properties of glycerol plasticized-pea starch/zinc oxide–starch bionanocomposites*, *Carbohydr. Polym.* 75, 472–478 (2009)
- [15]. Radhakrishnan, T., Georges, M.K., Nair, P.S., 2007. *Study of sago starch–CdS nanocomposite films: Fabrication, structure, optical and thermal properties*, *J. Nanosci. Nanotechnol.* 7, 986–993 (2007)
- [16]. Jiugao, Yu, Jingwen, Yang, Baoxiang, Liu, Xiaofei, Ma, *Preparation and characterization of glycerol plasticized-pea starch/ZnO–carboxymethylcellulose sodium nanocomposites*, *Bioresource Technology* 100, 2832–2841 (2009)
- [17]. F. Ollis, E. Pelizzetti, and N. Serpone, “Photocatalyzed destruction of water contaminants,” *Environ. Sci. Tech.*, vol. 25, no. 9, pp. 1522–1529, Sept. 1991.
- [18]. D. Y. Goswami, “Engineering of the solar photocatalytic detoxification and disinfection processes,” in *Advances in Solar Energy*, vol. 10,
- [19]. K. W. Böer, Ed. Boulder: American Solar Energy Society Inc., 1995, pp.165–209.

INVESTIGATING AND OPTIMIZATIONS SOLUTION BY MEANS OF SCANING TYPE SENSOR-SURFACE

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ABSTRACT

Scanning Probe Microscopy has been developed as surface characterization technique for nearly 20 years. Atomic Force Microscopy, a widely used SPM subset, can be used in ambient conditions with minimum sample preparation. Atomic Force Microscopy is able to measure three-dimensional topography information from the angstrom level to the micron scale. Major advantages of Atomic Force Microscopy are that it has a combination of high resolution in three dimensions, the sample does not have to be conductive, and there is no requirement for operation within a vacuum.

KEYWORDS: scanning, investigation, optimization

1. Introduction

During the scanning process the scanning area is initially set at step 1 by

Xmin, Ymin, Xmax and Ymax values. The scanning is automatically performed by the program row by row. The scanning path is demonstrated in figure 1.

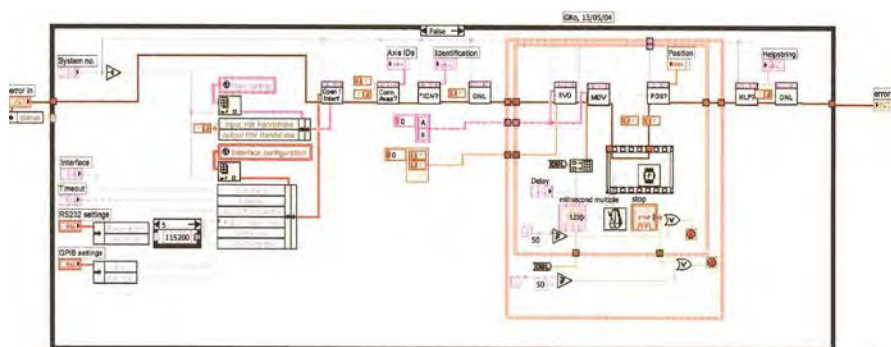


Fig. 1. The block diagram of the instrument

If zooming function is not chosen the default steps in x and y directions are incremented by 0.0096 V. The following zoom options that are available in the program can be seen in figure 2 (b). The user

can select the value before running the program, but it cannot be changed while the program is running. The front panel and the block diagram used to set zooming are shown in figure 2.

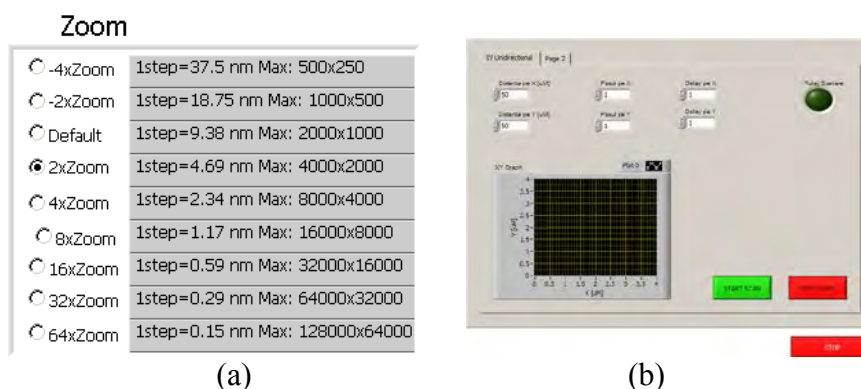


Fig. 2. Zooming Options (a) Front Panel (b) Block Diagram in LabVIEW

The maximum resolution (64x zoom) results in steps incremented by $0.0096 \text{ V}/64=0.00015 \text{ V}$. The step increment in x and a y direction exploit the highest possible resolution with the NI ELVIS system, and it is calculated according to the following formula [2]:

$$\frac{M}{R} \frac{a}{e} \frac{v}{-1} \frac{x}{s} = \frac{o}{2} \frac{1}{-1} \frac{iV}{l} \frac{n}{l} \frac{t}{u} \frac{a}{0.0} \frac{u}{0} \frac{g}{V} \quad (1)$$

Ten volts is the maximum voltage output of the NI ELVIS system. This will be amplified 10 times to the maximum of 100 V by the Physik Instrumente piezo driver device before it is applied to x, y and z expansion of the piezo crystal of the Molecular Imaging scanner head. 0.000153 V is the resolution resulting from the 16 bit output of the NI ELVIS system [1].

Descriptions of surface topography were the main objective of earlier studies of scanning probe microscopy. In the past few years, however, more and more quantitative analyses have been performed by means of scanning probe microscopes.

In this overview, results will be discussed of nine cases of surface modification and quantitative analysis by scanning tunneling (AFM) and scanning force microscopes (SFM, AFM). SPM has a considerable impact now on research and development in micro- and nanotechnology. Scanning force microscopes have become important tools for controlling the topography of electronic chips in the

production process, and for analysis of the topography of micromechanical components. One of the most promising applications of scanning probe microscopy is in the elucidation of the fundamentals of future nanotechnology [2].

In nanotechnology, materials science and solid state physics on an atomic scale should meet. Also studies of chemical and biological nanosystems will contribute to the fundamentals of future nanotechnology. Two aspects are of special interest: Firstly, the self-organization processes occurring in nature and secondly, the creation of nanosystems by surface modification and by manipulation of atoms, molecules or clusters, and the characterization of such artificial systems. It is worthwhile studying biological molecular systems, such as motors, sieves, and electrical conductors, to find ways of designing nanosystems for practical use.

2. Examples of modification and structuring of surfaces

Local Material Deposition and Single Electron Tunneling. Deposition of materials from the tip of the AFM was demonstrated nicely, for example, by for the case of Au cluster deposition on polycrystalline Au surfaces. The investigations described in this article are about the generation of small metal clusters on Si (111) surfaces, their thermal stability, and single electron

tunneling through them. When the dimension of the metal clusters are on the order of 10 nm or smaller, single electron tunneling effects can be observed even at room temperature [4].

Al- and Au-clusters with diameters between three and several hundred nanometers were generated on Si(111) surfaces by the application of voltage pulses between the tip and the sample.

The clusters were stable for more than 24h at room temperature; for small clusters, Coulomb staircase effects were observed in the current versus voltage curves (I(V)).

The Al tips, for example, require a bias voltage below -6 V or above +6 V for the deposition process by field evaporation to take place.

Figure 3 shows a typical Au cluster as deposited with the AFM, and the I(V)-curve together with its derivative demonstrating staircase effects at room temperature.

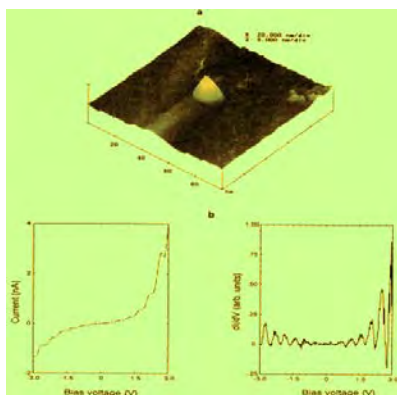


Fig. 3. Au cluster deposited on an Si (111)

3. Mechanical structuring of surfaces

Nanostructures can be generated by ploughing furrows with SFM tips. Also thin Au films deposited on nonconducting substrates were structured to demonstrate the possibility to create conducting nanostructures on an insulating substrate.

Figure 4 shows a periodic grid generated on the surface of polycrystalline Au. The profile is quite homogeneous over the area of 2 μm x 2 μm . The cantilever tip (Si) shows no

pronounced abrasion in the structuring process, as can be concluded from the homogeneity of the structure generated and from the analysis of the tips by scanning electron microscopy. Such periodic grids have been used for measuring the surface self-diffusion constant.

Structures generated with the SFM could also be used as molds for making nanostructures out of molecules or clusters as building blocks [3].

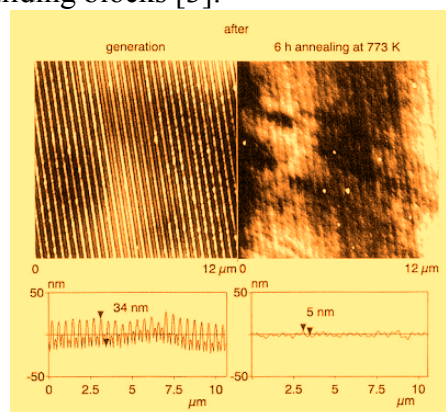


Fig. 4. Mechanical structuring of a polycrystalline Au surface with a stiff SFM-cantilever (Si).

temperature, however, these procedures are not as sensitive as the periodic grid method. In these cases, the time dependence of the depth of the profiles, $d(t)$, is given by

$$d(t) \sim (c_d t)^{3/4}, \text{ and } d(t) \sim (c_d t)^{1/4}, \text{ respectively.} \quad (2)$$

The latter methods are less sensitive because the time dependence is much weaker and no dependence on k exists. Another advantage of studying a periodic grid to determine the diffusion constant is the possibility to derive the grid parameters as a function of temperature by two dimensional Fourier transformation. The results of such analyses represent mean values averaged over the entire area analyzed.

The use of the SFM allows the surface self-diffusion constant to be measured for materials that are soft enough to allow grid

generation with a hard cantilever tip, if the surface can be kept clean throughout the measurement so that the diffusion is not altered by contamination.

For general application, the measurements would have to be performed in UHV or, at least, in an inert atmosphere [4].

Cluster Dynamics and Ostwald Ripening. Epitaxial growth of islands were studied in great detail on surfaces of single crystals by means of AFM.

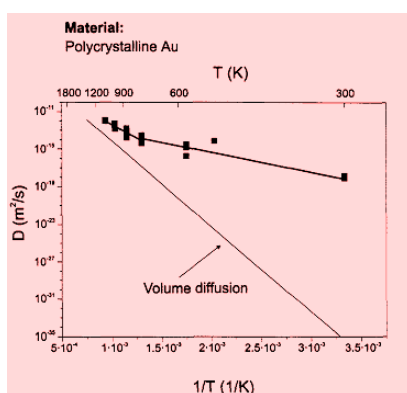


Fig. 5. Self-diffusion constant at the surface of polycrystalline Au as a function of temperature.

Metal clusters and cluster systems were deposited also on different disordered substrate surfaces, and their structure was analyzed mostly by transmission electron microscopy (TEM). Here we are discussing the dynamics of clusters grown out of ultrathin (10 nm thick) Au films deposited on native SiO_x surfaces of Si wafers by annealing the films at relatively low temperatures (50-100° C).

The dynamics of these Au cluster systems is determined by the Ostwald ripening process on the substrate surface, characterized, for example, by the growth of the large clusters and the appearance of depletion zones around the growing clusters, as recently observed in SFM experiments.

Ostwald ripening is regulated by the vapor pressure, $P(r)$, on surfaces of clusters depending on the curvature of the surface. For spherical clusters with a radius of r , it is

given, according to the Gibbs-Thomson equation, by the relation,

$$P(r) = P_{\infty} \exp(2\gamma_s \Omega / r k_B T) \approx P_{\infty} (1 + c/r). \quad (3)$$

A consequence of depending on the radius of the vapor pressure at the cluster surface is that particles will be transferred from small to large clusters. The large clusters will grow at the expense of the smaller ones which, finally, will dissolve. The largest clusters produced in the generation process have the highest probability of survival during ripening. General theory yields the following time dependence for the growth of the cluster radius, r :

$$r(t) = r_0 t^x \quad (4)$$

The exponent, x , depends on detailed assumptions about the growth process as, for example, discussed in the framework of theories of the ripening process proceeding in two dimensions.

In general, two characteristic zones around a growing cluster can be distinguished: a depletion zone defining the area in which material is removed by dissolution of small clusters and a nucleation zone around a growing cluster in which additional clusters may grow, whereas outside nucleation is excluded [1].

If the interaction of the diffusing atoms with the substrate is isotropic, the borderlines between the different zones will be circles whose radii will depend on the diffusion length and the capture probability as a function of the radius of the clusters.

Cluster size distribution, cluster density, cluster growth as a function of annealing time and temperature were studied by SFM analysis.

Cluster size and pair distributions as well as the mean cluster diameter as a function of annealing times are shown in Figure 6.

The diameter distributions indicate an increase of the number large clusters with increasing annealing time. This change may be a precursor of Ostwald ripening processes. If the ripening processes occur, then the cluster diameter will rise much faster, as observed in another experiment.

By characterizing cluster growth dynamics on the substrate surface, one could probably learn how the right kind of metal cluster systems for practical use in catalysis or in single electron tunneling systems could be generated.

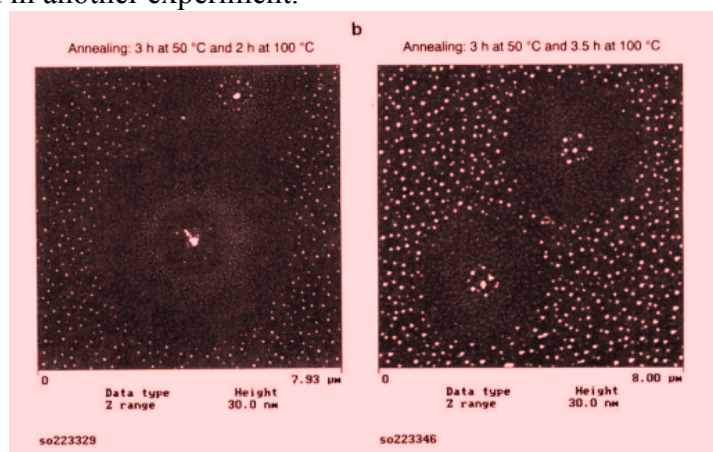


Fig. 6. Ostwald ripening at the surface of an ultra thin Au film from which clusters have been developed.

4. Conclusion

In recent years, scanning probe microscopy (SPM) has become an important tool in materials science. It not only allows ultimate analyses of surface structures to be conducted, but also unique procedures to be performed, such as material deposition, initiation of chemical reactions (e.g. oxidation, lithographic reactions), mechanical structuring as well as manipulation of atoms, molecules, and clusters.

Phenomena of practical importance, such as friction, adhesion, local magnetism, and surface diffusion can be studied on a microscopic scale. Several special types of instruments are now available for surface modification and for studying the surface properties of materials.

Among other methods of interest in materials science are electrolytic SPM techniques, and SPM techniques using magnetic and optical sensors.

References

- [1]. G. Binnig, C.F. Quate, and Ch. Gerber, *Atomic force microscope*, Phys. Rev. Lett. 56,930-933 (1986).
- [2]. G. Binnig, H. Rohrer, Ch. Gerber, and E. Weibel, *Surface studies by scanning tunneling microscopy*, Phys. Rev. Lett. 49, 57-61 (1982).
- [3]. Helen Hansma, James Vesenka, C. Siegerist, G. Kelderman, H. Morret, R.L. Sinsheimer, V. Elings, C. Bustamante, and P.K. Hansma, *Reproducible imaging and dissection of plasmid DNA under liquid with the atomic force microscope*, Science, 256, 1180-1184 (1992).
- [4]. E. Henderson, *Imaging and nanodissection of individual supercoiled plasmids by atomic force microscopy*, Nuc. Acids Res. 20,445-447 (1992).

THE INFLUENCE OF SURFACE MORPHOLOGY INVESTIGATED VIA SEM UPON THE MECHANICAL PROPERTIES OF STAINLESS STEEL SAMPLES

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ABSTRACT

This paper contains the investigation of metallic surfaces using SEM technology. This method provide the possibility to map out surface topography with atomic resolution in all three dimensions.

KEYWORDS: measured, laser, sensors, SEM

1. Introduction

Wire-bonding is a main interconnection process in the packaging industry. Wires are bonded to Al pads using combined thermal and ultrasonic activation. Gold wires are the widely used and well characterized media for this process [1]. Recently, the use of copper wires is of interest to the industry due to its electrical and mechanical properties. Since copper is relatively hard and readily oxidized, the use of copper wires in industrial interconnection processes requires special bonding procedures and equipment. Moreover, due to the relatively slow formation of Al-Cu intermetallics, examination of the as bonded Al-Cu interface by conventional characterization such as optical microscopy (OM) and scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS), provide almost no information related to the deterioration of the wire-bonds as a function of the bond life.

Until today, the Al-Cu wirebond interface was investigated by OM and SEM in samples which were mechanically polished, making it difficult to distinguish between the different Al-Cu intermetallics. Attempts were also made to resolve the

intermetallic composition of the bonds via EDS incorporated in SEM [2].

2. Experimental procedure

In the present study, transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM) and TEM-EDS were used for quantitative analysis of the intermetallic composition of as-bonded and heat-treated Al-Cu wire-bonds. A dual beam focused ion beam (FIB) was used to prepare site-specific TEM samples. FIB was also used for preliminary analysis of cross-sections by ion-beam and high-resolution SEM. In order to understand the processes that occur at the Al-Cu interface, as-bonded samples and samples annealed in air and argon were prepared. The channeling effect may occur for incident ions if a crystal in the sample is oriented in a low index zone axis. In these conditions, the ion beam will penetrate deeper into the target before significant inelastic scattering occurs, resulting in a lower probability of secondary electrons escaping from the sample due to their limited mean-free-path. As a result, grains oriented in a low index zone-axis will have a darker contrast than randomly oriented grains (Figure 1).

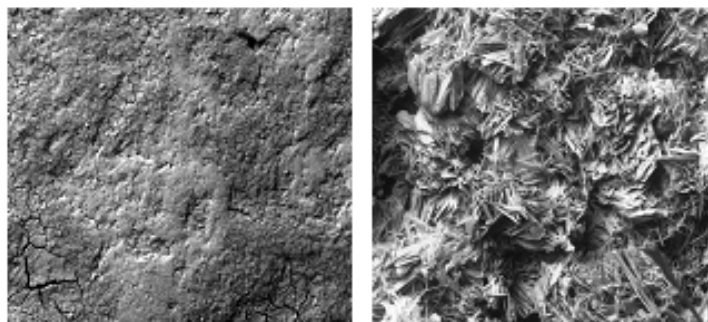


Fig. 1. (a) Secondary electron SEM micrograph of the as-bonded Al-Cu interface and (b) ion induced secondary electron micrograph of the same specimen, showing the Cu grain morphology.

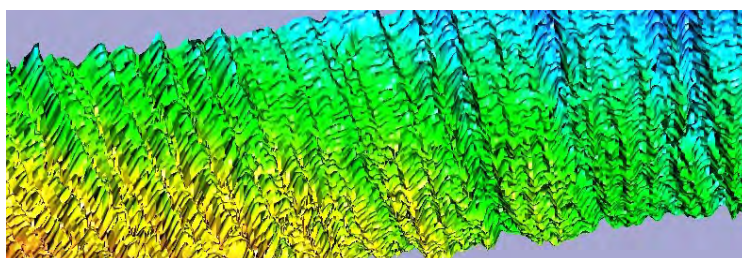


Fig. 2. HAADF-STEM micrograph of the asbonded Al-Cu wire-bond cross-section. A nonuniform intermetallic region is evident.

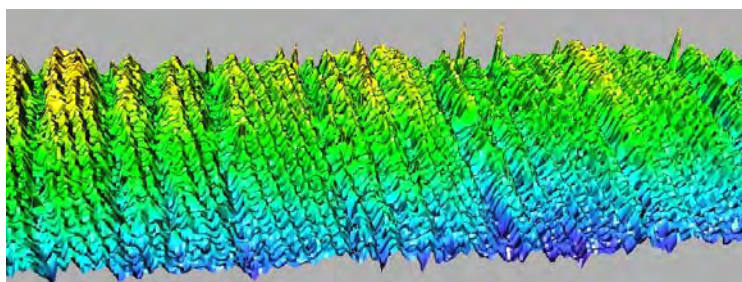


Fig. 3. Bright field TEM micrograph of a central region of a Al-Cu wire-bond annealed for 24 hours in argon at 175°C. The inset diffraction pattern is of the dark intermetallic grain.

Figure 2 presents high angle annular dark field (HAADF) STEM micrograph of an area of the as-bonded Al-Cu wire bond, indicating that intermetallic phases are formed in the as bonded samples [3]. EDS analysis confirmed the presence of Al-Cu intermetallics, and that changes in the Cu concentration in the large intermetallic region was not monotonic as a function of a distance from the copper layer. The composition of the intermetallic regions in heat-treated samples was evaluated by TEM-EDS and, wherever possible, confirmed by selected area electron diffraction patterns (Figure 3).

2. Tape Automated Bonding (TAB). They will accommodate the flat TAB tape lead and provide the proper material for a reliable connection to the tape [4]. The bump fabrication process uses a metal deposition and plating process. First a series of barrier and seed layers of metal are deposited over the surface of the wafer. A layer of photoresist is deposited over these barrier and seed layers. A photomask is used to pattern the locations over each of the pads that will be bumped. An etching process exposes the pads, and the open resist hole defines the shape and height of the bump. The bump, which is typically gold, is then electroplated over the pad and the deposited

barrier metals. Once the plating is complete, a series of etching steps are used to protect the underlying materials from being etched. While gold bumping is the most common, copper, tin-lead, as well as layered combinations of these materials are used for

bumping. An alternative to die bumping is to create bumps on the tape.

For high leadcounts, wafer bumping is more common. Figure 4.1 illustrates a completed bump and a TAB tape lead.

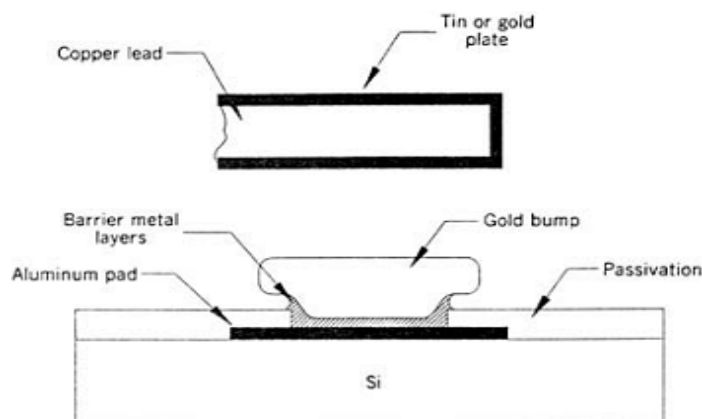


Fig. 4. Tab with wafer bumping

Gold top wafer metallurgy had been practiced in the past. With exception of GaAs and TAB, gold had been replaced by aluminum interconnects and then by advanced copper interconnects. Lower material cost plus ultra-fine line capabilities of both aluminum and copper were reasons for the displacement of gold as interconnect. However, to enter high temperature IC applications, to achieve superior reliability or to dissipate greater power, the resurrection of gold as the top metal is both practical and effective. This protective gold top is coined Power Au for the ability of gold to increase power capabilities of ICs, packages and systems. Au wire bonded to aluminum forms many Au-Al intermetallics. This interdiffusion of Au atoms into Al bond pads is well studied. At higher temperature, diffusion and growth rate of intermetallics also accelerate. If the entire thickness of aluminum bond pad were converted into Au₄Al intermetallic, then the poor adhesion of Au₄Al to barrier metal between aluminum layers can result in wire bond separation and electrically open failure. Even as Au₄Al intermetallic is growing,

Kirkendall's voids coalesce into hairline crack at intermetallic interface. These weakened interfaces are susceptible to stress failure and again result in electrically open failure. The metal between Power Au and Al is not a perfect barrier however. Under higher temperature testing, barrier metal does eventually break down. Above 250°C plus self heating from 860mA current, gold atoms punch through the barrier metal and then gold diffuse into aluminum. Rapid diffusion of Au into Al Power Au line immediately above contact to aluminum.

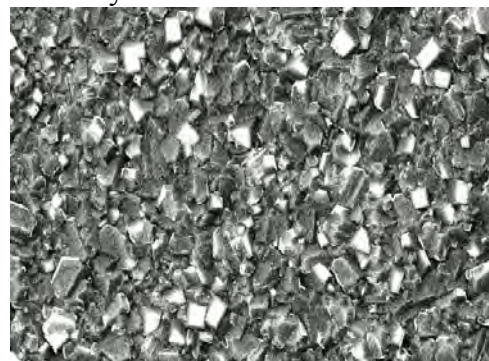


Fig. 5. Power Au line with void above contact to aluminum after extremely high temperature testing and 860mA current. Gold diffused into aluminum and left a void.

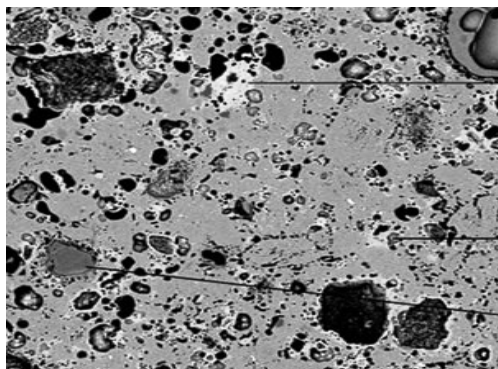


Fig. 6. Shows a cross section of a Au-Al bond

The wire pull test is used to measure the strength and failure mode of the wire bond. A small hook is bond to gauge the strength of the 1st bond or next to the wedge at the 2nd bond to ensure a reliable weld. Generally, if the hook is placed at the mid span of the wire, then the test will show the weakest link of the bond. This is typically either the neck of the ball bond (right above the ball) or at the heel of the wedge bond. The Pull test is basically a function of the wire diameter. Loop height & wire span are the most significant factors that determines the strength of a wire for a given wire diameter. Shorter span & a lower loop will result in a lower pull strength. As opposed to a longer span & a higher loop height which will result in higher pull strength. Copper wire bonding is normally formed by a copper ball onto an aluminum based bond pad in microelectronic package. However, copper oxidation at the interface of Cu- Al bonding area causes the cracks, decreases the interfacial shear strength, and weakens the Cu-Al bonding. Surface analysis of ball-peeled pad of Cu-Al bonding using XPS demonstrates the copper oxidation in the Cu-Al interface after autoclave test (at 121oC and 100% relative humidity). The binding energy scans for Cu 2p on the specimen after 0, 192, 384, and 576 hours in autoclave test chamber is carried out.

After 576 hours corrosion, the chemical change of copper in a few atomic layers of surface from Cu to CuO. Furthermore, there are two major copper oxides peaks observed in the study, CuO and Cu(OH)₂. Cu₂O is not stable in air and change to CuO immediately. Therefore, Cu₂O is not expected to be detected at the specimen [7].

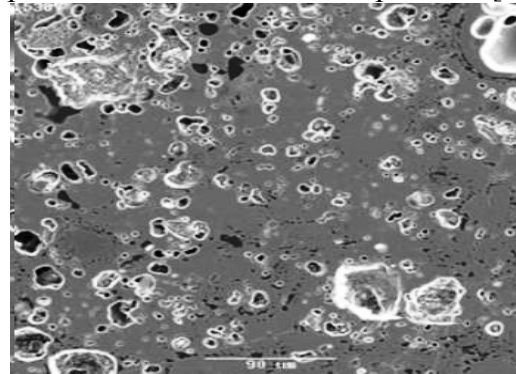


Fig. 7. SEM pictures show corrosion and a crack after test hour increase (X1000)

Low cost, high thermal and electric conductivity, easy fabricating and joining, and wide range of attainable mechanical properties have made copper widely used in electronic packaging, such as lead frames, interconnection wires, foils for flexible circuits, heat sinks, and WPB traces. However, unlike the aluminum oxide, the copper oxide layer is not self-protect. Therefore, copper is readily oxidized, especially at elevated temperature. Copper oxidation interface of Cu-Al bonding area causes the cracks, decreases the interfacial shear strength, and weakens the Cu-Al bonding. Also, Copper oxidation in the area of the lead frames die pad and mold compound causes the delamination of packages. Furthermore, the moisture penetrates through the crevices because copper oxidation induces poor adhesion in the area of the copper lead frames and molding compound, creating corrosion problem in the packages.

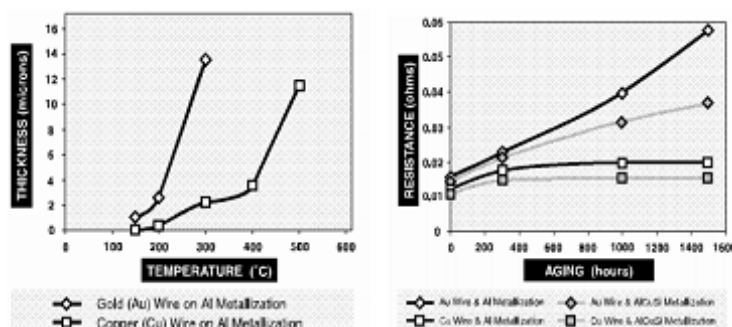


Fig. 8. Intermetallic thickness vs. exposure for 6 hrs at respective temperature b) effect of wire material & substrate metallization on electrical resistance after aging

Tests show that, after exposure at various temperatures, intermetallic growth is significantly slower in copper wire bonds than in gold wire bonds. and device performance. Tests also show that despite a lower amount of intermetallic penetration, pull force and shear testing show values that are equivalent to, or greater than, those obtained with gold wire. Potential for maximum conductivity, device performance (tact frequencies of <500 MHz) and resistance to degradation in a mono-metallic system are the driving forces for the use of Cu wire in packages with Cu pads. DHF and iCu wire have been successfully ball-bonded to bare Cu lead frames and also AlSiCu metallized pads [8].

3. Conclusions

Recent studies have shown that, in many applications, copper wire bonding can provide better performance and reliability than gold wire bonding. While copper wire and ribbon have been used in discrete and power devices for many years, these latest studies also show that successes in ball bonding thin copper wire to aluminum, silver-nickel plating and even bare copper, provide the potential for its use in high-end, fine-pitch packages with higher lead counts and smaller pad sizes. For these reasons, along with the lower inherent cost of copper material, Kulicke & Soffa Bonding Wire [8] has developed and optimised two copper wire products: DHF copper wire for ball and

wedge bonds in power devices and discrete packages; and iCu for fine-pitch or high-end IC applications.

Acknowledgment

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References

- [1]. M. Drozdov, G. Gur, Z. Atzmon, and W.D. Kaplan *Microstructural Evaluation of Al-Cu Intermetallic Phases in Wire-Bonding*;
- [2]. G. Harman, "Wire Bonding in Microelectronics Materials, Processes, Reliability and Yield", 2 ed., *Electronic Packaging and Interconnection*, ed. C.A. Harper. 1997: McGraw-Hill;
- [3]. F.W. Wulff, C.D. Breach, D. Stephan, Saraswati and K.J. Dittmer, *Characterization of Intermetallic Growth in Copper and Gold Ball Bonds on Aluminum Metallization*, *Proceedings of Electronics Packaging Technology Conference*, 6th, Singapore, Dec. 8-10, 2004: 348-353, 2004.
- [4]. *** *Semiconductor Packaging Module II*;
- [5]. James J. Wang and Bob Baird *Power gold for 175°C Tj max* ;
- [6]. *** *Semiconductor Packaging Assembly Technology 2000 National Semiconductor Corporation*;
- [7]. Ying Zheng *Study Of Copper Applications And Effects Of Copper Oxidation In Microelectronic Package In Partial Fulfillment of MatE 234 2003*;
- [8]. Kulicke & Soffa *Complete Connection DHF & iCu Copper Bonding Wire for Power Devices and High-End ICs*.

OPPORTUNITIES TO ANALYSE THE POLLUTION IN METALLURGICAL INDUSTRY

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ABSTRACT

The metallurgical industry is a highly polluting economic sector. In order to establish measures to minimise the pollution, new methods are needed to analyse such processes.

This article analyses the following possibilities:

- *thermodynamic analysis;*
- *analysis with system theory elements;*
- *characterization of pollution as global phenomenon of soiling;*
- *possibilities of maintaining a balance between the economic development and pollution.*

KEYWORDS: pollution, analysis, life cycle

1. Introduction

In metallurgy, the life cycle phases of a product we are mostly interested in are:

- **product manufacturing**, in which the material resources and energy, through the technological process, are transformed into product;
- **use of the product**, in which, through the *disintegration of the material and scrapping* (by destruction) of the product, it is transformed into secondary material (waste).

Both phases, objectively, generate pollutants. Some of pollution assessment methodologies that can be used for scientific and practical purposes are represented by:

- thermodynamic analysis;
- analysis with system theory elements;
- characterization of pollution as global phenomenon of pollution;
- possibilities of maintaining a balance between the economic development and pollution.

2. Thermodynamic analysis

The evolution of manufacturing processes, use and generation of pollutants (among which enters and wastes) is governed by the laws of thermodynamics.

2.1. Analysis using the first principle of thermodynamics

It is recommended that pollution analysis using first principle of thermodynamics to be made by taking into account the considerations below.

- The scheme of the simplest operating system includes the following metallurgical measures (Fig. 1):

- * input measures;
- * output measures, which consist of:
 - useful measures;
 - losses

- It is proposed that the pollutants (materials and energy transferred to the external environment) to be considered losses [1].

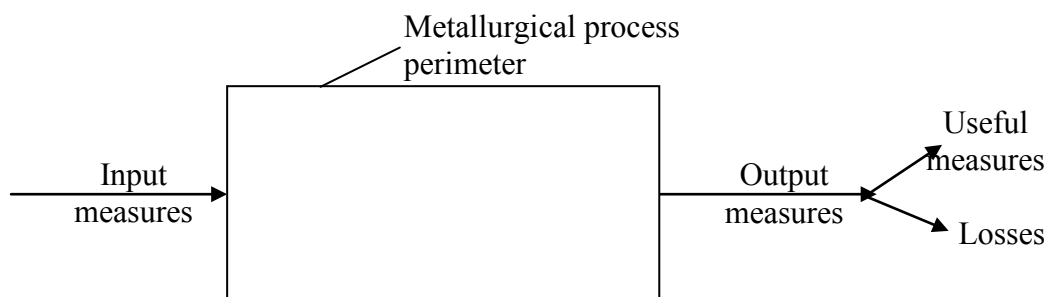


Fig. 1. Scheme of thermodynamic operation of a technological process.

- The idea that pollutants are system losses should be reported to the first principle of thermodynamics, that there is no system to function without losses (*zero losses*). In these circumstances, the concept of zero waste plant (launched also in metallurgy), but not justified in terms of thermodynamic. It must be accepted and operationalised as target [2].

- The zero waste status can result only in case of cancellation of the technological process (production stoppage).

- A similar situation concerns the risk analysis. Any industrial activity is associated with risks, reason why the target of environmental policy, of **zero risk** level, is unrealistic, because it can only be achieved by stopping the production [3]. To run the industrial activity, ***we should be aware of the existence of potential risks, to accept the consequences of some of them and / or to take measures to minimize unacceptable risks.***

2.2. Analysis using the second principle of thermodynamics

In this case, it is an entropic analysis, where two important thermodynamic measures are used:

- *Entropy*, S , which is a measure of the degree of disorder (chaos) in the organization of matter; where the growth of

S characterizes the spontaneous tend of the systems to chaos;

- *Negentropy* (*antientropia*), nS , which characterises the level of the ordered organisation of matter and energy.

For analyses of pollution phenomena using the second principle, we make some recommendations:

- As losses to the environment, *the pollutants represent a state of disorder*. It follows that the generation of pollutants is an anti-entropic phenomenon, inadvisable in terms of the second principle of thermodynamics [1].

- The manufacturing phase (process technology) is an activity to increase the degree of order on the path *natural resources - metal product*. It concludes that *advanced processing* of natural resources is recommended in the pollution minimize policies.

- The degree of disorder (entropy S) of pollutants increases with increasing the duration of keeping them in the environment. It is recommended that into a flow designed with the reintegration (recirculation, recycling, or regeneration) of wastes *to reduce the number of reintegration*.

- The degree of disorder (entropy S) of wastes increases with increasing the distance between the location of generation and the location of reintegration.

•

In this situation, it is recommended:

- To decrease the distance between the two locations;
- To use internal reintegration (waste recovery inside the perimeter of the facility that generated them) detrimental the external reintegration (recovery of wastes in other locations).

3. Analysis with system theory elements

Analysis of pollution phenomena and pollutants can be also done by using the systems theory. We take into account the aspects presented below.

- It is proposed that in the structure of the natural system, the pollution to be considered as *disturbance process*, and the

pollutants – *disturbance measures (noises)*, (Fig. 2).

- According to the systems theory, *a certain amount of noise must exist to maintain the order*, because it provides information on system status. It concludes that to *maintain the life* of the system requires a certain minimal amount of disturbance.

It is argued in this way that **zero pollution** is not only impossible to be reached, but a certain amount of pollution must be kept to a minimum rate.

- It is proposed that the routes of the secondary materials reintegration to be considered *feedback paths* (Fig. 3).

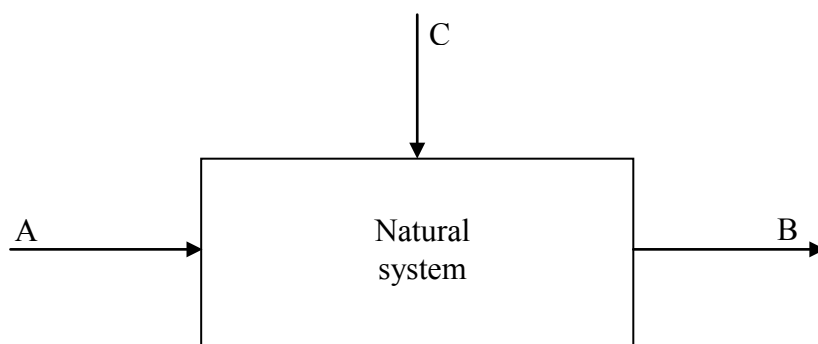


Fig.2. The simple structure of the natural system.

A – input measures (control measures; measures to transform the natural ecosystems);
B – output measures (parameters regarding the productive capacity in resources, parameters for rational use of resources, parameters on carrying capacity); C – disturbance measures (pollutants, including wastes)

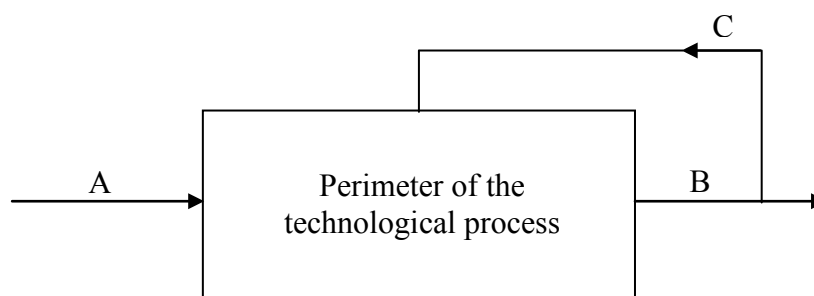


Fig.3. Diagram of the technological process as a system.

A – input measures; B – output measures; C – feet-back path of the wastes

- If the reintegrated secondary materials (wastes) are subject of feed-back, they can perform two functions:

- Transport of materials (secondary material resources) and energy (secondary energy resources);

- Information transportation represented by the technological deviations that led to wastes; reintroduced in the primary sequences of the flow, such information becomes levers of the system (self) control.

- The self-adjustment ability of a system, i.e. the capacity of self-sustainability of the natural system in its relations with the economic and social system, depends on the diversity of its behaviour. We deduct from this the *need to diversify* the base of raw materials and energy of metallurgy, on the one hand, and the *metallurgical production*, on the other one.

- The need to exist losses to the environment (pollution) must be correlated with another rule of systems theory showing that in a systemic evolution, *the presence of losses stimulates the development*.

4. Characterization of pollution as a global phenomenon of soiling

One of the meanings that can be given to pollution is the soiling. Etymologically, by its Latin origin (poluo-polluere), the term *to pollute* means *to soil*, and *pollution* can be interpreted as soiling.

There are many situations (economic, social and environmental) that can be treated as soiling phenomena (quality deterioration). So, it becomes possible a new approach of the phenomena of pollution, by extending the application of the environmental laws in other areas (industrial and even social). In this context, we can say that exist:

- *conventional pollution phenomena* including the known classic cases on the relation environmental pollutants → environmental factors → quality of life;

- *unconventional pollution phenomena* relating to the process interaction between environments and special items, of which qualitative alteration can be studied based on principles of ecology.

For the second case, this article refers to two situations: use of metallic implants and the use of metal ornaments. The interactions between them and the substances of human body are considered to be a process of pollution. The process of interaction between human body and the objects mentioned above is in fact a process of soiling them or their bodies.

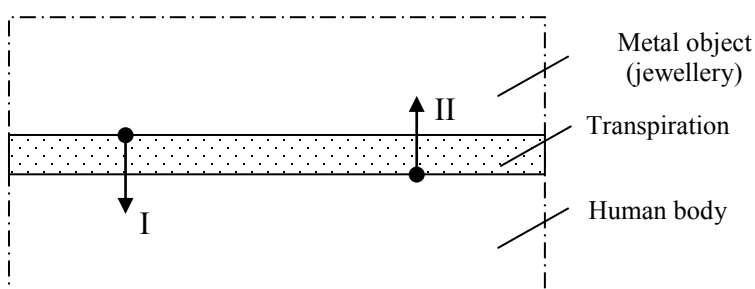


Fig. 4. Examples of unconventional pollution (soiling):
 I) direct pollution; II) indirect pollution.

It concludes that it is a process of bi-univocal pollution (Fig. 4):

- *unconventional direct pollution*, which means pollution on the relation metal object → *human body* and refers to the negative impact of the object on the body;

unconventional indirect pollution, which means pollution on the relation *human body* → *object* and refers to the negative impact of body on the object, with direct implications on the duration of its social utility.

5. Possibilities of maintaining a balance between the economic development and pollution

Optimizing the correlation between development and pollution is a fundamental issue of knowledge in today's society. It is also known as the *contradiction* between the *human activity* and *environmental conditions*.

The currently recommended measures to mitigate this contradiction are placed in two categories:

- measures of technical and technological nature;
- measures of social-political-administrative nature.

In this article, we analyse a possible situation in metallurgy.

- The target-binding development in metallurgy can be characterized by the production of steel P [tonnes of steel / year].

Under development strategies, it must have an upward trend (Fig. 5, trend 1).

- Manufacture of steel is accompanied by CO_2 generation. The process is evaluated using the emission factor $f_{\text{CO}_2} [t \cdot \text{CO}_2 / t \cdot \text{steel}]$. Where no action is taken to minimize the CO_2 emissions, the factor f_{CO_2} has constant values (Fig. 5, trend 2).

- The CO_2 quantity is Q_{CO_2} :

$$Q_{\text{CO}_2} = P \cdot f_{\text{CO}_2}, [t \cdot \text{CO}_2 / \text{year}]$$

Where no action is taken to minimize the CO_2 emissions, this indicator is trending upward (Fig. 5, trend 3).

- By taking measures to decrease the CO_2 emissions, the factor f_{CO_2} is trending downward (Fig. 5, trend 4).

- By reducing f_{CO_2} , we can also reduce Q_{CO_2} (Fig. 5, trend 5), although P increases.

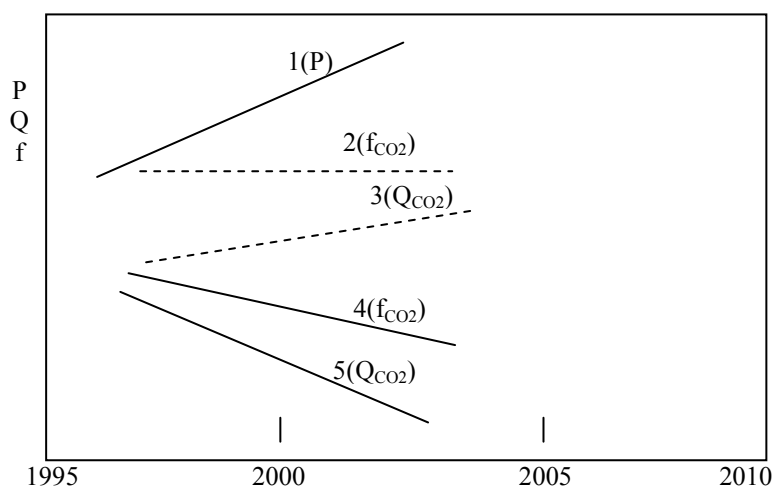


Fig.5. The dynamics of relationship between development and pollution.

6. Conclusions

- * It is proposed that pollutants to be considered *losses* from the technological process perimeter to the environment.

- * It is proposed that pollutants to be considered disturbances (noises) in the natural system.

- * The activities and the anti-entropy actions determine the reduction of the pollutants quantities.

- * To use the environmental laws to analyze the phenomena in different areas, it is recommended that pollution to be considered a soiling process.

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References

* To solve the contradiction between development and pollution, it becomes necessary to minimize the emission factors given by the industrial activities.

- [1]. Nicolae A., et. a. (2009), *Econologie metalurgică*, Ed. Printech, București.
- [2]. Nicolae A., et. a. (2001), *Management ecometalurgic*, Ed. Fair Partners, București.
- [3]. Ursul A., Rusandu I., Capvelea A., (2009), *Dezvoltarea durabilă: abordări metalurgice și de operaționalizare*, Ed. Științifică, Chișinău.
- [4]. Vădineanu A., (2004), *Managementul dezvoltării: o abordare ecosistemică*, Ed. Ars Docendi, București.

A STUDY OF THE REMOVAL CHARACTERISTICS OF Cu(II) FROM WASTEWATER BY ASPERGILLUS ORYZAE

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ABSTRACT

In this study, the biosorption behavior of Aspergillus oryzae ATCC (American Type Culture Collection) biomass, with respect to Cu²⁺ ions, has been studied in order to consider its application to the purification of copper containing wastewater. The batch method was employed: parameters such as pH, contact time, and initial metal concentration were studied. The influence of the pH of the metal ion solutions on the uptake levels of the copper ions from wastewaters containing CuS nanoparticles by fungus biomass used were carried out between pH 3.5 and pH 7.5. The optimum pH was 6. An equilibrium time of 5 days was required for the biosorption and biosolubilization of Cu(II) ions onto Aspergillus oryzae biomass. The results showed that Aspergillus oryzae biomass has potential to remove cationic heavy metal species from industrial wastewaters.

KEYWORDS: copper removal, biosorption, bioleaching

1. Introduction

Water and soil are receivers of thousands of contaminants such as inorganic and organic compounds. These contaminants enter in natural systems as a result of actions like improper disposal of wastes, wastewaters and waste accidental and intentional discharges, spills. All the contaminants have negative effects to the ecosystems, and human health.

The effects depend on the nature of the contaminants, their concentration or composition, and on the receptor characteristics.

Consequently, the treatment of polluted industrial and municipal wastewater and wastes remains a topic of global concern since wastewaters must ultimately be returned to receiving waters or to the land

[1-4]. Heavy metals found in wastewaters in dissolved form and as nanoparticle suspensions are harmful to a variety of living organisms. Through the food chain they can accumulate in organisms.

The removal of heavy metals from wastewaters and wastes is essential not only to protect the water, and soil resources, but also to slow down the fast depletion of heavy metals sources.

Conventional methods such as: chemical precipitation, electrochemical treatment, ion exchange processes, solvent extraction, membrane separation and evaporation [5] were applied in order to remove heavy metals from industrial effluents. These conventional methods have many advantages and disadvantages.

Some of them are ineffective and unfavorable because they determine huge

amounts of sludge that involve disposal problem, and some of them are expensive and determine incomplete removal of heavy metals [6].

Adsorption is most widely used in removal of metal ions from aqueous solutions because as adsorbent can be used numerous materials such as: clays, zeolites, activated carbon.

Biosorption is considered as an alternative process for the removal of heavy metals, metalloid species, compounds and particles from aqueous solution by biological materials [7, 8]. Biomaterials are adsorbent materials with high heavy metals adsorption capacity. They have many advantages such as reusability, low operating cost, improved selectivity for specific metals of interests, removal of heavy metals found in low concentrations in wastewaters, short operation time, and no production of secondary compounds which can be toxic [7].

The high biosorption capacity of fungal biomass is due to the fact that fungal cell walls mainly have in composition compounds such as polysaccharides, proteins and lipids whose functional groups can be involved in heavy metals bonding. In addition they can tolerate adverse conditions like low pH medium.

Many fungal strains such as *Aspergillus niger* [1], *Aspergillus flavus* [8], *Aspergillus versicolor* [9], *Fusarium* [10], *Gliomastix murorum* [11], *Pleurotus ostreatus* (a macro-fungus) [3], *Pleurotus pulmonarius* [12], *Trametes versicolor* [5], *Penicillium* [13], *Schizophyllum commune* [12], *Rhizopus arrhizus* [14], were used in copper removal from wastewater.

The objective of the present study was to investigate the use of *Aspergillus oryzae* biomass as a biosorbent for the removal of Cu(II) from an aqueous solution that contains nanoparticles of CuS. The quantity of biomass grown in the presence of CuS was determined. The optimum biosorption conditions were determined as a function of

initial pH, initial metal ion concentration and time.

The choice of metal was made with regard to its industrial use and potential pollution impact. It is well-known that copper is not acutely toxic to humans but its extensive use and increasing levels in the environment may cause serious health problems [8].

2. Materials and methods

2.1. Growth of culture

The fungus strain was propagated on potato dextrose agar (PDA) 39 g·L⁻¹ and malt extract 0.1 g·L⁻¹ for 5-7 days at 30°C. Copper(II) uptake studies were carried out in liquid minimal medium containing 30 g·L⁻¹ dextrose, 10 g·L⁻¹ peptone, 0.4 g·L⁻¹ KH₂PO₄, 0.2 g·L⁻¹ MgSO₄·7H₂O. The pH of the growth medium was 6.24. After inoculation, flasks were incubated at 150 rpm for 8 days at 30°C using Thermoshake (an Incubator Shaker).

2.2. Copper containing effluents

Copper was used in the form of copper sulfide nanoparticles. These nanoparticles were previously obtained and characterized [15, 16]. CuS nanoparticles used have an average diameter of about 20-30 nm [17].

2.3. Analytical procedures

Metal content in final solution after the biomass growth was determined after the filtration of biomass with the use of atomic absorption spectroscopy (AAS) (ANALYTIK-JENA – AAS Multi-Element with Continuum Source ContraAA®700).

2.4. Biosorption

Aspergillus oryzae ATCC fungal strain was inoculated into 100 mL copper solution with an initial concentration of 25 mg Cu(II)·L⁻¹ obtained in liquid minimal medium containing 30 g·L⁻¹ dextrose, 10 g·L⁻¹ peptone, 0.4 g·L⁻¹ KH₂PO₄, 0.2 g·L⁻¹

KH_2PO_4 , $0.2 \text{ g} \cdot \text{L}^{-1}$ $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. The pH of the growth medium was 6.24. Controls were run with a fungal biomass system without copper. After the biosorption experiments samples were taken and filtered. The supernatant was used to analyze the residual copper ion concentration. Equilibrium time and its conditions were determined through the kinetic studies.

2.5. Effect of initial ion concentration on biosorption of Cu(II) by *Aspergillus oryzae*

Experiments were carried out at different Cu(II) concentrations varying from 25 to 100 mg/L at 6.45 pH to establish the effect of initial Cu(II) ion concentration onto *Aspergillus oryzae* biosorption capacity.

2.6. Effect of contact time

The fungal strain used in this study was inoculated into a glass vial which contains 100 mL of copper 25 mg/L and minimum liquid medium growth. The initial pH was 6.45, and the temperature was $30 \pm 1^\circ\text{C}$. The time varied between 24 and 192 h. After the contact between solutions containing CuS and fungal biomass each sample was filtered, and tested for copper ion concentration.

2.7. Effect of temperature

Aspergillus oryzae ATCC fungal strain was inoculated into 100 mL solutions containing $25 \text{ mg Cu(II)} \cdot \text{L}^{-1}$ at 20, 25, 30, 35, 40°C . The mixtures were shaken at 150 rpm until reaching the equilibrium.

2.8. Effect of pH solution

Aspergillus oryzae fungal strain was inoculated into 100 mL solutions containing $25 \text{ mg Cu(II)} \cdot \text{L}^{-1}$ with an initial pH of 3.5, 4, 4.5, 5, 5.5, 6, 6.5, and 7.5. The pH was varied using HCl 1M, and NH_4OH 25% solutions. The mixtures were shaken at 150 rpm until reaching the equilibrium.

2.9. Elution study

At the end of biosorption, biomass of *Aspergillus oryzae* was contacted with 100

mL of 0.05 HNO_3 in deionized water. The mixture was shaken at 150 rpm on Thermoshake at $30 \pm 1^\circ\text{C}$ for 24 hours. After elution, the mixture was filtered, and the copper ion concentration of supernatant was determined.

3. Results and discussion

Kinetic studies of *Aspergillus oryzae* fungal strain were performed as batch tests. These tests were performed in order to establish the factors which influence copper removal processes from wastewaters by *Aspergillus oryzae* fungal strain.

The quantity of biomass grown in presence of liquid medium growth that contains different quantities of CuS nanoparticles (different Cu(II) concentrations), and dry substances content of biomass is presented in Table 1.

Table 1. Biomass quantity and dry substance content of biomass grown in absence and in presence of different concentrations of Cu(II)

Cu(II) concentration, mg/L	0	25	50	75	100
Biomass quantity, g	22.8282	23.0517	17.8123	13.3592	7.3025
Dry substance content, %	9.37	4.26	5.39	6.42	12.22

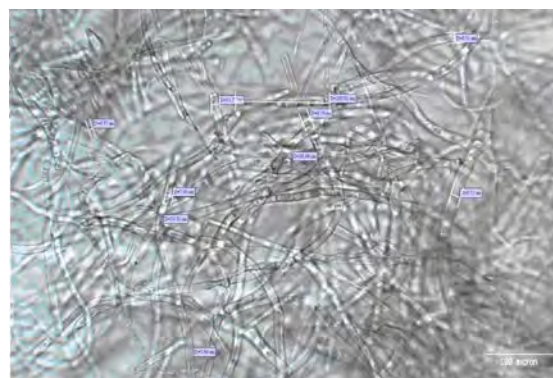


Fig. 1. *Aspergillus oryzae* grown in presence of CuS

From Table 1 it can be concluded that the quantity of biomass decreases with the increasing of copper content in the aqueous solution, and the dry substance content increases with increasing of copper content. In Figure 1 are presented fungal strain grown in presence of CuS. The fungal hife have a diameter of 4-15 μm , and the length of the hife between 30 to 140 μm (Figure 1).

3.1. Effect of initial ion concentrations on biosorption of Cu(II) by *Aspergillus oryzae*

The quantity of Cu(II) removed by *Aspergillus oryzae* fungal strain was determined using the following equation:

$$Q = \frac{(C_i - C_e) \cdot V}{m} \quad (1)$$

where:

Q – copper uptake per unit of dry biomass ($\text{mg} \cdot \text{g}^{-1}$);

C_i – initial copper concentration ($\text{mg} \cdot \text{L}^{-1}$);

C_e – equilibrium copper concentration ($\text{mg} \cdot \text{L}^{-1}$);

V – suspension solution volume (L);

m – quantity of dry biomass (g).

Removal efficiency was calculated using the equation no. 2:

$$\text{Removal efficiency} = \left[\frac{\text{mg Cu(II) removed}}{\text{mg Cu(II) available}} \right] \cdot 100 \quad (2)$$

Table 2 presents data obtained in case of Cu(II) biosorption by *Aspergillus oryzae* ATCC fungus strain.

Table 2. The effect of initial Cu(II)

Cu(II) concentration, $\text{mg} \cdot \text{L}^{-1}$	Copper quantity uptake, $\text{mg} \cdot \text{g}^{-1}$	Removal efficiency, %
25	2.1395	84.04
50	4.6784	86.07
75	7.1512	89.83
100	8.8724	90.95

concentration to the biosorption capacity and removal efficiency

As can be seen from Table 2, biosorption of Cu(II) ions increased with increasing initial concentration of metal ions. These values of biosorption capacities are consistent with literature data. Thus are mentioned the following values of biosorption capacities of *Rhizopus arrhizus*, *Aspergillus niger*, and *Aspergillus flavus* for Cu(II): 10.76 mg/g , 9.53 mg/g , and 10.82 mg/g biosorbent [18, 8]

3.2. Effect of contact time

The effect of the contact time on biosorption of Cu(II) on *Aspergillus oryzae* biomass is shown in Figure 2.

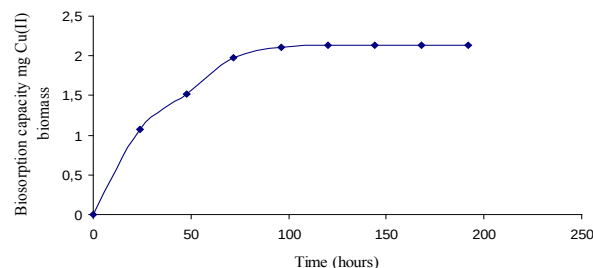


Fig. 2. Effect of contact time between biomass and solution with 25 $\text{mg Cu(II)} \cdot \text{L}^{-1}$ in the form of CuS

In this case biosorption is a lent process because equilibrium was reached after 5 days of contact between biomass and solution containing CuS.

The maximum removal occurred in 5 days. After this equilibrium period the amount of adsorbed Cu(II) ions did not change significantly with an increase in contact time.

3.3. Effect of temperature

The effect of temperature on the removal efficiency of *Aspergillus oryzae* ATCC is presented in Figure 3.

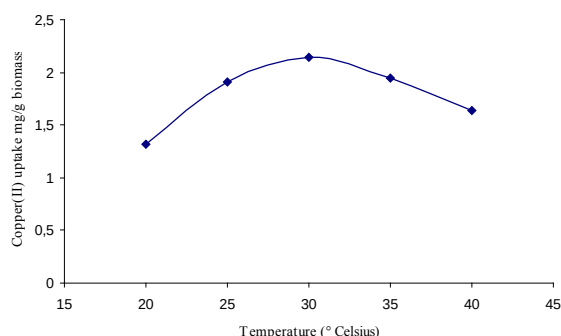


Fig. 3. Effect of temperature onto *Aspergillus oryzae* biosorption capacity

From this Figure it can be seen that copper uptake increases with increasing of the temperature to a maximum value of biosorption capacity at 30°C. After this temperature the biosorption capacity decreases.

3.4. Effect of pH solution

Biosorption capacity was determined in function of pH value. pH range used was 3.5 - 7.5. In Figure 4 are presented results obtained about the effect of solution pH to the biosorption capacity. From this figure it can be seen that biosorption capacity increases with increasing of pH from 3.5 to 6.

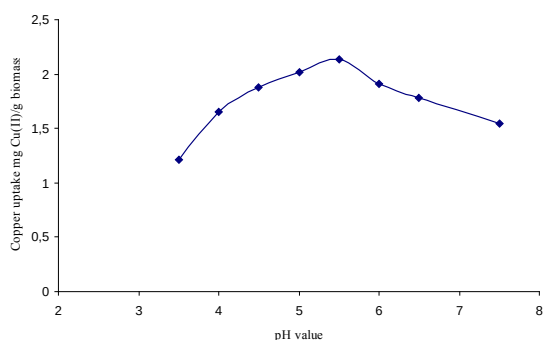


Fig. 4. Effect of pH on the removal efficiency of *Aspergillus oryzae* fungal strain

Maximum biosorption occurs at pH 6. After this value of pH, biosorption capacity decreases due to the formation of copper hydroxides.

These results are in concordance with literature data which mentioned the following values of pH for maximum Cu(II) adsorption: 6.5 for *Aspergillus niger* [3], 5 for *Trametes versicolor* [5], 6 for pretreated *Aspergillus niger* biomass [19].

3.5. Elution study

After biosorption process occurs it was made experiments to remove copper from biomass. The biomass of *Aspergillus oryzae* ATCC loaded with Cu(II) was contacted with 100 mL of 0.05 HNO₃ in deionized water at 150 rpm on Thermoshake at 30±1°C for 24 hours. After elution, the mixture was filtered, and the copper ion concentration of supernatant was determined. Copper ion concentration removed from biomass was 3.21 mg/L.

4. Conclusions

Optimum conditions was determined for Cu(II) removal from aqueous solutions containing nanoparticles of CuS by *Aspergillus oryzae* ATCC.

The results obtained showed that in case of aqueous solution that contains 25 mg Cu(II)/L in the form of CuS nanoparticles the maximum biosorption was reached at 120 hours of contact, 30°C and 6 value of pH.

Acknowledgements

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References

- [1]. Tsekova T., Todorova D., Ganeva S., *Removal of heavy metals from industrial wastewater by free and immobilized cells of Aspergillus niger*, International Biodeterioration & Biodegradation 64, p. 447, 2010.
- [2]. Tsekova T., Todorova D., Dencheva V., Ganeva S., *Biosorption of copper(II) and cadmium(II) from aqueous solutions by free and immobilized biomass of Aspergillus niger*, Bioresource Technol. 101, p. 1727, 2010.
- [3]. Javaid A., Bajwa R., Manzoor T., *Biosorption of heavy metals by pretreated biomass of Aspergillus niger*, Pak. J. Bot., 43(1), p. 419, 2011.
- [4]. Javanbakht V., Zilouei H., Karimi K., *Lead Biosorption by different morphologies of fungus Mucor indicus*, International Biodeterioration & Biodegradation, 65, p. 294, 2011.
- [5]. Subbaiah M.V., Vijaya Y., Reddy A.S., Yuvaraja G., Krishnaiah A., *Equilibrium, kinetic and thermodynamic studies on the biosorption of Cu(II) onto Trametes versicolor biomass*, Desalination doi:10.1016/j.desal.2011.03.067, 2011.
- [6]. Tuzun I., Bayramoglu G., Yalcin E., Basaran G., Celik G., Arica M.Y., *Equilibrium and kinetic studies on biosorption of Hg(II), Cd(II) and Pb(II) ions onto microalgae Chlamydomonas reinhardtii*, J. Environ. Manage., 77(2), p. 85, 2005.
- [7]. Mungasavalli D.P., Viraraghavan T., Chunglin Y., *Biosorption of chromium from aqueous solutions by pretreated Aspergillus niger: batch and column studies*, Colloids. Surf. A Physicochem. Eng. Aspects, 301, p. 214, 2007.
- [8]. Akar T., Tunalı S., *Biosorption characteristics of Aspergillus flavus biomass for removal of Pb(II) and Cu(II) ions from an aqueous solution*, Bioresource Technology, 97, p. 1780, 2006.
- [9]. Taştan B. E., Ertuğrul S., Dönmez G., *Effective bioremoval of reactive dye and heavy metals by Aspergillus versicolor*, Bioresource Technology, 101, p. 870, 2010.
- [10]. Pan R., Cao L., Zhang R., *Combined effects of Cu, Cd, Pb, and Zn on the growth and uptake of consortium of Cu-resistant Penicillium sp. A1 and Cd-resistant Fusarium sp. A19*, Journal of Hazardous Materials, 171, p. 761, 2009.
- [11]. Li X., Xu Q., Han G., Zhu W., Chen Z., He X., Tian X., *Equilibrium and kinetic studies of copper(II) removal by three species of dead fungal biomasses*, Journal of Hazardous Materials, 165, p. 469, 2009.
- [12]. Veit M. T., Tavares C. R. G., Gomes-da-Costa S. M., Guedes T. A., *Adsorption isotherms of copper(II) for two species of dead fungi biomasses*, Process Biochemistry, 40, p. 3303, 2005.
- [13]. Su X.Z.H., Xiao T.T.G., *Study of Thermodynamics and Dynamics of Removing Cu(II) by Biosorption Membrane of Penicillium Biomass*, Journal of Hazardous Materials doi:10.1016/j.jhazmat.2011.03.014, 2010.
- [14]. Preetha B., Viruthagiri T., *Application of response surface methodology for the biosorption of copper using Rhizopus arrhizus*, Journal of Hazardous Materials, 143, p. 506, 2007.
- [15]. Simonescu C.M., Teodorescu V.Ş., Brezeanu M., Melinescu A., *Morphology and Shape Evolution of the Copper Monosulfide Nanocrystallites with the Reaction Time*, Rev. Chim. (Bucureşti), 56(6), p. 611, 2005.
- [16]. Simonescu C.M., Patron L., Teodorescu V.Ş., Brezeanu M., Căpăţină C., *A facile chemical route to copper sulfide CuS nanocrystallites – pH effect of the morphology and the shape of them*, Journal of Optoelectronics and Advanced Materials, 8(2), p. 597, 2006.
- [17]. Simonescu C.M., Teodorescu V.Ş., Patron L., Giurginca M., Căpăţină C., *Unconventional method used to obtain copper sulfide nanocrystallites*, Rev. Chim. (Bucureşti), 56(8), p. 810, 2005.
- [18]. Dursun A.Y., Uslu G., Tepe O., Cuci Y., Ekiz, H.I., *A comparative investigation on the bioaccumulation of heavy metal ions by growing Rhizopus arrhizus and Aspergillus niger*. Biochem. Eng. J. 15, p. 87, 2003.
- [19]. Mukhopadhyay, M., Noronha, S.B., Suraishkumar, G.K., *Kinetic modeling for the biosorption of copper by pretreated Aspergillus niger biomass*, Bioresource Technology, 98(9), p. 1781, 2007.

ENVIRONMENTAL RISK ASSESSMENT ON COKE PLANT DECOMMISSIONING

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ABSTRACT

Dismantling and demolition work generates considerable quantities of waste that can be feedback, but some remain on the site of the former plant and materials may affect the environment for a short, medium and long periods of time. Emissions of dust and gas can degrade the quality of air, surface water and groundwater. It is also polluted the soil by rain water, sewage, toxic spills and leakages due to damage antacid coatings. There are other environmental factors acting during the decommissioning of the plant such as noise and odors, but is manifested in a short period of time and the impact on staff can be considered small or negligible consequences.

KEYWORD: dismantling, risk assessment, decommissioning, risk factor

1. Introduction

Environmental risk management is a relatively new component of risk management which covers both mitigation measures of environmental pollution, as well as the measures taken to mitigate their effects. Environmental risk management differs significantly from other types of risk management, due to environmental complexity [1]. Most times, the decisions relate to long periods of time and are based on many assumptions about the potential impact, such as, for example, the effect on future generations [2]. The starting point for optimization of prevention of environmental pollution and occupational diseases in an organization is the risk assessment of that system. Risk assessment is performed using analytical methods or by simulation. Risk assessment is carried out using qualitative and quantitative techniques. Qualitative risk assessment techniques are used when hazards cannot be quantified or are not available sufficiently reliable information needed for quantitative assessment, or data

collection is not efficient in terms of costs. Quantitative assessment techniques are used in more complex activities to complement qualitative techniques. Quantitative assessment is usually preceded by the qualitative one [3].

2. Stages of risk assessment

A risk assessment involves identifying all risk factors and quantifies their size. The analysis system is based on the combination of two parameters: the severity and frequency event occurs. Risk assessment is required the following steps: a) identification of risk factors, b) setting out the consequences, c) determining the probability of occurrence; d) assignment of risk levels depending on the severity and likelihood of consequences of risk factors. Determination was made qualitative consequences for each risk category in part determining the maximum foreseeable consequence. We can determine the severity of the consequences of several classes, appreciation is the more precise if the number is higher. The largest

number is seven classes: Class 1 - negligible consequences, Class 2 - small consequences, Class 3 - medium consequences, Class 4 - large consequences, Class 5 - serious consequences, Class 6 - very serious consequences, Class 7 - maximum consequences [4].

Establishing the probability (P) that occurs cannot be done for each risk factor. Therefore it is considered the intervals as follows: extremely rare ($P < 10^{-7}/h$), very rare ($10^{-7}/h < P < 10^{-5}/h$); rare ($10^{-5}/h < P < 10^{-4}/h$), Uncommon ($10^{-4}/h < P < 10^{-3}/h$), common ($10^{-3}/h < P < 10^{-2}/h$), very common ($P > 10^{-2}/h$). Probability classes were noted as follows: Class 1 event frequency > 10 years, Class 2 occur rate of once every 5 ÷ 10 years, Class 3 occur rate of once every 2 ÷ 5 years, Class 4 occur rate of once every 1 ÷ 2 years, Class 5 once every 1 year ÷ 1 month, Class 6 once < 1 month.

3. Environmental risk assessment

Level of risk associated with each factor was considered at risk of a couple of elements of the system: gravity - probability. Thus for seven classes of severity were established seven risk levels, in ascending order: 1 - minimal risk, 2 - very low level of risk, 3 - low level of risk, 4 - medium risk, 5 - high level of risk, 6 - very high level of risk, 7 - maximum level of risk [5]. If we consider all possible combinations of the variables, two, we get a matrix of risks, $M_{g,p}$, with 7 lines - g, which will be grades severity classes and 6 columns - p - which will be grades probability classes:

$$M_{g,p} = \begin{pmatrix} (1,1) & (1,2) & (1,3) & (1,4) & (1,5) & (1,6) \\ (2,1) & (2,2) & (2,3) & (2,4) & (2,5) & (2,6) \\ (3,1) & (3,2) & (3,3) & (3,4) & (3,5) & (3,6) \\ (4,1) & (4,2) & (4,3) & (4,4) & (4,5) & (4,6) \\ (5,1) & (5,2) & (5,3) & (5,4) & (5,5) & (5,6) \\ (6,1) & (6,2) & (6,3) & (6,4) & (6,5) & (6,6) \\ (7,1) & (7,2) & (7,3) & (7,4) & (7,5) & (7,6) \end{pmatrix}$$

- Risk level 2 - couples g-p: (1,1) (1,2) (1,3) (1,4) (1,5) (1,6) (2,1);
- Risk level 2 - couples g-p g-p: (2,2) (2,3) (2,4) (3,1) (3,2) (4,1);
- Risk level 3 - couples g-p g-p: (2,5) (2,6) (3,3) (3,4) (4,2) (5,1) (6,1) (7,1);
- Risk level 4 - couples g-p: (3,5) (3,6) (4,3) (4,4) (5,2) (5,3) (6,2) (7,2);
- Risk level 5 - couples g-p: ((4,5) (4,6) (5,4) (5,5) (6,3) (7,3);
- Risk level 6 - couples g-p: (5,6) (6,4) (6,5) (7,4);
- Risk level 7 - couples g-p: (6,6) (7,5) (7,6).

The overall risk level is calculated as a weighted average risk levels established for the factors identified. For the result to reflect reality as accurately as possible, will be used as a weighting factor rank risk factor, which is equal to the level of risk. Factor with the highest level of risk will have the highest rank.

Calculating global risk level is the relationship the level of risk. Factor with the highest level of risk will have the highest rank.

Calculating global risk level is done by the relationship:

$$Nr = \frac{\sum_{i=1}^n r_i \cdot R_i}{\sum_{i=1}^n r_i} \quad (1)$$

where:

Nr = the global risk level on the workplace;

r_i = risk factor rank "i";

R_i = risk level for the risk factor "i";

n = number of risk factors identified at the workplace.

Water, soil and air are the main environmental factors considered in assessing the risk.

3.1. Risk factors for water

Site waters are contained in sewage, water pipeline or partially dismantled water

pipeline, or open tanks with various toxic substances that accumulate water from precipitation. Table 1 shows the dangers of

water pollution and risk levels, and Figure 3 shows levels of risk of dangerous factors identified for water.

Table 1. Partial risk levels for water

No.	Risk	Consequences	Severity	Probability	Part of risk level
A ₁₁ .	Industrial water supply routes partially removed from water containing precipitation.	negligible	2	1	1
A ₁₂ .	Gross ammonia water tank containing water from precipitation.	very serious	5	6	6
A ₁₃ .	Accumulation of rain water through open manholes	serious	4	5	5
A ₁₄ .	Partially dismantled industrial water networks in the primary coolers and coolers we removed in the final.	small	3	2	2
A ₁₅ .	water networks on energy fluid scaffold.	small	3	1	2
A ₁₆ .	Sewage degradation.	very serious	5	5	5

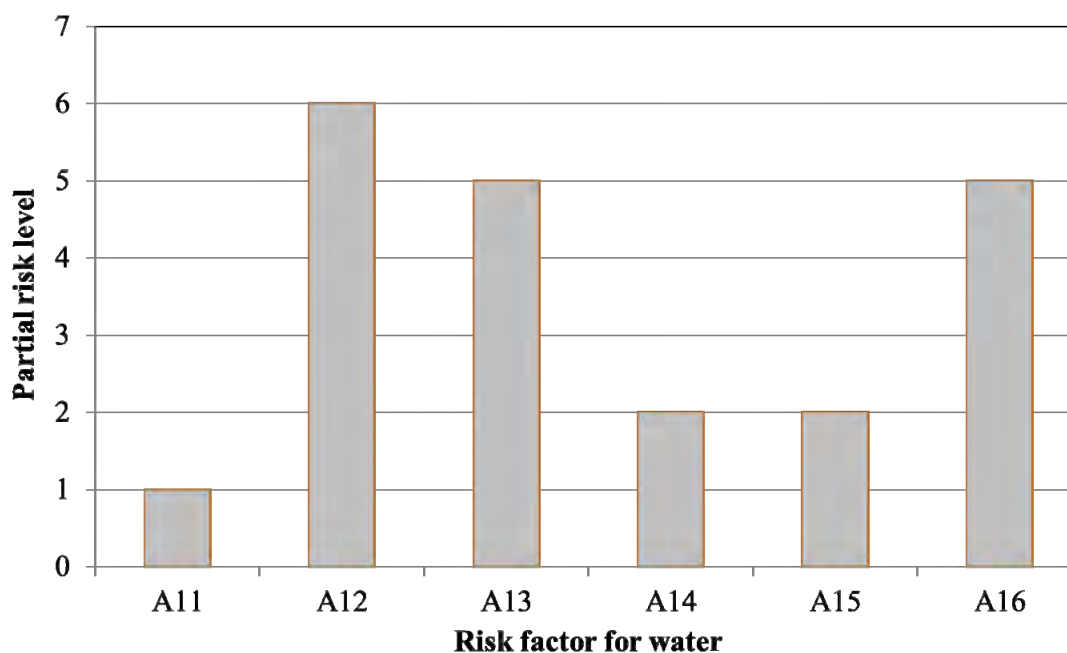


Fig. 1. Partial risk levels diagram for water

In Figure 1 is observed at high level risk and very high level risk for risk factors A12, A13, A16. To these factors must be taken measures to eliminate hazards or

reduce the level of risk. Highest risk level (6) for water pollution comes from ammonia water tanks left on site. The overall environmental risk level for water:

$$N_{rA1} = \frac{\sum_{i=1}^6 r_i \cdot R_i}{\sum_{i=1}^6 r_i} = \frac{1(6 \times 6) + 2(5 \times 5) + 2(2 \times 2) + 1(1 \times 1)}{1 \times 6 + 2 \times 5 + 2 \times 2 + 1 \times 1} = 4,52$$

Value of 4.52 overall level of risk of water pollution is also high requiring measures to minimize.

3.2 Risk factors for soil.

Soil pollution is caused by remaining sludge in the tanks of benzene,

decanters and degrades over time, the hazardous chemicals stored in tanks in an advanced state of degradation, uncontrolled leakage from sewers damaged by large amounts of coal and coke remaining on the ground, floors or damaged bins. Table 2 shows the risk levels for soil, and Figure 3 show dangerous levels of risk factors identified.

Table 2. Risk level for soil

No.	Risk	Consequences	Severity	Probability	Part of risk level
A ₂₁ .	Quantities of coal in bunkers in covered warehouse..	medium	2	5	3
A ₂₂ .	Coke sludge in settling tanks.	small	3	2	2
A ₂₃ .	Sludge in decanter which had been mechanized.	medium	3	3	3
A ₂₄ .	Condensing water in tanks below ground level, in an advanced state of corrosion.	small	3	2	2
A ₂₅ .	Tar sludge in tanks.	very serious	5	5	6
A ₂₆ .	Discharge channels that are partially clogged.	serious	4	3	4
A ₂₇ .	Sludge or slurry mixture of water in the tanks for benzene.	serious	5	5	5
A ₂₈ .	Coal or coke on the floors or ground stations and the closed stations bunkers.	high	4	3	4
A ₂₉ .	Coal and coke mixed with sand, soil, plant debris, bodies stain due to inadequate storage conditions.	serious	4	5	5
A ₂₁₀ .	Large amounts of tar sludge deposited on the bottom of tanks and mechanized clarifiers.	very serious	5	6	6

No.	Risk	Consequences	Severity	Probability	Part of risk level
A ₂₁₁	Dangerous chemicals stored in tanks in an advanced state of decay.	very serious	5	6	6
A ₂₁₂	Uncontrolled leakage from damaged sewerage networks.	very serious	5	6	6

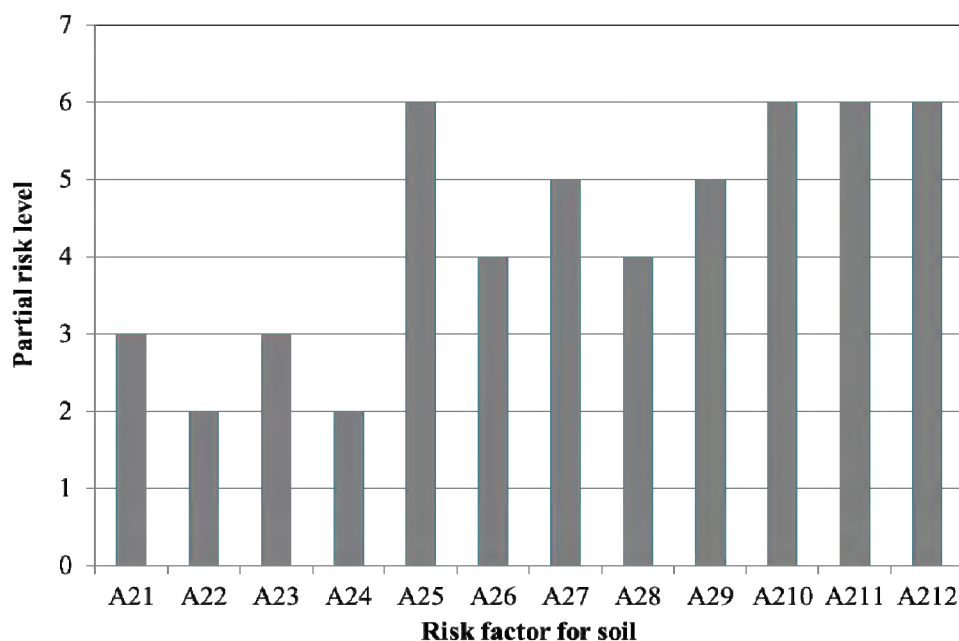


Fig. 2. Partial risk levels diagram for soil

From Figure 2 we can see that the small risk (2) is exceeded by most risk factors indicating a greater degree of soil pollution compared to water. Risk response to this environmental factor is complex since

$$N_{rA2} = \frac{\sum_{i=1}^{12} r_i \cdot R_i}{\sum_{i=1}^{12} r_i} = \frac{1(6 \times 6) + 2(5 \times 5) + 2(4 \times 4) + 2(3 \times 3) + 2(2 \times 2)}{4 \times 6 + 2 \times 5 + 2 \times 4 + 3 \times 3 + 2 \times 2} = 4,58$$

3.3 Risk factors for air

The air also suffers from contamination due to coal dust left on the ground in large quantities, tar from

pollution is both directly and through other environmental factors: water and air. Level of risk for soil environmental factor will be:

degradable tanks, gas from pipelines and damaged. Table 3 shows the risk levels for air and Figure 3 shows levels of risk of dangerous factors identified.

Table 3. Partial risk levels for air

No.	Risk	Consequences	Severity	Probability	Part of risk level
A ₃₁ .	Steam network dismantled.	negligible	2	1	1
A ₃₂ .	Partially dismantled gas pipes.	medium	3	4	3
A ₃₃ .	Gas pipelines sludge (tar, naphthalene, coke breeze).	very serious	5	6	6
A ₃₄ .	The gas condensed (water, slurry of naphthalene, tar).	very serious	5	6	6
A ₃₅ .	Abandoned installation for capture ammonia and benzene .	very serious	5	6	6
A ₃₆ .	Coal dust in large quantities.	very serious	5	6	6
A ₃₇ .	The tar remained in the tanks.	serious	5	6	6
A ₃₈ .	Coal dust in mechanized settling tanks.	medium	3	4	3

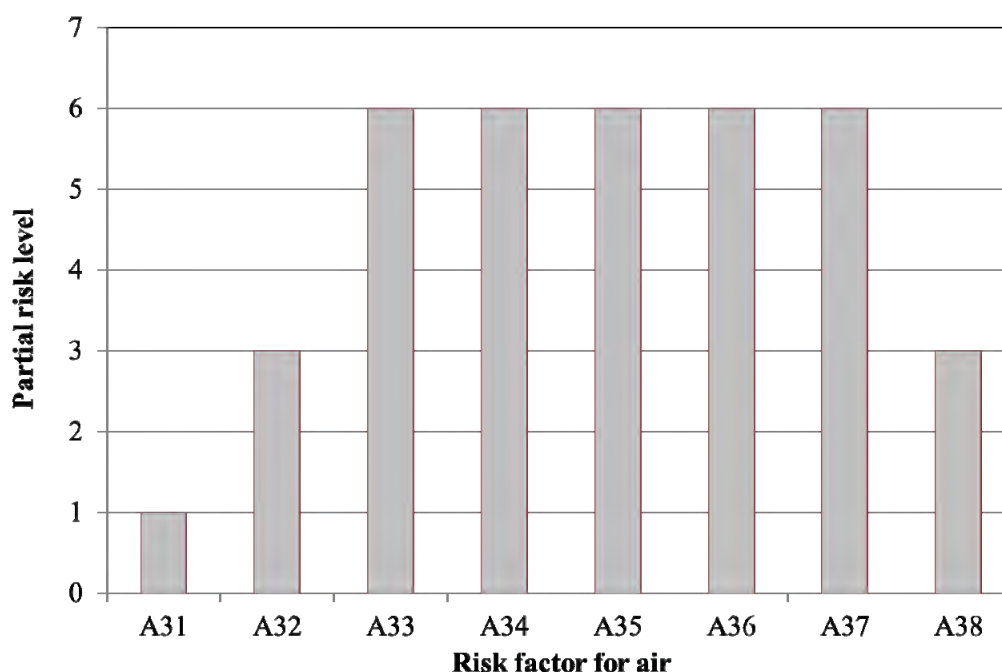


Fig. 3. Diagram of partially risk level for air.

Air pollution, as shown in Figure 3 and the overall risk level (5.37) is as expected the highest. The presence of coal and coke dust, toxic vapours of different substances (benzene, ammonia, naphthalene, etc.), significantly affect air

quality, requiring urgent action to reduce risk levels and hence part of overall risk level.

Air environmental Risk level factor will be:

$$N_{rA3} = \frac{\sum_{i=1}^8 r_i \cdot R_i}{\sum_{i=1}^8 r_i} = \frac{5(6 \times 6) + 2(3 \times 3) + 1(1 \times 1)}{5 \times 6 + 3 \times 3 + 1 \times 1} = 5,37$$

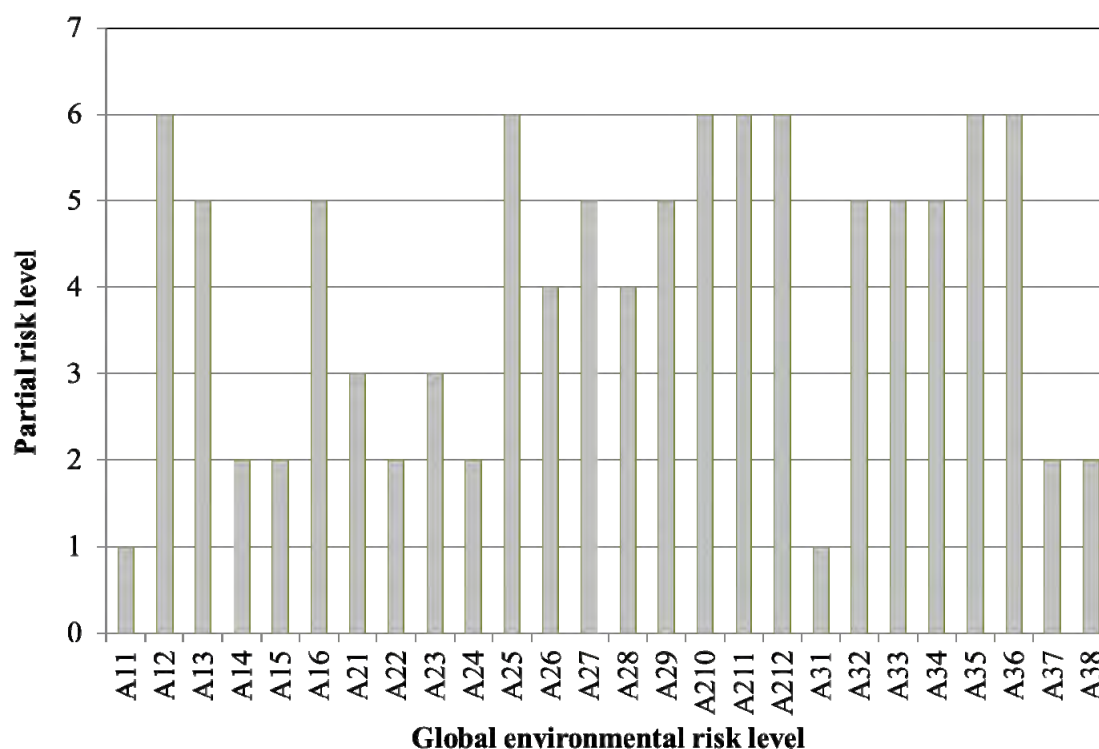


Fig. 4. Diagram of global environmental risk level (N_{GM})

As shown in Figure 4, the decommissioning of coke-chemical plant cause significant environmental pollution,

resulting in major risks which must be well managed.

The overall level of environmental risk is:

$$N_{GM} = \frac{\sum_{i=1}^{26} r_i \cdot R_i}{\sum_{i=1}^{26} r_i} = \frac{7(6 \times 6) + 7(5 \times 5) + 2(4 \times 4) + 2(3 \times 3) + 6(2 \times 2) + 2(1 \times 1)}{8 \times 6 + 6 \times 5 + 2 \times 4 + 2 \times 3 + 6 \times 2 + 2 \times 1} = 4,74$$

4. Conclusion

During decommissioning of coke-chemical plant there are many environmental problems to be pursued with caution and responsibility to be reduced and eliminated.

Polluted water infiltration has indirect and cumulative impacts on

groundwater due to degraded sewage and water tank ammonia. Highest risk level (6) for water pollution comes from ammonia water tanks left on site.

Dust can affect indirect and cumulative surface water to wash the air by precipitation and groundwater by infiltration of rainwater into the soil and degraded sewerage leak. 4.52 risk levels

indicate the need for immediate action to reduce pollution.

In the case of soil, most factors indicate a high risk level of contamination, being affected by more toxic substances in water and air. Sewage and rain from washing the flue gas emissions (CO, NO_x, SO_x, CO₂), generates cumulative and irreversible indirect pollution on soil.

Leakage of tar, ammonia water, sodium hydroxide, due to leakages, antacid coating damage from the storage areas and ramp handling the products has direct and irreversible impact on soil pollution.

Leakage tar in deposits generates hazardous waste and has an indirect, cumulative and irreversible impact on soil. 4.58 risk levels of soil are higher than water, therefore is very necessary to take measures to reduce pollution.

Emissions of dust and gas generate a direct and irreversible impact on local

air. 5.37 overall level of risk is the highest, requiring urgent action to reduce partial risk levels and therefore part of the overall risk level.

References

- [1]. **Moraru R., Băbuț G.**, *Cadrul general al managementului riscului de mediu*, Buletinul AGIR nr. 3/2006, iulie-septembrie, p. 103-107.
- [2]. **Băbuț G., Moraru R.**, *Environmental risk characterization principles*, Proceedings of the 6th Conference on Environment and Mineral Processing, part. I, p. 17-21, VŠB-TU Ostrava, Cehia, 27 - 29.06.2002.
- [3]. **Ozunu A., Anghel C. I.**, *Evaluarea riscului tehnologic și securitatea mediului*, Editura Accent, Cluj-Napoca, 2007, ISBN 978-973-8915-35-0.
- [4]. **Radu Tamara, Maria Vlad, Marius Bodor**, *Environmental risk management at hot-dip galvanizing*, The Annals of 'Dunărea De Jos' University Of Galați, Fascicle IX Metallurgy and Material Science, special ISUE, May 2011, pag. 263.
- [5]. **SR EN 292-1/1996.**

BIOSORPTION CHARACTERISTICS OF PENICILLIUM HIRSUTUM BIOMASS FOR REMOVAL OF Cu(II) IONS FROM AQUEOUS SOLUTION THAT CONTAINS CuS NANOPARTICLES

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ABSTRACT

*Pollution with inorganic compounds such as heavy metal is one of the most important problems with negative consequences to the environment and life. Wastewaters contain metals in dissolved form or in the form of nanoparticles of their compounds. Industries that generate wastewater with heavy metal content are: electroplating, paints, textile, chemical, mining and smelting of metalliferous, surface finishing industry, energy and fuel production, fertilizer and pesticide industry, metallurgy, iron and steel, electroplating, electrolysis, electro-osmosis, leatherworking, photography, electric appliance manufacturing, metal surface treating, aerospace and atomic energy installation. Wastes with heavy metal content are discharged direct or indirect in environment determined negative effects for organisms, important environment problems, becoming increasingly rare being exhaustible. Copper in high concentration causes significant health problems such as "Wilson's Disease" is caused by accumulation of copper in the brain, skin, liver, pancreas and myocardium. Copper toxicity increases in the presence of small amounts of Mo^{+2} ions, Zn^{+2} and SO_4^{2-} . The main acute and chronic disorders caused by copper are hemochromatosis and gastrointestinal diseases. Therefore copper must be removed from wastewater using various methods. Biosorption is a more effective alternative to decrease the concentration of heavy metal ions in solution from ppm to ppb level by using low cost materials. Usually this process is one faster than the other heavy metals removal processes such as: precipitation, ion exchange, reverse osmosis, adsorption. *Penicillium hirsutum* ATCC (American Type Culture Collection) was used in order to remove Cu(II) from wastewaters which contain copper sulfide nanoparticles. In this case Cu(II) removal involves in a first stage bioleaching followed by biosorption. The optimum biosorption conditions were determined.*

KEYWORDS: copper removal, biosorption, bioleaching

1. Introduction

Heavy metals such as copper are the main toxic pollutants in industrial wastewaters that can result in severe health and environmental problems [1-4].

They are non-degradable and harmful to a variety of living organisms. Through the food chain they can accumulate in organisms. They are found in wastewaters in dissolved form and in nanoparticle suspensions.

Nanoparticles are more toxic to environment and health due to their properties such as small size and large surface area. Their similar dimensions with cellular components determine their interaction with protein and nucleic acids. These interactions have negative effects on vital processes such as enzyme function and gene transcription and translation.

Therefore, removal of heavy metals (dissolved or in suspension) from industrial effluents is essential not only to protect the water, and soil resources, but also to slow down the fast depletion of heavy metals sources.

For removal of heavy metals from industrial wastewaters were applied conventional methods such as: chemical precipitation, electrochemical treatment, ion exchange processes, solvent extraction, membrane separation and evaporation [5]. Some of these conventional methods are ineffective and unfavorable as they cause sludge disposal problem, expensive and incomplete removal [6].

Adsorption plays an important role in the removal of metal ions from aqueous solutions. During the last years many research works have been focused on development of some new adsorbent materials with high adsorption capacity, and which can be reused. Using of biomaterials in heavy metals removal from wastewaters has many advantages such as reusability, low operating cost, improved selectivity for specific metals of interests, removal of heavy metals found in low concentrations in wastewaters, short operation time, and no production of secondary compounds which can be toxic [7].

Fungal biomasses are capable of treating metal-contaminated effluents with efficiencies several orders of magnitude superior to conventional adsorbent materials such as activated carbon, clays, zeolites. This high biosorption capacity is due to the fact that fungal cell walls mainly have in composition compounds such as

polysaccharides, proteins and lipids whose functional groups can be involved in heavy metals bonding. In addition they can tolerate adverse conditions like low pH medium.

Various fungal strains such as *Aspergillus niger* [1], *Aspergillus flavus* [8], *Aspergillus versicolor* [9], *Fusarium* [10], *Gliomastix murorum* [11], *Pleurotus ostreatus* (a macro-fungus) [3], *Pleurotus pulmonarius* [12], *Trametes versicolor* [5], *Penicillium* [13], *Schizophyllum commune* [12], *Rhizopus arrhizus* [14], *Pycnoporus sanguineus* (a white-rot fungus) [15] were used in copper removal from wastewater.

The purpose of this study was to determine the ability of *Penicillium hirsutum* ATCC to remove Cu(II) from wastewaters which contain copper sulfide nanoparticles by batch system. In this case Cu(II) removal involves in a first stage bioleaching followed by biosorption. The optimum biosorption conditions were determined as a function of initial pH, initial metal ion concentration and contact time.

2. Materials and methods

2.1. Growth of culture

The fungus strain was propagated on potato dextrose agar (PDA) 39 g·L⁻¹ and malt extract 0.1 g·L⁻¹ for 5-7 days at 30°C. Copper(II) uptake studies were carried out in liquid minimal medium containing 30 g·L⁻¹ dextrose, 10 g·L⁻¹ peptone, 0.4 g·L⁻¹ KH₂PO₄, 0.2 g·L⁻¹ KH₂PO₄, 0.2 g·L⁻¹ MgSO₄·7H₂O. The pH of the growth medium was 6.24. After inoculation, flasks were incubated at 150 rpm for 8 days at 30°C using Thermoshake (an Incubator Shaker).

2.2. Copper containing effluents

In this study copper was used in the form of copper sulfide nanoparticles. These nanoparticles were previously obtained and characterized [16, 17]. CuS nanoparticles

used have an average diameter of about 20-30 nm [18].

2.3. Analytical procedures

The copper content in final solution after the biomass growth was determined after the filtration of biomass with the use of atomic absorption spectroscopy (AAS) (ANALYTIK-JENA – AAS Multi-Element with Continuum Source ContraAA®700).

2.4. Biosorption

Penicillium hirsutum fungal strain was inoculated into 100 mL copper solution with an initial concentration of 25 mg Cu(II)·L⁻¹ obtained in liquid minimal medium containing 30 g·L⁻¹ dextrose, 10 g·L⁻¹ peptone, 0.4 g·L⁻¹ KH₂PO₄, 0.2 g·L⁻¹ KH₂PO₄, 0.2 g·L⁻¹ MgSO₄·7H₂O. The pH of the growth medium was 6.24. Controls were run with a fungal biomass system without copper. After the biosorption experiments samples were taken and filtered. The supernatant was used to analyze the residual copper ion concentration. Equilibrium time and its conditions were determined through the kinetic studies.

2.5. Effect of contact time

Penicillium hirsutum fungal strain was inoculated into a glass vial which contains 100 mL of copper 25 mg/L and minimum liquid medium growth. The initial pH was 6.45, and the temperature was 30±1°C. The time varied between 24 and 192 h. After the contact between solutions containing CuS and fungal biomass each sample was filtered, and tested for copper ion concentration.

2.6. Effect of initial ion concentration on biosorption of Cu(II) by *Penicillium hirsutum*

Experiments were carried out at different Cu(II) concentrations varying from 25 to 100 mg/L at 6.45 pH to establish the effect of initial Cu(II) ion concentration onto *Penicillium hirsutum* removal efficiency

2.7. Effect of temperature

Penicillium hirsutum fungal strain was inoculated into 100 mL solutions containing 25 mg Cu(II)·L⁻¹ at 20, 25, 30, 35, 40°C.

The mixtures were shaken at 150 rpm until reaching the equilibrium.

2.8. Effect of pH solution

Penicillium hirsutum fungal strain was inoculated into 100 mL solutions containing 25 mg Cu(II)·L⁻¹ with an initial pH of 3.5, 4, 4.5, 5.5, 6.5, and 7.5. The pH was varied using HCl 1M, and NH₄OH 25% solutions. The mixtures were shaken at 150 rpm until reaching the equilibrium.

2.9. Elution study

At the end of biosorption, biomass of *Penicillium hirsutum* was contacted with 100 mL of 0.05 HNO₃ in deionized water. The mixture was shaken at 150 rpm on Thermoshake at 30±1°C for 24 hours. After elution, the mixture was filtered, and the copper ion concentration of supernatant was determined.

3. Results and discussion

Kinetic studies of *Penicillium hirsutum* fungal strain were performed as batch tests. These tests were performed in order to establish the factors which influence copper removal processes from wastewaters by *Penicillium hirsutum* fungal strain. The fungal strain of *Penicillium hirsutum* was growing rapidly in the presence of CuS attaining a diameter of 10-36 µm, and the length of the hife between 30 to 100 µm (Figure 1).

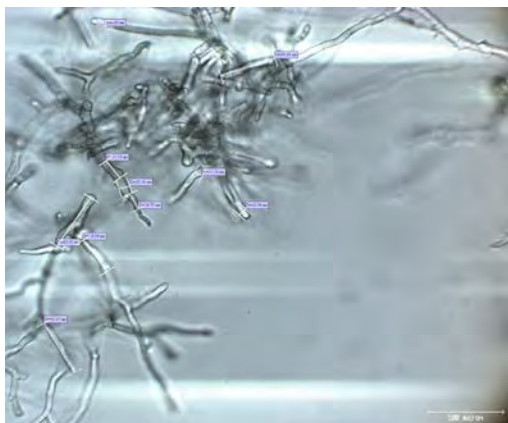


Fig. 1. *Penicillium hirsutum* grown in presence of CuS

3.1. Effect of contact time

Removal efficiency of *Penicillium hirsutum* fungal strain was determined using the following equation:

$$\text{Removal efficiency} = \left[\frac{\text{mg Cu(II) removed}}{\text{mg Cu(II) available}} \right] \cdot 100 \quad (1)$$

Results obtained for the removal efficiency of *Penicillium hirsutum* fungal strain in function of contact time are presented in Figure 2.

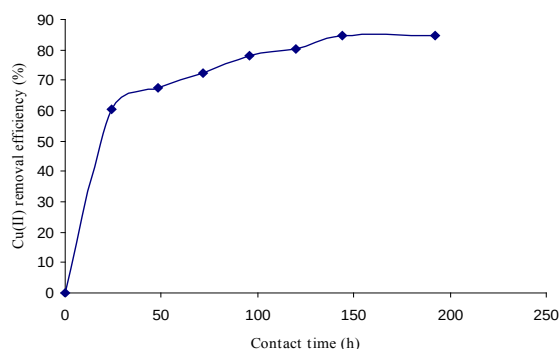


Fig. 2. Effect of contact time between biomass and solution with 25 mg Cu(II)L⁻¹ in the form of CuS

As it can be seen in the Figure 2 the removal efficiency increases with the increasing of the time. The time to reach equilibrium state is 144 hours (6 days), and the maximum removal efficiency registered is 84.77%.

3.2. Effect of initial ion concentrations on biosorption of Cu(II) by *Penicillium hirsutum*

Figure 3 shows the effect of initial Cu(II) concentration onto removal efficiency of *Penicillium hirsutum* fungal strain. The biosorption of Cu(II) ions onto *Penicillium hirsutum* was carried out at different Cu(II) concentrations varying from 25 to 100 mg/L at 6.45 pH.

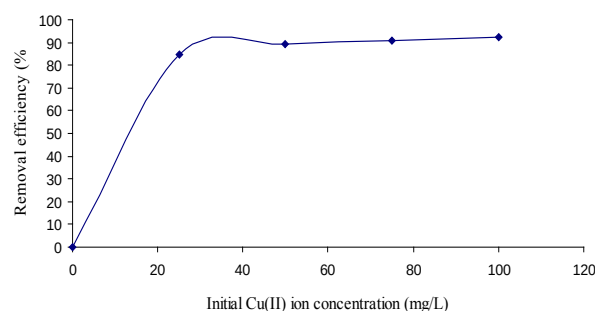


Fig 3. Effect of initial Cu(II) ion concentration onto *Penicillium hirsutum* removal efficiency

Results showed that as the initial Cu(II) concentrations increased, removal efficiency increased. Higher Cu(II) ions concentration increased the overall mass transfer driving force and thus the Cu(II) uptake onto the biosorbent.

3.3. Effect of temperature

Penicillium hirsutum fungal strain was inoculated into 100 mL solutions containing 25 mg Cu(II)L⁻¹ at 20, 25, 30, 35, 40°C. The effect of temperature on the removal efficiency of *Penicillium hirsutum* is presented in Figure 4.

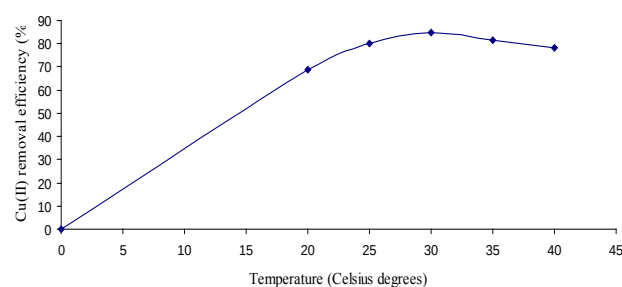


Fig. 4. Effect of temperature onto *Penicillium hirsutum* removal efficiency

From this Figure it can be seen that removal efficiency increases with increasing of the temperature to a maximum value of removal efficiency at 30°C. After this temperature the removal efficiency decreases.

3.4. Effect of pH solution

The removal efficiency was determined in function of pH value. pH range used was 3.5 - 7.5. Results obtained are presented in Figure 5. From this figure it can be seen that the copper removal efficiency increases with increasing of pH from 3.5 to 5.5.

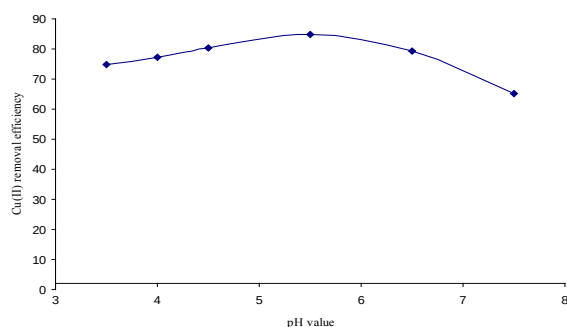


Fig. 5. Effect of pH on the removal efficiency of *Penicillium hirsutum* fungal strain

Maximum removal efficiency occurs at pH 5.5. After this value of pH, removal capacity decreases due to the formation of copper hydroxides.

These results are in concordance with literature data which mentioned the following values of pH for maximum Cu(II) adsorption: 6.5 for *Aspergillus niger* [3], 5 for *Trametes versicolor* [5], 6 for pretreated *Aspergillus niger* biomass [19].

3.5. Elution study

Biomass of *Penicillium hirsutum* loaded with Cu(II) was contacted with 100 mL of 0.05 HNO₃ in deionized water at 150 rpm on Thermoshake at 30±1°C for 24 hours. After elution, the mixture was filtered, and the copper ion concentration of supernatant

was determined. Copper ion concentration removed from biomass was 6.54 mg/L.

4. Conclusions

Cu(II) removal efficiency of *Penicillium hirsutum* ATCC was determined in function of contact time, initial Cu(II) concentration, temperature and pH value. The results obtained showed that in case of aqueous solution that contains 25 mg Cu(II)/L in the form of CuS nanoparticles the maximum removal efficiency was reached at 144 hours of contact, 30°C and 5.5 value of pH.

Acknowledgements

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References

- [1]. Tsekova T., Todorova D., Ganeva S., Removal of heavy metals from industrial wastewater by free and immobilized cells of *Aspergillus niger*, International Biodeterioration & Biodegradation 64, p. 447, 2010.
- [2]. Tsekova T., Todorova D., Dencheva V., Ganeva S., Biosorption of copper(II) and cadmium(II) from aqueous solutions by free and immobilized biomass of *Aspergillus niger*, Bioresource Technol. 101, p. 1727, 2010.
- [3]. Javaid A., Bajwa R., Manzoor T., Biosorption of heavy metals by pretreated biomass of *Aspergillus niger*, Pak. J. Bot., 43(1), p. 419, 2011.
- [4]. Javanbakht V., Zilouei H., Karimi K., Lead Biosorption by different morphologies of fungus *Mucor indicus*, International Biodeterioration & Biodegradation, 65, p. 294, 2011.
- [5]. Subbaiah M.V., Vijaya Y., Reddy A.S., Yuvaraja G., Krishnaiah A., Equilibrium, kinetic and thermodynamic studies on the biosorption of Cu(II) onto *Trametes versicolor* biomass, Desalination doi:10.1016/j.desal.2011. 03.067, 2011.

- [6]. **Tuzun I., Bayramoglu G., Yalcin E., Basaran G., Celik G., Arica M.Y.**, *Equilibrium and kinetic studies on biosorption of Hg(II), Cd(II) and Pb(II) ions onto microalgae Chlamydomonas reinhardtii*, J. Environ. Manage, 77(2), p. 85, 2005.
- [7]. **Mungasavalli D.P., Viraraghavan T., Chunglin Y.**, *Biosorption of chromium from aqueous solutions by pretreated Aspergillus niger: batch and column studies*, Colloids. Surf. A Physicochem. Eng. Aspects, 301, p. 214, 2007.
- [8]. **Akar T., Tunali S.**, *Biosorption characteristics of Aspergillus flavus biomass for removal of Pb(II) and Cu(II) ions from an aqueous solution*, Bioresource Technology, 97, p. 1780, 2006.
- [9]. **Taştan B. E., Ertuğrul S., Dönmez G.**, *Effective bioremoval of reactive dye and heavy metals by Aspergillus versicolor*, Bioresource Technology, 101, p. 870, 2010.
- [10]. **Pan R., Cao L., Zhang R.**, *Combined effects of Cu, Cd, Pb, and Zn on the growth and uptake of consortium of Cu-resistant Penicillium sp. A1 and Cd-resistant Fusarium sp. A19*, Journal of Hazardous Materials, 171, p. 761, 2009.
- [11]. **Li X., Xu Q., Han G., Zhu W., Chen Z., He X., Tian X.**, *Equilibrium and kinetic studies of copper(II) removal by three species of dead fungal biomasses*, Journal of Hazardous Materials, 165, p. 469, 2009.
- [12]. **Veit M. T., Tavares C. R. G., Gomes-da-Costa S. M., Guedes T. A.**, *Adsorption isotherms of copper(II) for two species of dead fungi biomasses*, Process Biochemistry, 40, p. 3303, 2005.
- [13]. **Su X.Z.H., Xiao T.T.G.**, *Study of Thermodynamics and Dynamics of Removing Cu(II) by Biosorption Membrane of Penicillium Biomass*, Journal of Hazardous Materials doi:10.1016/j.jhazmat.2011.03.014, 2010.
- [14]. **Preetha B., Viruthagiri T.**, *Application of response surface methodology for the biosorption of copper using Rhizopus arrhizus*, Journal of Hazardous Materials, 143, p. 506, 2007.
- [15]. **Yahaya Y. A., Don M. M., Bhatia S.**, *Biosorption of copper (II) onto immobilized cells of Pycnoporus sanguineus from aqueous solution: Equilibrium and kinetic studies*, Journal of Hazardous Materials, 161, p. 189, 2009.
- [16]. **Simonescu C.M., Teodorescu V.Ş., Brezeanu M., Melinescu A.**, *Morphology and Shape Evolution of the Copper Monosulfide Nanocrystallites with the Reaction Time*, Rev. Chim. (Bucureşti), 56(6), p. 611, 2005.
- [17]. **Simonescu C.M., Patron L., Teodorescu V.Ş., Brezeanu M., Căpăţină C.**, *A facile chemical route to copper sulfide CuS nanocrystallites – pH effect of the morphology and the shape of them*, Journal of Optoelectronics and Advanced Materials, 8(2), p. 597, 2006.
- [18]. **Simonescu C.M., Teodorescu V.Ş., Patron L., Giurginca M., Căpăţină C.**, *Unconventional method used to obtain copper sulfide nanocrystallites*, Rev. Chim. (Bucureşti), 56(8), p. 810, 2005.
- [19]. **Mukhopadhyay, M., Noronha, S.B., Suraishkumar, G.K.**, *Kinetic modeling for the biosorption of copper by pretreated Aspergillus niger biomass*, Bioresource Technology, 98(9), p. 1781, 2007.

INVESTIGATION OF LAYERS METAL ATOMIC FORCE MICROSCOPY

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ABSTRACT

The article presents the scanning technology based on scanning with the sensor-surface interaction. It shows the scanning possibilities given by applying such a method within technologies, allowing a measurement at a nano-level, as well as the advantages of implementing this type of investigation method.

KEYWORDS: sensor-surface, atomic force microscopy

Wire-bonding is a main interconnection process in the packaging industry. Wires are bonded to Al pads using combined thermal and ultrasonic activation. Gold wires are the widely used and well characterized media for this process [1].

Recently, the use of copper wires is of interest to the industry due to its electrical and mechanical properties. Since copper is relatively hard and readily oxidized, the use of copper wires in industrial interconnection processes requires special bonding procedures and equipment. Moreover, due to the relatively slow formation of Al-Cu intermetallics, examination of the as bonded Al-Cu interface by conventional characterization such as optical microscopy (OM) and scanning electron microscopy (AFM) with energy dispersive spectroscopy (EDS), provide almost no information related to the deterioration of the wire-bonds as a function of the bond life.

Until today, the Al-Cu wirebond interface was investigated by OM and AFM in samples which were mechanically polished, making it difficult to distinguish between the different Al-Cu intermetallics. Attempts were also made to resolve the intermetallic composition of the bonds via EDS incorporated in AFM [2]. In the present study,

transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM) and TEM-EDS were used for quantitative analysis of the intermetallic composition of as-bonded and heat treated Al-Cu wire-bonds. A dual beam focused ion beam (FIB) was used to prepare sitespecific TEM samples. FIB was also used for preliminary analysis of cross-sections by ion-beam and high-resolution AFM. In order to understand the processes that occur at the Al-Cu interface, as-bonded samples and samples annealed in air and argon were prepared.

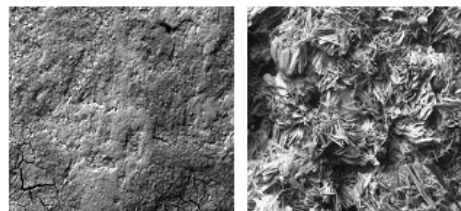


Fig. 1. (a) Secondary electron AFM micrograph of the as-bonded Al-Cu interface and (b) ion induced secondary electron micrograph of the same specimen, showing the Cu grain morphology.

The channeling effect may occur for incident ions if a crystal in the sample is oriented in a low index zoneaxis. In these conditions, the ion beam will penetrate deeper into the target

before significant inelastic scattering occurs, resulting in a lower probability of secondary electrons escaping from the sample due to their limited mean-free-path. As a result, grains oriented in a low index zone-axis will have a darker contrast than randomly oriented grains (Figure 1).

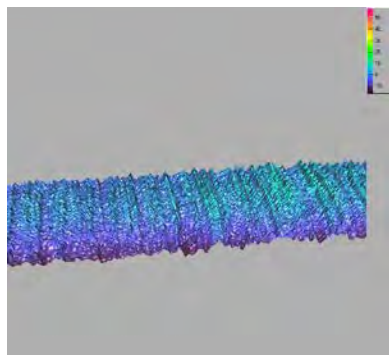


Fig. 2. HAADF-STEM micrograph of the asbonded Al-Cu wire-bond cross-section. A nonuniform intermetallic region is evident.

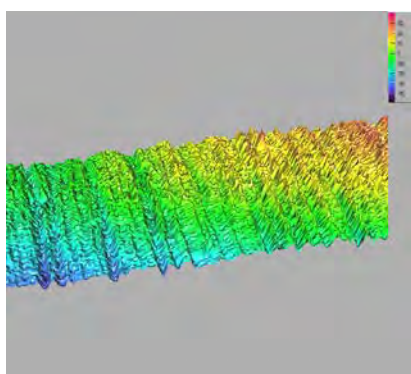


Fig. 3. Bright field TEM micrograph of a central region of a Al-Cu wire-bond annealed for 24 hours in argon at 175°C. The inset diffraction pattern is of the dark intermetallic grain.

Figure 2 presents high angle annular dark field (HAADF) STEM micrograph of an area of the as-bonded Al-Cu wire bond, indicating that intermetallic phases are formed in the as bonded samples [3]. EDS analysis confirmed the presence of Al-Cu intermetallics, and that changes in the Cu concentration in the large intermetallic region was not monotonic as a function of a distance from the copper layer. The composition of the intermetallic regions in heat-treated samples was evaluated by TEM-EDS and, wherever possible, confirmed by selected area electron diffraction patterns (Figure 3).

2. Tape Automated Bonding (TAB). They will accommodate the flat TAB tape lead and provide the proper material for a reliable connection to the tape [4]. The bump fabrication process uses a metal deposition and plating process. First a series of barrier and seed layers of metal are deposited over the surface of the wafer. A layer of photoresist is deposited over these barrier and seed layers. A photomask is used to pattern the locations over each of the pads that will be bumped. An etching process exposes the pads, and the open resist hole defines the shape and height of the bump. The bump, which is typically gold, is then electroplated over the pad and the deposited barrier metals. Once the plating is complete, a series of etching steps are used to protect the underlying materials from being etched. While gold bumping is the most common, copper, tin-lead, as well as layered combinations of these materials are used for bumping. An alternative to die bumping is to create bumps on the tape. For high leadcounts, wafer bumping is more common. Figure 4. illustrates a completed bump and a TAB tape lead.

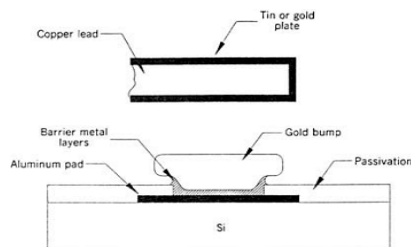


Fig. 4. Tab with wafer bumping

Gold top wafer metallurgy had been practiced in the past. With exception of GaAs and TAB, gold had been replaced by aluminum interconnects and then by advanced copper interconnects. Lower material cost plus ultra-fine line capabilities of both aluminum and copper were reasons for the displacement of gold as interconnect. However, to enter high temperature IC applications, to achieve superior reliability or to dissipate greater power, the resurrection of gold as the top metal is both practical and effective. This protective gold top is coined Power Au for the ability of gold to increase power capabilities of ICs, packages and systems. Au wire bonded to aluminum forms many Au-Al intermetallics. This interdiffusion of Au atoms into Al bond

pads is well studied. At higher temperature, diffusion and growth rate of intermetallics also accelerate. If the entire thickness of aluminum bond pad were converted into Au4 Al intermetallic, then the poor adhesion of Au4 Al to barrier metal between aluminum layers can result in wire bond separation and electrically open failure. Even as Au4 Al intermetallic is growing, Kirkendall's voids coalesce into hairline crack at intermetallics interface. These weakened interfaces are susceptible to stress failure and again result in electrically open failure. The metal between Power Au and Al is not a perfect barrier however. Under higher temperature testing, barrier metal does eventually break down. Above 250°C plus self heating from 860mA current, gold atoms punch through the barrier metal and then gold diffuse into aluminum. Rapid diffusion of Au into Al Power Au line immediately above contact to aluminum.



Fig. 5. Power Au line with void above contact to aluminum after extremely high temperature testing and 860mA current. Gold diffused into aluminum and left a void.

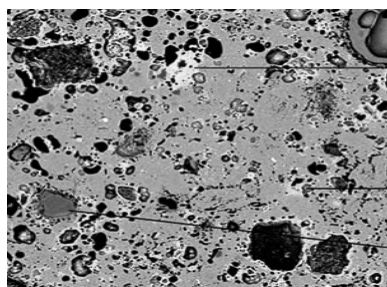


Fig. 6. Shows a cross section of a Au-Al bond

The wire pull test is used to measure the strength and failure mode of the wire bond. A small hook is bond to gauge the strength of the

1st bond or next to the wedge at the 2nd bond to ensure a reliable weld. Generally, if the hook is placed at the mid span of the wire, then the test will show the weakest link of the bond. This is typically either the neck of the ball bond (right above the ball) or at the heel of the wedge bond. The Pull test is basically a function of the wire diameter. Loop height & wire span are the most significant factors that determines the strength of a wire for a given wire diameter. Shorter span & a lower loop will result in a lower pull strength. As opposed to a longer span & a higher loop height which will result in higher pull strength. Copper wire bonding is normally formed by a copper ball onto an aluminum based bond pad in microelectronic package. However, copper oxidation at the interface of Cu- Al bonding area causes the cracks, decreases the interfacial shear strength, and weakens the Cu-Al bonding. Surface analysis of ball-peeled pad of Cu-Al bonding using XPS demonstrates the copper oxidation in the Cu-Al interface after autoclave test (at 121oC and 100% relative humidity). The binding energy scans for Cu 2p on the specimen after 0, 192, 384, and 576 hours in autoclave test chamber is carried out.

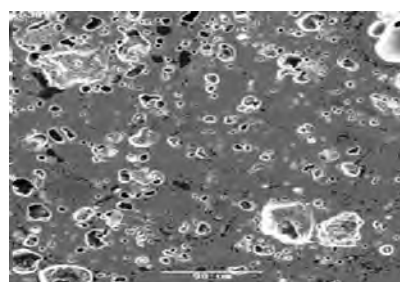


Fig. 7. AFM pictures show corrosion and a crack after test hour increase (X1000)

After 576 hours corrosion, the chemical change of copper in a few atomic layers of surface from Cu to CuO. Furthermore, there are two major copper oxides peaks observed in the study, CuO and Cu(OH)₂. Cu₂O is not stable in air and change to CuO immediately. Therefore, Cu₂O is not expected to be detected at the specimen [7]. Low cost, high thermal

and electric conductivity, easy fabricating and joining, and wide range of attainable mechanical properties have made copper widely used in electronic packaging, such as lead frames, interconnection wires, foils for flexible circuits, heat sinks, and WPB traces. However, unlike the aluminum oxide, the copper oxide layer is not self-protect. Therefore, copper is readily oxidized, especially at elevated temperature. Copper oxidation interface of Cu-Al bonding area causes the cracks, decreases the interfacial shear strength, and weakens the Cu-Al bonding. Also, Copper oxidation in the area of the lead frames die pad and mold compound causes the delamination of packages. Furthermore, the moisture penetrates through the crevices because copper oxidation induces poor adhesion in the area of the copper lead frames and molding compound, creating corrosion problem in the packages.

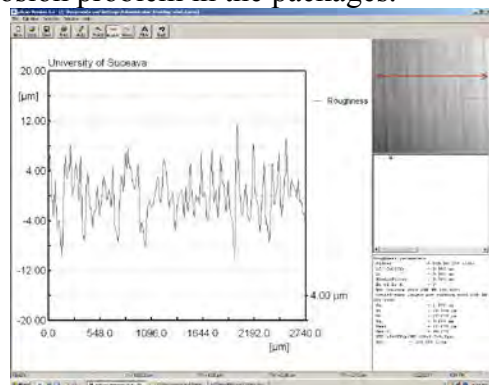


Fig. 8. Intermetallic thickness vs. exposure for 6 hrs at respective temperature b) effect of wire material & substrate metallization on electrical resistance after aging

Tests show that, after exposure at various temperatures, intermetallic growth is significantly slower in copper wire bonds than in gold wire bonds. Tests also show that despite a lower amount of intermetallic penetration, pull force and shear testing show values that are equivalent to, or greater than, those obtained with gold wire. Potential for maximum conductivity, device performance (at frequencies of <500 MHz) and resistance to degradation in a monometallic system are the driving forces for the

use of Cu wire in packages with Cu pads. DHF and iCu wire have been successfully ball-bonded to bare Cu lead frames and also AlSiCu metallized pads [8].

2. Conclusions

Recent studies have shown that, in many applications, copper wire bonding can provide better performance and reliability than gold wire bonding. While copper wire and ribbon have been used in discrete and power devices for many years, these latest studies also show that successes in ball bonding thin copper wire to aluminum, silver-nickel plating and even bare copper, provide the potential for its use in high-end, fine-pitch packages with higher lead counts and smaller pad sizes. For these reasons, along with the lower inherent cost of copper material, Kulicke & Soffa Bonding Wire [8] has developed and optimised two copper wire products: DHF copper wire for ball and wedge bonds in power devices and discrete packages; and iCu for fine-pitch or high-end IC applications.

References

- [1]. **M. Drozdov, G. Gur, Z. Atzmon, and W.D. Kapla**, *Microstructural Evaluation of Al-Cu Intermetallic Phases in Wire-Bonding*;
- [2]. **G. Harman**, "Wire Bonding in Microelectronics Materials, Processes, Reliability and Yield", 2 ed., *Electronic Packaging and Interconnection*, ed. C.A. Harper. 1997: McGraw-Hill;
- [3]. **F.W. Wulff, C.D. Breach, D. Stephan, Saraswati and K.J. Dittmer**, *Characterization of Intermetallic Growth in Copper and Gold Ball Bonds on Aluminum Metallization*, *Proceedings of Electronics Packaging Technology Conference*, 6th, Singapore, Dec. 8-10, 2004: 348-353, 2004.
- [4]. *** *Semiconductor Packaging Module II*;
- [5]. **James J. Wang and Bob Baird**, *Power gold for 175°C Tj max* ;
- [6]. *** *Semiconductor Packaging Assembly Technology 2000 National Semiconductor Corporation*;
- [7]. **Ying Zheng**, *Study Of Copper Applications And Effects Of Copper Oxidation In Microelectronic Package In Partial Fulfillment of MatE 234 2003*;
- [8]. **Kulicke & Soffa**, *Complete Connection DHF & iCu Copper Bonding Wire for Power Devices and High-End ICs*.

RISK FACTORS IN THE ELECTRO-DEPOSITION OF METALLIC MATERIALS

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ABSTRACT

Depending on their nature, metals can be obtained from solution, by well-determined potential electrolytic reduction. In practice, the electrolytic deposition of metals is used due to the two purposes: obtaining and refining metals from solutions and, namely, coatings of metallic or non-metallic materials. The electrolytic process must account for: the density of the deposited material, its structure, deposition potentials, current density and not last, temperature. The risk factors that can occur during the electro-deposition process comprise the risk factors on environment and humans. The risk factors on environment and people are represented by the prime materials used, by the vapors released further to the organic degreasing etc.

KEYWORDS: electro-deposition, metals, risk factors

➤ The production and processing of metals is done in industrial facilities, using electrochemical procedures where the total tank volume exceeds 30 m³. The main prime and auxiliary matters used consumptions are: chrome anhydride, sulfuric acid, phosphoric acid, sodium, potassium, metallic cadmium cyanides, sodium hydroxide, trichloroethylene, lead etc. Among these, most have a high toxicity degree.

❖ The treatment of cyanide-contaminated waters is done by oxidation reaction with the sodium hypochlorite (powerful oxidant agent and also bleacher due to its decomposition with the release of atomic oxygen).

❖ The treatment of chromium-contaminated waters (used waters containing chromium compounds and especially hexavalent chromium compounds, very noxious, as chromic, dichromic acid) basically consists in the reduction of hexavalent chromium to trivalent chromium by means of a reduction agent such as the sodium bisulfite and the further depositions

of the trivalent chromium as hydroxide, usually together with the heavy metals present in the used waters. The treatment of concentrated bases or acids is done by a neutralization reaction obtaining a chemically neutral solution. From the reaction pools used waters pass into the decanting pool for the separation of the mud containing deposited heavy metals from the used water, and then, after a final laboratory verification, they are dumped into the sewage of the industrial facility and then into the city sewage.

❖ The pollutants that may cause quality modifications of the soil in the area are the heavy metal ions generated by the activities within the objective; they may get into the soil either from the used waters directed to the own water treatment station – if the used waters sewage network is not maintained in the proper condition – or by aerosols containing heavy metals driven by the gas flows exhausted into the atmosphere.

Further to the current activities measurements should be performed: loss on

ignition, pH, heavy metal ion charging level (Cr, Zn, Cd, Cu), cyanides.

❖ Substance vapors are eliminated via the necessary ventilation of each technological tank and/or technological line. These emissions are considered to be fugitive emissions that are not monitored. But these emissions may contain small pollutant quantities that should have a significant impact on environment. To this end, the best available techniques must be applied to reduce these emissions as well as to reduce the consumptions of materials and utilities.

➤ Chemical risk factors on people depend on the chemical properties, as the substances used in the working process become sources of accidents and professional diseases, we mainly distinguish the toxic, caustic, flammable, explosive, carcinogenic substances.

Toxic substances are the substances that once having penetrated the organism, have a harmful action, disturbing its functions and causing acute or chronic intoxications. The acute intoxication takes place when the toxic substance enters the body in a large amount within a short period of time; otherwise – small quantities within a large period of time – a chronic intoxication occurs. Toxic substances may enter the organism most frequently via the respiratory path (inhaling) and through the skin (dermally) or via the digestive tube (accidentally). The ingress of toxic substances on respiratory path is the most frequent case (around 90% of intoxications) and has the most severe consequences, as their absorption at cellular and molecular level is done faster. As physical condition, such substances are found as gases, vapors, fumes, fog, aerosols or dust.

The dermal ingress of toxic substances especially takes place in the case of liquid toxic substances (gasoline, toluene, xylene, halogenated derivatives of methane and benzene etc.).

The ingestion of toxic substances is more rarely encountered, being possible only by negligence. The action of toxic substances on the organism may be local, only on certain organs or general, when it affects all tissues and organs (for instance the hydrocyanic acid or hydrogen sulfite). Yet an accurate delimitation according to the action criterion cannot be made, as most of the toxic substances have concurrently a general and a local action on the organism. .

❖ The air in the working places always contains powders, some of the most dangerous being the invisible ones, with the diameter less than 5 microns. It was found that some of them may cause pulmonary transformations generically called “pneumoconiosis”. There are many pneumoconiotic powders, both mineral and vegetal, causing irreversible pathological transformations (pulmonary fibrosis) within the lung, which reduce the life duration, being one of the most serious professional diseases.

❖ Noise sources are generally motors and equipments that have working rotating elements such as: ventilators, compressors, pumps etc.

The maximum admissible limits on the basis of which the environment is assessed from the acoustic point of view within an objective are specified at the limit of an industrial facility is of maximum 65dB.

❖ Due to the special working conditions there may occur the psychic overload which reduces the working efficiency, going to even depressive manifestations that may endanger the entire activity but also the life of the suffering person. The risk factors inherent to the social working environment are the nature of the interpersonal relations. These factors appeared as a new concept as there was found that the deficiencies in the communication system lead to the disturbance of the activity, and even to direct repercussions within the work security.

Conclusions

For an effective management it is necessary to analyze the existing risks and to track down other potentially risky situations throughout the technological process, the estimation of the risk level using objective criteria, the elaboration and application of a plan of measures that should reduce as much as possible the impact of the risk factors on people and environment.

The risks assumed during the electro-deposition process involve both the environment and the people, which causes the elaboration of an effective risk management and its practical application so as risky situations occur very rarely.

References

- [1]. **Cornel Florea Gabrian, Corneliu Horaicu**, *Environmental protection in the European Union – challenge for the sustainable development of economic activities*, TIPO Moldova Publishing house, Iasi, 2010
- [2]. **Alfa Xenia, Lupea Alina, Ghariben Branic, Aurel Ardelean, Dorina Ardelean**, *Environmental chemistry elements*, Didactic and Pedagogical Publishing House, Bucharest, 2008
- [3]. **Andrei Ciolac Ardelean**, *Fundamental notions of ecology and environmental protection*, Didactic and Pedagogical Publishing House, Bucharest, 2004
- [4]. **Marcel Dragan**, *Analysis of technological processes impacting on environment*, “Dunarea de Jos” University of Galati
- [5]. **Gheorghe Nemtoi**, *Electrochemistry, Fundamental aspects*, Tehnopress Publishing House, Iasi 2011
- [6]. **Horea Iustin Nascu, Lorentz Jantschi**, *Analytical and instrumental chemistry*, Academic Press & Academic Direct Publishing House, 2006
- [7]. **L. Onici**, *Physical Chemistry. Electrochemistry*, Didactic and Pedagogical Publishing House, Bucharest, 1974

THE IMPACT OF REFRIGERANT AGENTS ON THE ENVIRONMENT

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ABSTRACT

Freon was proven to have a significant role in the depletion of Earth's ozone shield. The excessive use of Freon in the cooling installations, in preparing the cosmetic aerosols makes the most harmful UVB wavelengths of UV light pass through Earth's atmosphere. The continuous degradation of this natural shield between us and the hazardous UV radiation that streams from the surface of the Sun, it is believed to have a variety of biological consequences, the most dramatic one is considered to be the extinction of any life form on Earth.

KEYWORD: ozone, refrigerant, recycling

1. Introduction

1.1. Sources and types of air pollution

Air pollution is any activity that causes pollutants to be emitted into the air. Any chemical substance released into to atmosphere at a specific concentration can have an unwanted negative effect on any living organisms, thus producing an unbalance to any ecosystem.

Some important air pollutants are classified based on their chemical composition as follows:

a. Inorganic compounds:

- Compounds of carbon (smoke black, carbon oxides);
- Sulphur compounds (oxides, H₂SO₄, sulphur);
- Nitrogen compounds (NH₃, metal oxides, HNO₃, nitrogen);
- Halogen compounds (chlorine and chloride, hydrogen fluoride and fluoride);
- Metals (Pb, Cd, Hg);
- Chemically inactive powders (silicates, carbonates, natural minerals).

b. Organic compounds:

- Hydrocarbons (saturated, unsaturated, aromatic);
- Oxygenated compounds (alcohols, aldehydes and ketone);
- Halogenated compounds (Freon, Halon);
- Radioactive substances;
- Bio aerosols (pollen, mould spores).

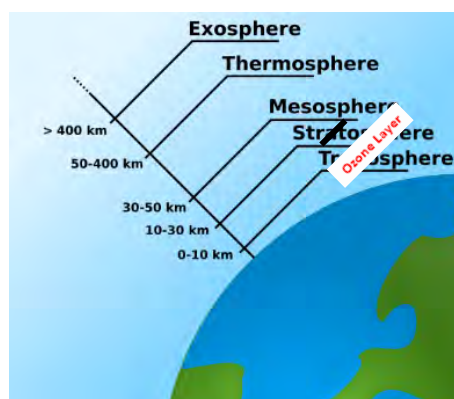


Fig.1. Atmosphere layers

1.2. Layers of the Earth's Atmosphere

1.2.1. The ozone layer

The ozone layer is a layer in Earth's atmosphere which contains relatively high

concentrations of ozone (O_3). This layer absorbs 97–99% of the Sun's high frequency ultraviolet light and it is situated in the lower portion of the stratosphere at approximately 30 kilometres from Earth. Acting as a filter which retains almost completely the harmful UV radiations to which the surface of the Earth is exposed to, regulating the atmosphere's temperature, this natural thin layer called the ozone layer is an extremely important element in protecting all forms of life.

The drop in ozone's concentration with 1% results in amplifying the intensity of the UV radiation with 2% at ground level. In 1974 was proven that particular chemical substances used by humans to produce different types of cooling installation and

aerosols are carried up to the stratosphere by the movement of the air masses and are destroying the ozone layer. Another contributor to the degradation of the ozone layer is the methyl bromide; tones of CFC are thrown into the atmosphere every day. All these elements caused the generation of the ozone hole.

The ozone hole is not exactly a 'hole' where ozone lacks completely, actually represents a region situated from stratosphere where the concentration of ozone has significantly decreased over the last past years. Satellite images shows that the ozone hole is situated above the Antarctic region. This is constantly moving over Antarctica as shown in *Fig.2*.

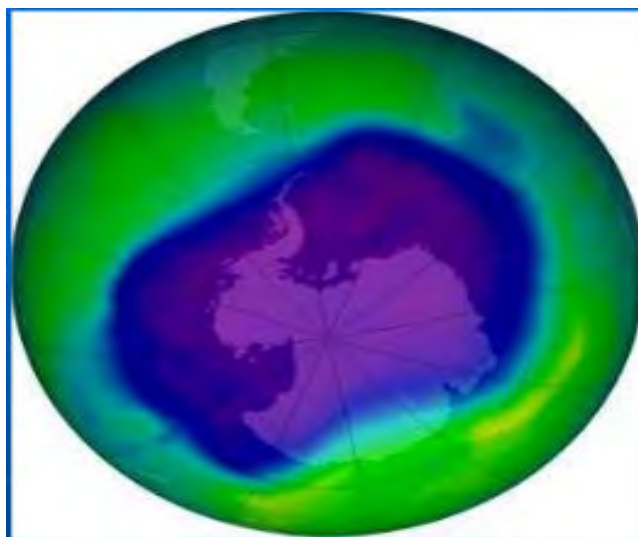


Fig.2. Ozone Hole (satellite image)

By exposing Freon molecules to UV rays generated by the Sun, results the monatomic chlorine (Cl) (see *Fig. 3.*). Cl chemically reacts with the ozone (O_3), present in the stratosphere, and produces diatomic oxygen and oxides of chlorine (O_2).

The ozone layer is a layer in Earth's atmosphere which contains relatively high concentrations of ozone (O_3). This layer absorbs 97–99% of the Sun's high frequency ultraviolet light and it is situated in the lower portion of the stratosphere at approximately

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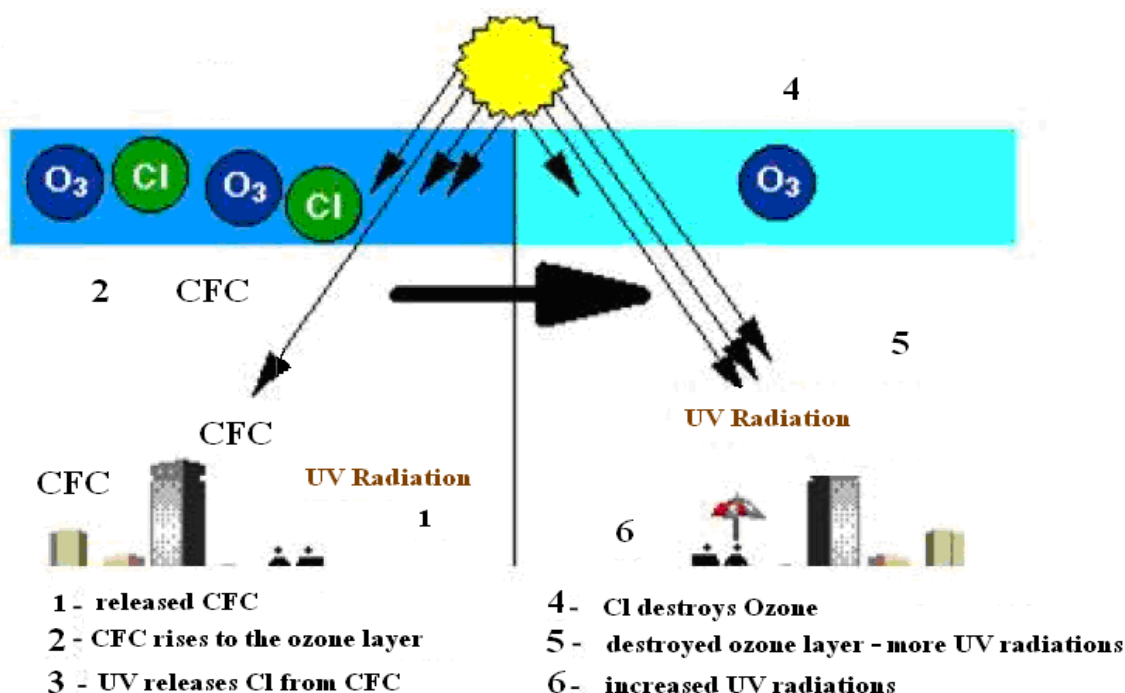


Fig.3. Ozone depletion process

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3. Chemical composition of Freon

Freon is the commercial name for the odourless, colourless, non-flammable and non-corrosive fluid which is used for air conditioning, for cooling installation and some fire extinguishing systems. Freon is

considered to produce major health problems and in excessive concentrations can even cause asphyxiation. The most common representative is dichlorodifluoromethane also known as R-12 or Freon-12.

Chemical speaking Freon represents fluorinated hydrocarbons can be divided in three main categories as described in Fig.4:

- Chlorofluorocarbons (CFCs) – their molecule contains very instable Cl;
- Hydrochlorofluorocarbons (HCFCs) – their molecule contains also hydrogen and makes Cl more stable and not easily decomposing when exposed to UV rays;
- Hydrofluorocarbons (HFC's) – their molecules doesn't contain Cl.

CFC		HCFC		HFC	
			Hydrogen		Hydrogen
	Chlorine		Chlorine		
	Fluorine		Fluorine		Fluorine
	Carbon		Carbon		Carbon

Fig.4. Three types of Freon

Table 1. Alternative refrigerants containing HCFC

Agent	Formula + mass composition (%)	$T_N/\Delta T$ (°C)	ODP (R11=1)	GWP (CO ₂ =1)	Substitutes	Commercial Name
R22	CHClF ₂	- 40.9	0,055	1700	R502	R22
R123	CHCl ₂ -CF ₃	27.9	0,020	93	CFC11	R123
R124	CHClF-CF ₃	- 13.2	0,022	480	CFC114	R124
R141b	CH ₃ -CCl ₂ F	32.2	0,110	630	CFC11	R141b
R142b	CH ₃ -CClF ₂	- 9.1	0,065	2000		R142b
R401A	R22/152a/124 (53/13/34)	(-33.0/6.3)	0,037	1100	CFC12	Suva MP 39
R401B	R22/152a/124 (61/11/28)	(-34.6/5.9)	0,040	1200	CFC12 R500	Suva MP 66
R401C	R22/152a/124 (33/15/52)	(-28.3/4.7)	0,030	850	CFC12	Suva MP 52
R402A	R125/290/22 (60/2/38)	(-48.9/2.0)	0,021	2600	R502	Suva HP 80
R402B	R125/290/22 (38/2/60)	(-47.1/2.3)	0,033	2200	R502	Suva HP 81
R403A	R290/22/218 (5/75/20)	(-50.0/2.5)	0,041	2700 ¹ >8000 ²	R502	Isceon 69-S
R403b	R290/22/218 (5/56/39)	(-49.5/0.9)	0,030	3700 ¹ >14000 ²	R502	Isceon 69-L
R405A	R22/152a/142b /C318 (45/7/5.5/42.5)	(-35.5/5/5)	0,028		CFC12	Greencool ATG-405A
R406A	R22/600a/142b (55/4/41)	(-36.0/9.9)	0,057	1800	CFC12	GHG 406A
R408A	R125/143a/22 (7/46/47)	(-44.4/0.7)	0,026	3000	R502	Forane FX 10
	R125/143a/290/22 (72/6/2/50)	(-50.6/1.0)	0,027	2500	R502	Meforex DI 44
R409A	R22/124/142b (60/25/15)	(-34.3/8.5)	0,048	1400	CFC12	Forane FX 56
	R22/124/142b (65/25/10)	(-35.5/7.7)	0,048	1400	CFC12	Forane FX 57
	R22/124/600 (50/47/3)	(-32.1/6.1)	0,038	1100	CFC12	Meforex DI 36
R509	R22/218 (44/56)	-47.5 (azeotrop)	0,024	4700 ¹ >19000 ²	R502	Arcton TP5R2
R411A	R1270/22/152a (1.5/87.5/11)		0,048	1500	HCFC22	Greencool G2018A

Agent	Formula + m ass composition (%)	$T_N/\Delta T_F$ (°C)	ODP (R11=1)	GWP (CO ₂ =1)	Substitutes	Commercial Name
R411B	R1270/22/152a (3/94/3)		0,052	1600	R502	Greencool G2018B
R412A	R22/218/142b (70/5/25)	(-40.1/8.1)	0,055	2000 ¹ >3300 ²	R500	Arcton TP5R

¹ - where: FC218: GWP₁₀₀=7000 ² - where: FC218: GWP₁₀₀>34000

Table 2. Alternative refrigerants

Agent	Formula + m ass composition (%)	$T_N/\Delta T_F$ (°C)	GWP (CO ₂ =1)	Substitutes	Commercial Name
R23	CHF ₃	- 82.1	12100	*CFC13/BFC13B1 *R503	
R32	CH ₂ F ₂	- 51.7	580		
R125	CHF ₂ -CF ₃	- 48.6	3200		
R134a	CF ₃ -CH ₂ F	- 26.1	1300	*CFC12/HCF22	
R143a	CH ₃ -CF ₃	- 47.4	4400		
R152a	CHF ₂ -CH ₃	- 24.7	150		
	R218/134a/600a (9/88/3)	(-35.0/5.2)	1800 ¹ >4200 ²	*CFC12	Isceon49 (RX2)
R404a	R125/143a/134a (44/52/4)	(-46.5/0.8)	3700	*R502/HCF22	Forane FX70 Suva HP62
R-407A	R32/125/134a (20/40/40)	(-45.5/6.6)	1900	*R502	Klea 07A
R-407B	R32/125/134a (10/70/20)	(-47.3/4.4)	2600	CFC12/*R502	Klea 07B
R-407C	R32/125/134a (23/25/52)	(-44.0/7.2)	1600	*HCFC22	Klea 407C Suva 9000
	R32/125/143a (10/45/45)	(-49.7/0.9)	3500	*R502	Forane FX 40
R-410A	R32/125 (50/50)	(-52.7/<0.1)	1900	HCFC22	Genetron AZ20 Solkane 410A
R-410b	R32/125 (45/55)	(-51.8/<0.1)	2000	HCFC22	Suva 9100
	R32/125/143a/134a (10/33/36/21)	(-49.4/4.1)	3000	HCFC22/*R502	Reclin HX4
	R32/125/134a (4.5/21.5/74)	(-43.0/10.2)	1600	*HCFC22	Forane FX 220
R507	R125/143a (50/50)	-46.7(azeo)	3800	R502	Genetron AZ50 Meforex M57
	R125/290/218	-54.6 (neaz)		*BFC13B1	Isceon 89 (RX4)
R508	R23/116 (39/61)	- 85.7 (azeo)	12300	*CFC13/*R503	Klea 508
	R23/116 (46/54)	- 88 (near)	12300	*CFC13/*R503	Suva 95
	R32/134a (25/75)	(-40/7.2)	1100	*HCFC22	
	R290/600 (50/50)	(-31.6/12.3)	3	*CFC12	OZ 12
R717	NH ₃	- 33.3		HCFC22/R502	

Table 3. Applicability for refrigerants

Application	Refrigerant	Transition agents	Permanent agents
Home appliances	R12	R401A (MP39) R409A (FX56)	R134a R290 (Propane) R600a (Isobutane)
Water coolers	R11 R12 R114 R22 R117(NH3)	R123 R142b R22	R134a R404A R117(NH3)
Commercial refrigeration (positive temperatures)	R12	R401A (MP39) R409A (FX56) R22	R134a R404A R507 R413A
Commercial refrigeration (negative temperatures)	R502	R402A (HP80) R408A (FX10) R403B R22	R404A R125 AZ50 - R407B
Industrial refrigeration	R717(NH3) R22	R22	R717 (NH3) R404A
Deep-freeze refrigeration	R13B1 R13 R503		ES20 R23 R32
Conditioning	R22 R500	R409B (FX57) R401B (HP66)	R124a R407C Klea66
Auto Air Conditioning	R12 R500	R401C (MP52) R409B (FX57) R401B (HP66)	R134a

The impact of refrigerant agents on the environment can be divided in the following categories:

- Human and animal toxicity;
- The influence upon biological and genetic domains;

- The influence upon olfaction;
- the flammability and explosion limits;
- Impact on global warming – energy production and usage, CO₂ emission;

- Impact on the ozone layer.

3. Refrigerants Conservation

3.1. Refrigerants Recovery

To recover the refrigerant agent represents the capability of collecting and storing it into an external container. Refrigerants are taking out from an installation and are placed in a gas cylinder.

3.2. Refrigerants recycling

To recycle the refrigerant agent means

to extract it from an installation and clean it by separating the oils and by passing through a filter dryer, one or multiple times, if needed.

This process is basically used to remove oils and acid, particles and chlorides, and the air inside the used refrigerant.

It is prohibited the usage of substances in the process of maintenance the cooling systems and air conditioning, that can affect the ozone layer.

3.3. Equipments for recovery, recycling and disposal of refrigerants

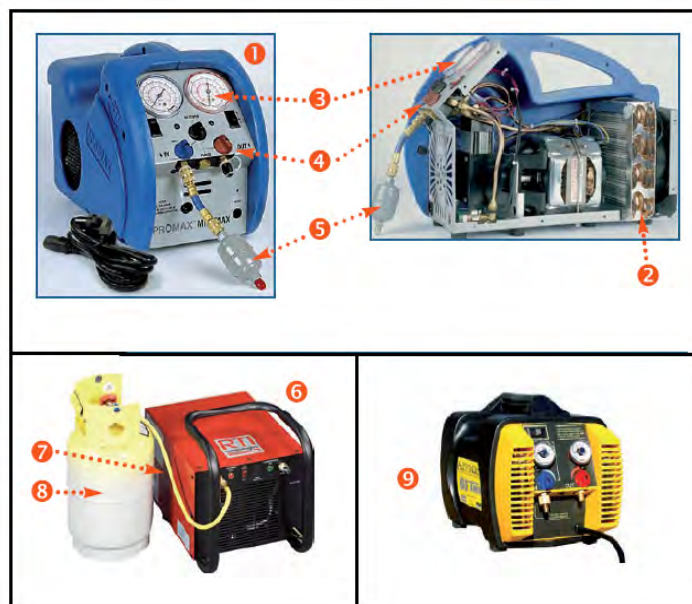


Fig.5. Refrigerant recovery unit

- 1- recovery unit "oil less" commercial refrigeration and air-conditioning;
2-condenser and ventilator; 3-high and low pressure gauges; 4-refrigerant inlet and outlet valves;
5-inline filter-drier; 6-recovery unit "oil based" for small commercial, AC and domestic;
7- access cord for overfill protection (OFP); 8-recovery cylinder;
9- recovery unit "oil less" for all refrigerants including CFC-R11.

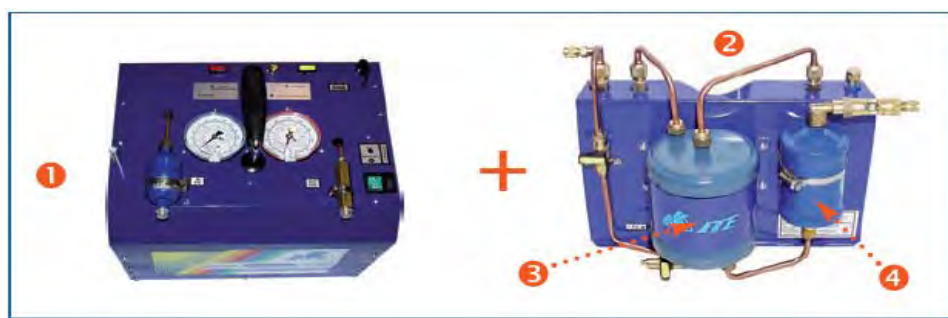




Fig.6. Refrigerant recovery and recycling unit

1- recovery unit "oil less" commercial refrigeration and air-conditioning equipped with connective facilities for refrigerant recycling; 2-refrigerant cleaning module for recovery unit; 3-oil separator with oil drainage valve; 4-filter-drier with sight glass; 5- recovery unit "oil based" for small commercial, AC and domestic; 6- refrigerant cleaning module for recovery unit; 7-cleaning module for all recovery units; 8- oil separator with oil drainage valve; 9-manifold gauge set with high and low pressure gauges; 10- filter-drier with sight glass

3.4. Refrigerant Charging

Charge the system with. Cautious should be taken not overcharge. (80-90% of the CFC charge as a starting point)
CFC:CFC>halone based refrigerants; Developed over 60 years ago; Major cause of ozone damaging; R11,R12,R502.

HCFC:HCFC>halogenated refrigerants; Called Hydrochlorofluorocarbons; Causes less of ozone damaging than R11/R12; Effect on global warming; R22, R23. (4.5 Kg of R22 are equal to 8100 Kg of CO₂; Medium-class car exposes approx. 0.200Kg/Km CO₂; You can drive 40500Km for the same CO₂ ; Emission of 4,5 Kg HCFC-R22)

HFC: No chlorine atoms; Called Hydrochlorofluorocarbons; Zero potential of ozone damaging; Slight effect on global warming; R134a, R23, R125, R407C, R410.

HC:Natural refrigerant; Called Hydrocarbons; Zero potential of ozone damaging; Very low effect on global warming; Flammable, explosive; R290, R600.

RETROFIT

Refrigerants R134a, R404A and R507 are NOT "drop-in" replacement for CFC-based refrigeration systems.

Mineral oils and Alkylbenzene lubricants are immiscible with the refrigerants above and must therefore be replaced with new lubricants.

The retrofit procedures listed at the following pages, have been developed to address these issues and to help technicians perform successful retrofits of refrigerating systems utilizing positive-displacement (reciprocating, rotary, scroll or screw) compressors with HFC Refrigerants.

HFC- Refrigerants 134a: Refrigerants 134a is a good alternative refrigerant to

replace CFC-12 in most medium-temperature refrigeration system.

This products an HFC and therefore is not scheduled for phaseout under current law.

Stationary Applications where R134a is a suitable retrofit refrigerant include supermarket cases, walk-in coolers, beverage dispensers, vending machines, coolers and home refrigerants.

The use of R134a should be limited to applications where the evaporator is above-23°C.

HCF- Refrigerants 404A: Refrigerants 404A is a blend(HCF-125/HCF-143a/HCF-134a-with glide)designed to serve as a alternative to R-502 and HCFC-22 in low-and medium-temperature commercial refrigeration applications.

This product contains three HFCs and therefore is not scheduled for phaseout under current law.

Applications where 404A is a suitable retrofit refrigerant include supermarket freezer cases, reach-in coolers, display cases, transport refrigeration and ice machines.

HCF- Refrigerants 504: Refrigerants 504 is a azeotrope (without glide)mixture(HFC 125/HFC143a)designed to serve as a alternative to CFC R- 502 and HCFC R-22 in low-and medium-temperature commercial refrigeration applications.

This product contains two HFC's and therefore is not scheduled for phase-out under current law.

Applications where R 507 is a suitable retrofit refrigerant include supermarket freezer cases, reach in coolers, display cases, and ice machines.

SAFETY:R-134A,R404 and R507 can be safely used in all its intendent applications, based on data developed by the Program for Alternative Fluorocarbon Toxicity Testing.(toxicity).

If a lange release of vapour occurs, the evacuated immediately. Vapours may

concentrate near the floor, displacing available oxygen.

Once the orea is evacuated, it must be ventilated using blowers or fans to circulate the air at floor-level (leaks).

According to ASHRAE Standard 34 the refrigerants are classified in safety group A1, i.e., it is non-flammable at 1 atm.

Pressure (101.3kPa) and 18 ° C (flammability).

Special Considerations with R134a:R134a has been shown to be non-flammable at ambient temperature and atmospheric pressure. However, tests under controlled conditions have indicated that at pressures above atmospheric and with air concentrations grated than 60 pe rcnt by volume, R134a can form combustible mixtures.

While it is recognized that an ignition source is also required for combustible mixtures is a potentially dangerous and should be avoided. Under no circumstances should any equipment be pressure tested or leak tested with Air and R134a mixtures. Most national standards follow either European norms (CE) or US/Canadian standards.

Table.4. CE or US/Canadian standards

Equipment type	European	US/Canadian
Recovery and Recycling equipment Safety	CE marking EN378, EN60335	UL marking,UL1 963
Recovery and Recycling Performance	ISO 11650	ARI 740 SAE-J1991 SAE-J2210 SAE-J2788
Reclaim equipment safety	CE marking EN292, EN60204	Various UL
Reclaim equipment Perfomance	ARI used	ARI700

4. Conclusions

Following the scientific researches of harmful effects on the ozone layer caused by Freon, the international community has taken several measurements to reduce and even forbid their use.

Although, internationally, drastic measures regarding the prohibition of CFC (chlorofluorocarbon) use have been adopted, in the scientific world there are also opinions which claim that the destructive potential of these substances is not by far so high as it is asserted. Consequently, several situations which refute the anterior assumptions concerning the role of CFC in destroying the ozone layer and, as a result, the increase of the ultraviolet radiations level, were declared.

In the South of Latin America, several communities are struggling for decades to survive the devastating effects caused by the hole in the ozone layer.

Scientists say that if the provisions of the Montreal Protocol will be carried out,

the ozone layer will fully recover by year 2050.

Earth's future depends on our attitude and actions towards environmental issues.

5. References

- [1]. **Viorel Munteanu** – *Calitatea mediului*, Editura Fundației Universitare “Dunărea de Jos”, Galați, 2008;
- [2]. **Fl. Chiriac** – *Instalații frigorifice*, Editura Didactică și Pedagogică, București, 1981;
- [3]. **Popescu Gh., Apostol V., Porneala S.**, – *Echipamente și instalații frigorifice*, Editura Printec, București, 2005;
- [4]. **L.I. Ciplea, Al. Ciplea** - *Poluarea mediului ambiant*, Ed Tehnică, București, 1978;
- [5]. **Lixandru, B.** - *Ecologie și protecția mediului*, Timișoara, Editura Presa Universitară, 1999;
- [6]. **Ardelean, Florinela** - *Ecologie și protecția mediului* 2007;
- [7]. **Kaposta, Iosif** - *Ecologie și protecția mediului*, 2009;
- [8]. <http://www.unep.fr> – *Agenți frigorifici*;
- [9]. www.metoffice.gov.org - *Compoziția atmosferei terestre*;
- [10]. <http://www.scientia.ro/>- *Atmosfera terestră*;
- [11]. www.needpedia.org – *Freonul*.

THE INFLUENCE OF ELECTRODEPOSITION PARAMETERS ON OBTAINING NICKEL-SILICON COMPOSITE LAYERS

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ABSTRACT

Nickel coatings are widely applied for high corrosion resistance, decorative or to increase hardness, resistance to wear and abrasion. Electrodeposition parameters nickel-silicon composite layers analysed in this paper during the deposition was current density and speed of rotation of the agitator in the electrolyte. Nickel - silicon composite coatings obtained by electrochemical dispersed phase particles are the silicon with sizes $< 5\mu\text{m}$. Increasing electrodeposition time and current density have increased the deposited layer thickness, while increasing the rotational speed of agitator electrodeposited layer thickness decreased.

KEYWORD: electrodeposition, composite, current density, deposition time, rotation speed

1. Introduction

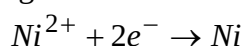
The electrochemical method is used to obtain a large number of types of materials with superior characteristics and low cost. Achieving competitive coatings by this method need carefully analyse for determining the limits of variation of the production parameters: current density, electrolyte pH, temperature, electrolyte mixing by stirring, etc.

The current density increased speed of migration of ions in the cathodic layer increases. Increasing current density results in most cases the formation of coatings with fine structure due to the multiplication of germs of crystallization of the cathode. The influence of current density is explained by the increase of the cathode active surface, forming crystalline germs on inactive or less active sections above. In some cases, the change in crystal size with increasing current density passes through a maximum at first ascertaining the crystal growth and from a given current density, whose size depends on the nature and composition of electrolyte, temperature and

other factors, deposit structure becomes more and more fine. The current high density increase hardness layer and deposition rate.

However, the current density cannot be increased without limit. At very high current densities, especially in an electrolyte that is not shaken, because rapid depletion of the layer of metal ions around the cathode, there is the formation of loose deposits in the form of dendrites, the corners and in other prominent places cathode or compact form of a spongy mass over the entire surface of the cathode. These deposits consist of separate particles that are aggregates of crystals related to each other or with weak support surface. After removal of electrolyte they separate easily from the cathode surface, and sometimes. If a high current density off the cathode falls to the bottom even during electrolysis bath. The lower density depositing process is slow, the crystals will grow larger, and the layer will have low hardness. A good correlation between current density and deposition time can lead to desired results [1-3].

Electrolyte agitation is used in electrodeposition processes in order to maintain constant concentration of the solution to the electrode and to prevent concentration polarization. Because of this, the bath agitation is applied to obtain compact storage, smooth and fine grain at higher current densities and higher current efficiency in terms of quantity of metal produced. If the current density is higher, the electrolyte and agitation should be more intense. In solutions of nickel salts, nickel ions are present in the form of bivalent ions. Nickel ion is reduced at the cathode. The process can be described by the following reaction:



Since the normal potential of nickel ions is more negative than hydrogen ($E_{\text{Ni}}^0 = -0,25 \text{ V}$, $E_{\text{H}}^0 = -0,23 \text{ V}$), in solution would be to deposit a large amount of hydrogen: $2\text{H}^{+} + 2e^{-} \rightarrow \text{H}_2$, but the deposit is prevented because the voltage peak of the nickel surface is high.

Nickel baths are sensitive to pH, which must be included between 5.4 - 6. To stabilize the solution pH, electrolyte, nickel salts in addition, have to contain an acid: sulphuric, boric or citric. The electrical conductivity of solutions of nickel salts is relatively low, which does not allow use of higher current intensities, in order to accelerate the deposition process.

To remedy this situation are used the electrolytic solution and the so-called "salt of leadership" that contain cations with a redox potential more negative than nickel (Ni^{2+}), which are reduced with nickel on the cathode, but have a high mobility, providing an abundant electrical charge transport. Examples of such salts are $(\text{NH}_4)_2\text{SO}_4$, NH_4Cl , Na_2SO_4 , NaCl , etc. Chlorides, helps dissolve the nickel anode and used in "fast bath". But they give macro crystalline nickel deposit, which does not provide good protection against corrosion. Therefore using nickel sulphate [4-6].

2. Experiments and results

This study refers to the layers obtained composite layers in nickel matrix by electrochemical method, by using silicon powder at a concentration in solution of 20 g / L and width of particles < 5 mm. Embedding particles was achieved with a variable speed mechanical stirrer. By incorporating these particles in nickel matrix composite coatings was intended to obtain the best corrosion properties, decorative, to increase hardness, resistance to wear and abrasion, than pure nickel.

Chemical composition and working parameters of electrolytes test is shown in Table 1.

Table 1. Chemical composition and working parameters of electrolytes

Electrolyte composition	Electrodeposition parameters
- $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$; 110 g/L - $\text{Na}_2\text{SO}_4 \times 10\text{H}_2\text{O}$; 110 g/L - NH_4Cl; 25 g/L - H_3BO_3; 15 g/L	- Temperature: 20 – 30 °C - Current density: 0.5 to 3 A/dm² - pH: 5-6 - Electrodeposition time: 30 to 60 min - Stirring speed: 500, 750 and 1000 rpm

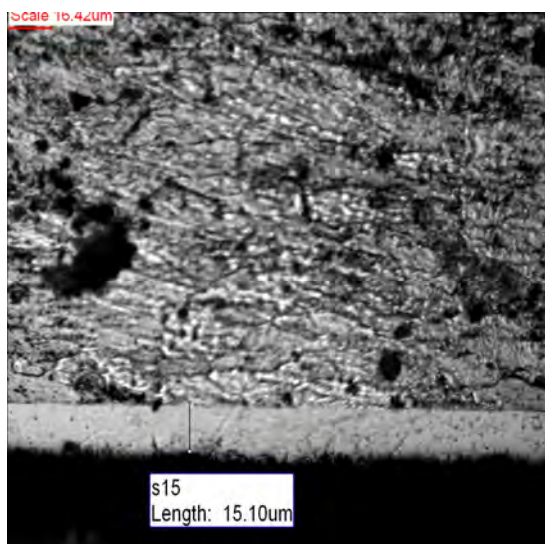
Nickel coatings obtained showed good adhesion and were uniform. Nickel sulphate provides the bulk of nickel ions and nickel chloride improved anode dissolution, by reducing overvoltage and increased electrolyte conductivity. Decrease of

Cl^- ions concentrations occurs in the cathodic film can produce "burn" deposits. This was avoided by the permanent correction of Cl^- ion concentration in electrolysis baths. Boric acid has stabilized the electrolyte pH. $\text{Na}_2\text{SO}_4 \times 10\text{H}_2\text{O}$ use in electrolyte solution was to

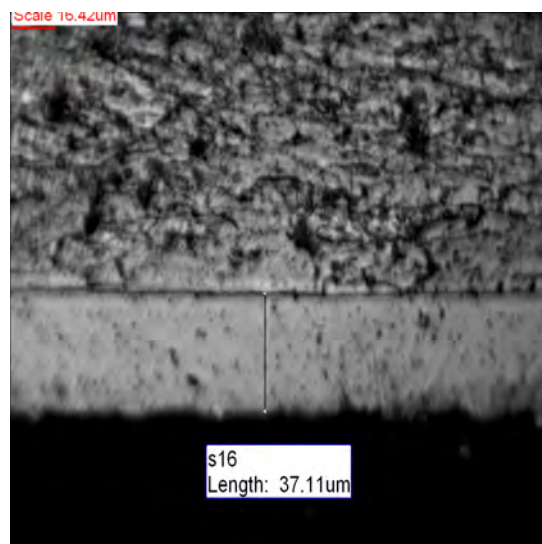
increase electrical conductivity, increase dispersion capacity and lower electrolysis voltage.

The thickness of coatings was determined by cross sectioning, mounting samples in epoxy, polishing and optical microscopy observation of the size layer.

After electrodeposition were made of composite nickel – silicon layer, compact and adherent, with a dispersed distribution of particles. Photo 1 present the layers obtained at a deposition time: 30 min and 60 min.



a)



b)

Photo 1. Thickness of electrodeposited nickel-silicon composite layers X 800;
a) 2A/dm², 30 min, 1000 rpm; b) 2A/dm², 60 min, 1000 rpm.

Layer thickness depends on the electrodeposition current density, figure 1.

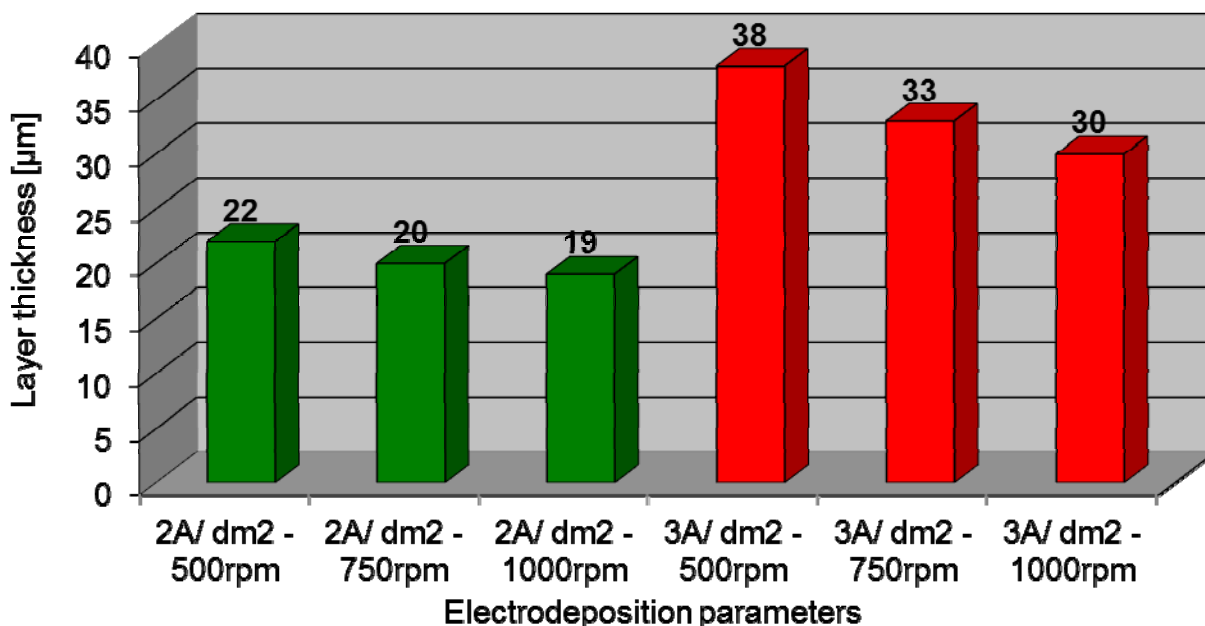


Fig. 1. Variation of thickness of nickel-silicon layers deposited with current density for the electrolyte I, during 60 minutes

The current density increased from 2 to 3 A/dm², there is an increase of layer thickness from 22 mm to 38 mm at 500 rpm; from 20 mm to 33 mm at 750 rpm and

19 mm to 30 mm at 1000 rpm. Also, there is a decrease a layer thickness with increasing stirring velocity.

3. Conclusion

1. Nickel coatings obtained showed good adhesion and were uniform.
2. Increasing electrodeposition time result an increase in the thickness of the layer of 15.10 mm to 37.11 mm, keeping the current density constant at 2 A/dm² and rotation speed mixer at 1000 rpm.
3. Increasing the current density from 2 to 3 A/dm², caused an increase of layer thickness by 16 mm, 13 mm and 11 mm, and increase the rotational speed from 500 rpm to 750 rpm, respectively at 1000 rpm.
4. Electrodeposited layer thickness decreased to increase stirring velocity.
5. The increased current density over 3 A/dm² the quality of deposited layer greatly decreases.

References

- [1]. **J.L. Stojak, J. Fraser, J.R Talbot**, *Rewiew of Electrodeposition*, Advances in Electrochemical Science and Engineering, vol. 3, p.193, 1994.
- [2]. **G. I. Desyatкова, L. M. Yagodkina, I. E. Savochkina, and G. V. Khaldeev†**, *Composite Nickel-Based Electroplates*, Protection of Metals, Vol. 38, No. 5, 2002, pp. 466–470. Translated from Zashchita Metallov, Vol. 38, No. 5, 2002, pp. 525–529.
- [3]. **M. Popczyk, J. Kubisztal, A. Budniok**, *Structure and electrochemical characterization of electrolytic Ni+Mo+Si composite coatings in an alkaline solution*, Electrochim. Acta 51, pp. 6140-6144 (2006).
- [4]. **M. Popczyk, A. Budniok, E. Łągiewka**, *Structure and corrosion resistance of nickel coatings containing tungsten and silicon powders*, Mater. Charact. **58**, pp. 371-375 (2007).
- [5]. **M. Popczyk, J. Kubisztal, A. Budniok**, *Electrodeposition and thermal treatment of nickel coatings containing molybdenum and silicon*, Mater. Sci. Forum **514-516**, pp. 1182-1185 (2006).
- [6]. **Alina-Crina Ciubotariu, Lidia Benea, Magda Lakatos - Varsanyi, Viorel Drăgan**, *Electrochemical Impedance Spectroscopy and Corrosion Behaviour of Al₂O₃-Ni Nano Composite Coatings*, Electrochimica Acta, vol. 53; p. 4557, 2008.

COMPARATIVE STUDY ON THE UNCONVENTIONAL SOURCES OF POWER GENERATION

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ABSTRACT

Growing need for electricity from clean sources determine the amplification of research in this field. The study presents some solutions to obtain electrical energy by unconventional means. The solutions presented allow to obtain a cheap and clean energy. It is the use of photoluminescence and photovoltaic panels, wind energy and water.

KEYWORD: Photovoltaic panel, parabolic concentrators, wind generator, radiant panel

1. Introduction

In the future energy needs to be minimized (the reasons are economic, environmental and political), including the buildings regardless of their use as living quarters or more.

The electricity consumed by human communities can be minimized by reducing the consumption of plants both inside and outside of the human habitat as well as by reducing all energy losses. The highest energy consumption are those with home heating, hot water, cooking and using household appliances.

The analysis of a human habitat in terms of energy efficiency, this energy can be thermal or electrical applications.

Electrical power required for some of these heating systems can be taken from public electricity grid or can be produced through the use of technological solutions applicable to renewable energy sources (solar, wind or hydraulic).

The choice of power supply of housing must be taken into account the efficiency of the plant, which produces poluareape,

energy consumption, space utilization, life, technology and safety, maintenance costs and installation.

2. Recovery equipments and technologies for solar radiation

Using solar radiation to produce electricity can be made through several methods:

- use of photovoltaic modules;
- use solar towers;
- use parabolic concentrator;
- use Dish-Stirling system.

2.1. Photovoltaics equipment

Photovoltaic generator (Figure 1) is organized as photovoltaic field covering all elements of interconnection (wiring), protection (or bypass anti-return diode) and / or specific parts (actuators for mobile billboards, automatic guidance devices, etc..) There are essentially two types of operation:

- Operation without storage (with network connection);
- Operating with storage (autonomous).



Fig.1. Photovoltaic panel

2.2. Solar tower systems

Solar tower systems involve a circular arrangement of photovoltaic panels, with the possibility of their orientation throughout the day depending on the position of the sun (figure 2). Electricity from photovoltaic panels is taken by cables and is directed towards the central tower.

Due to different exposure to solar radiation of the panels during the day, there

is a variation of electricity that is sent to the control tower.

The computer system of the command center is designed to balance energy transmitted from photovoltaic panels.

There is an electric energy storage system, when it is in excess.

This additional electricity will be issued in the national power system network when needed.



Fig.2. Electrical energy generation with solar tower system

2.3. Parabolic concentrator systems

Another way to capture solar radiation is the parabolic concentrators (Figure 3). This type of concentrator consists of a

parabolic mirror trough-shaped solar that focuses solar radiation on a pipe. In the pipe a fluid circulating which is usually oil. Heat of the oil is transmitted to the water. The

water is turns to steam which drives a turbine generator. This power generation system, requires a computer system to optimize the position solar concentrator

according to the maximum angle of incidence of solar radiation.

The system is equipped with batteries to store excess electricity produced.



Fig.3 Electrical energy obtained with parabolic concentrator systems

2.4. The Dish-Stirling system

They use Stirling engine (Figure 4) which is powered by heat energy supplied by a solar parabolic trap. The generation functioning of Dish-Stirling systems functioning, required heat that is taken from the parabolic solar panels.

Stirling heat engine is a system with closed-cycle regenerative of air heaters, where the working fluid is in a closed space. This is called the thermodynamic system. The open cycle machines such as internal combustion engine, it produces a permanent exchange with the working fluid thermodynamic cycle friendly as part of thermodynamic.

Stirling engine converts heat into mechanical work by the maximum Carnot efficiency. The coefficient of friction, thermal conductivity, melting point and plastic deformation would contribute significantly to reducing efficiency.

Stirling engines are quieter and more

economical than internal combustion, can be more reliable in operation and have no major maintenance requirements.

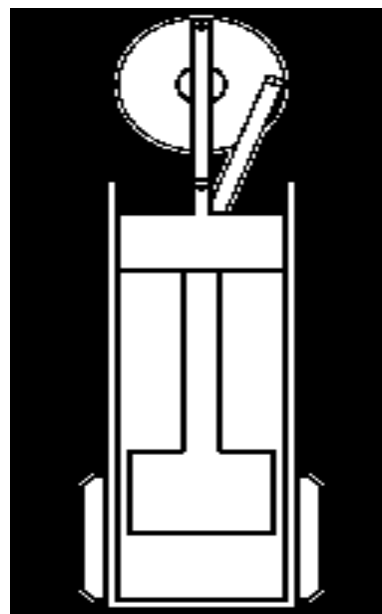


Fig.4. The principle of function for stirling engine.



Fig. 5. Dish-Stirling system for electrical energy produced.

In a complete cycle Stirling of pressure and volume the cost of this system is competitive up to about 100 kW of produced energy.

3. Wind technology and equipment

Almost all wind turbines installed for power generation until the last decade have been based on one of the three main types:

- a) speed induction generator with its rotor short-circuit directly coupled to the power grid;
- b) Variable speed induction generator with dual excitation;
- c) Variable speed based on synchronous generator rotor directly coupled to the wind.

Besides these main types, several manufacturers have developed other technologies over time; for wind turbines the range of power is between 600kW and 3MW.

Also, two technological solutions have emerged:

-Pitch turbines equipped with induction generators;

- Wind turbines operating with synchronous generator rotor directly coupled wind like in figure no.6.

For the second type of wind turbine, the shaft is supported by one bearing in each side of the generator.

This constructive solution provides greater reliability and is distinguished by much lower maintenance costs.



Fig.6. Wind turbine

Currently, this solution is applied to wind design with power ratings from 300 kW and reaching up to 4 MW power, the ECAC is conceptually aggregates with generators directly coupled wind turbine, să se asert more and more.

4. Autonom Systems

Mini / micro local networks: the small communities, some tourist attractions located in remote areas far from the distribution network can be powered with wind turbines integrated into the micro / mini local distribution network (LV). The basic structure of such a network include:

- * A group of wind turbine generator

forming EOL

- * Batteries charging unit (optional)
- GMG Group * (optional)

EOL for individual farms food system is presented in Figure 7.

Establishing these areas suitable for installing wind generators was based on the fact that all wind turbines will be located in Sub wind potential I-II (corresponding to the relief that: hills, plateaus, mountains and coastal plains with wind speeds over 5 m / s), according to data contained in the wind map of Romania.

Concrete specification of the location of wind turbines is made from field investigations, taking into account the plans of land, land configuration, etc..

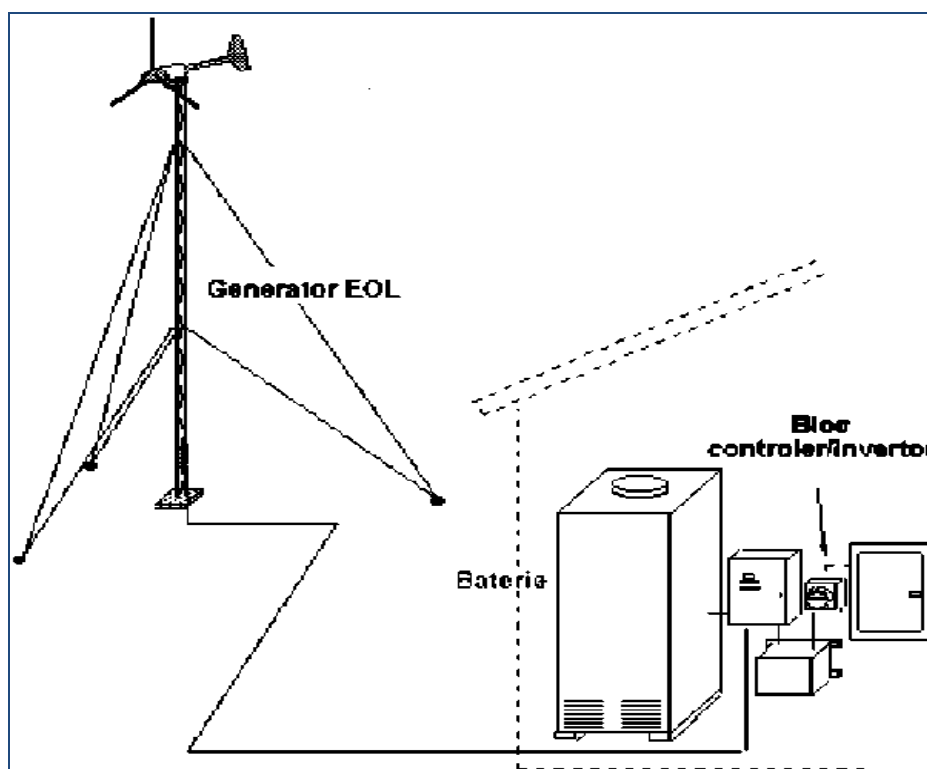


Fig. 7. EOL system

5. Hybride system

Given the unpredictable and intermittent nature of wind resources, to increase security in electricity supply is necessary to adopt solutions involving:

- * Use of unconventional resources, with complementary wind (solar, biomass)

- * Use of the motor - generator

In case of realization of autonomous power systems which exploit both solar and wind energy, the proposed technological

solution will include a photovoltaic-wind hybrid structure (PFV / EOL).

Some hybrid systems are the most common binary: GMG / photovoltaic / wind (PFV / EOL), wind / motor generator group (EOL / GMG) or tertiary PFV / EOL / GMG etc.

It is a food system that can ensure complete independence of the individual consumer of the national energy system. Generally meet two types of photovoltaic systems connected to the electricity grid, namely: embedded networks and distributed networks. The interconnection of the electricity grid photovoltaic various problems that may arise - whether photovoltaic system disconnecting the electricity grid fails (problem insulated) - power quality injected into the network - security officials measuring system of power transfer - technical risks and financial.

These connection systems are composed of a photovoltaic panel, wind generator and a diesel generator. The system has proven to be safe and highly efficient operation, resulting in a reduction in fuel consumption much higher than for other systems. To reduce dependence on fossil fuel can be used instead of vegetable fuel. For its production further investment, but they are recovered from future fuel savings that will result in lower costs. There are a PFV system / generator Wind / Water Generators, but is rarely used due to a drop of water dependency.

6. Radiant Panels

Radiant panels converts electricity into heat, which is distributed evenly in the room. Crystals provide heat for the entire playing surface with radiation having wavelengths of 4-14 mm.

This heat is the sun heats the Earth and is 99% absorbed by living creatures, to firing and UV radiation to microwave radiation. Panels have long wave radiation (infrared). Radiant panels generate heat at relatively

low temperatures that broadcast evenly on a relatively large area.

Radiant panel, thanks to its unique system, transforms electrical energy into heat and spreads the same amount of heat the entire surface. Basically, radiant panels heat spreads due to the difference in temperature between the panel and the body absorbs. Heat is directed to any body that has a temperature lower than the panel itself.

There are panels by convection, improperly called 'radiant', which are coil heating element inside a simple wire, the electrical resistance. These traditional systems are classified as convection heating. Heated surface which is at best half face of the radiation. Electric radiators are large consumers of electricity and their efficiency is very low. The new infrared technology will soon replace these devices; no space is needed, the panels are placed on the roof, but can be placed and walls. Rooms can be adjusted and separated Depending on the temperature. Installation is fast and clean, can be achieved within 1-2 days without disturbing the housing. Not produce a significant movement of air, and because of this operation is free of dust, does not cause chemical reactions and toxic fumes.

Radiant panel is a heating body as a billboard on the side designed so that heat, energy circulation is highest, and on the opposite side is minimal. This is done with ceramic granules stuck on the functional and insulated from the passive side. The heating system used is a combination of heat generator which is an exclusive application of nano-technology and glass "friendly environment" (97-98% heating efficiency). Given the big increases in gas prices, interest electric increased heating.

When we want save energy we think that infrared rays are emitted and reflected in wall, furniture, etc. Provides a good thermal comfort and a temperature of 2 - 4⁰ C, lower than the temperature considered optimal, performed by classical heating selecting the panel will consider the type and height

housing. Panel will use the full power to homes over 3m tall. At a height below 2.5 m height of the house will use low power radiant.

The power of the panel used in rooms where heat loss is of 0.8-1 W / m³, is about 1 kW. With this loss of heat in the room drops. The plaster is heated and provides a curtain of warmth. Heat given not out on the glass panels and thus made another economy. Low efficiency of the panels and their uniform distribution in the room makes it easy to classical heating, the yield to fall to 80% installed. Rapidly reached the highest yield (30-40 minutes) makes it possible to adjust the quality at lower temperatures. In addition there are infrared radiation emitting panels nanosilver particles with a strong antibacterial and odorless. In addition systems produce negative ions which have an important role in the annihilation of free radicals, the effects felt by the human body is very important as regards the occurrence of late effects of aging, a substantial improvement in psychological tone and strengthen the immune system.

7. Conclusions

The combined effect of these three actions (infrared and negative ions nanosilver) is a heat that penetrates the top layer of skin, an effect similar to that used in physiotherapy clinics, warming the person's body fluids (human body consists of 70% water) and generate greater physiological vitality. By this, the man felt a temperature 3-4 degrees Celsius higher than the real one in the room, which does not happen to any other traditional heating system.

Compared with other electrical appliances, heaters generate heat uniformly Plasma close environment. Heat is generated inside surfaces of wide glass panel and is radiated at an angle of 180 degrees, ensuring

an even distribution of heat without loss. Moreover, as long as heat is directed to the infrared radiant panels not only to objects in front (to the limited areas) and such objects around the Thermal Plasma heated. It creates a uniform and consistent heating called 'isothermal heat bath'.

Plasma heaters use less energy while working for long periods in which keeps the surface temperature.

Before choosing a power generation system that can be used for cooking, heating or to power home appliances, heat losses must be calculated into the room. The loss calculations to determine the required power input and then what kind of system meet energy needs.

References

- [1]. **F. Starr** (2001). "Power for the People: Stirling Engines for Domestic CHP" (PDF). *Ingenia* (8): 27–32. <http://www.ingenia.org.uk/ingenia/issues/issue8/Starr.pdf>. Retrieved 2009-01-18.
- [2]. **WADE** (a). "Stirling Engines". http://www.localpower.org/deb_tech_se.html. Retrieved 2009-01-18.
- [3]. **L.G. Thieme** (1981). "High-power baseline and motoring test results for the GPU-3 Stirling engine" (14.35 MB PDF). NASA. OSTI 6321358. http://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/1981023544_1981023544.pdf. Retrieved 2009-01-19.
- [4]. Y. Timoumi; I. Tlili; S.B. Nasrallah (2008). "Performance Optimization of Stirling Engines". *Renewable Energy* **33** (9): 2134–2144. doi:10.1016/j.renene.2007.12.012.
- [5]. **P. Fette**. "A Twice Double Acting α -Type Stirling Engine Able to Work with Compound Fluids Using Heat Energy of Low to Medium Temperatures". <http://home.germany.net/101-276996/english.htm>. Retrieved 2009-01-19.
- [6]. **D. Haywood**. "An Introduction to Stirling-Cycle Analysis" (PDF). http://www.mech.canterbury.ac.nz/documents/sc_intro.pdf. Retrieved 2009-01-19.¹
- [7]. **F. Kyei-Manu; A. Obodoako** (2005). "Solar Stirling-Engine Water Pump Proposal Draft" (PDF). http://www.engin.swarthmore.edu/academics/courses/e90/2005_6/E90Proposal/FK_AO.pdf. Retrieved 2009-01-19.

EFFECT OF FLUIDIZED- BED CARBURIZING ON MECHANICAL PORPERTIES AND ABRASIVE WEAR BEHAVIOR OF SINTERED STEELS

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ABSTRACT

In this paper is studied the influence of fluidized bed carburizing of sintered iron steels, for three different types of powder. Carburization is one of the most popular variety of temochemical treatment. Usually, carburization occurs in the temperature range of 850-950 °C. In powder metallurgy, the carburization had a great importance to establish the dependencies between porosity and their ability to take carbon.

KEYWORDS: powder metallurgy, fluidized bed carburizing, abrasive wear

1. Introduction

Growth of ferrous powder metallurgy (P/M) over the past three decades has been outstanding as this technology is proving itself as an alternate lower cost process to machining, casting, stamping, forging, and other similar metal working technologies. Parts manufactured by powder metallurgy (P/M) are widely used, especially in the automotive industry.

Powder metallurgy parts of complex shapes are obtained and close to final form, with precise surface so that the desired chemical and physical properties are obtained [1]. Also, specific parts made by powder metallurgy processing help to save time, energy, material, labor and money [2, 3]. Compared with classical metallurgy, additional processes (such as machining, forging, etc.) are minimized in powder metallurgy [4, 5].

Sintering is the process of compaction, consolidation by heat treatment, represented by a porous film made from powder.

Is a complex process representing a summation of physical and physicochemical phenomena that success or overlap.

Sintering process can be divided conventionally into three stages which follow each other at high temperature:

- initial stage - is the transformation of point contacts between particles in bridges and their expand to about 25-30% of the particle radius to form "necks" that cause hardening of the specimen. At this stage the particles retain their individuality, and contractions are small (max.4-5%).

- intermediate step is to extend necks between particles to particles losing their individuality. At this stage occurs 85-90% of total densification and grain growth of the particles.

- the final stage starts at a lower porosity, 10% and consist in transforming the network channels in isolated pores. The mechanisms involved in the transport of material to sintering is surface, intergranular limits and volume diffusion (Fig. 1).

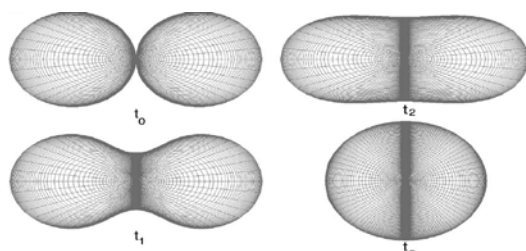


Fig.1. The schematic of two powder particles during sintering, carried out using finite element method at different sintering times, $t_0 < t_1 < t_2 < t_3$ [7].

Properties of sintered materials are determined both by the nature of the material's characteristics of powders used, pressing and sintering process parameters and subsequent processing procedures applied [6].

Fatigue resistance can be improved on increasing the density, reducing pore size and pore clustering and enlarging the sintered ligaments between pore, or, similarly to wrought steels, by

thermochemical (carburizing and nitriding) or mechanical treatments (shot peening). Carburizing consists in a surface carbon enrichment, which gradually decreases towards the core [8-14].

In this paper, the mechanical properties and abrasive wear behavior of carburized in fluidized bed sintered steels are analyzed. The abrasion tests were conducted under constant load and speed conditions.

2. Experimental procedure

2.1. Materials

Specimens prepared from atomized iron powder and from pre-alloyed iron base powders were analyzed in this paper. The chemical composition of the powder samples, pure iron and iron-based prealloyed powder with Cu, Ni and Mo is presented in Table 1.

Table 1. Chemical composition of analyzed powders

Powder type	Cu	Mo	Ni	C
P ₁	0.096	0.008	0.046	<0.01
P ₂	1.50	0.50	1.75	<0.01
P ₃	1.50	0.50	4.00	<0.01

To evaluate the mechanical properties, a die for making the samples in the form of a cylinder was produced. The samples were used to evaluate mechanical properties such as Vickers microhardness and abrasive wear.

The powders were mixed with 1% zinc stearate. The samples were compressed in a universal mechanical testing machine to a pressure of 600 MPa, the dimensions of disc specimens are $\phi 8 \times 6$ mm. Uniaxial pressing in the mold is used effectively for mass production of simple components.

The figure 2 shows the picture of the sample.

The green samples were sintering in a laboratory furnace, within a controlled atmosphere. The sintering temperature was

approximately 1150 °C and the sintering time was 60 min with a heating rate of 30-40 °C/min.



Fig. 2. Aspect of sintered sample

All the samples were kept in the furnace for slow cooling to room temperature. The microstructure depends on the amount of sintered carbon and cooling rate. Before the sintering temperature is reached, the parts

were maintained during 30 min at 500 °C to burn lubricant, respectively zinc stearate.

After cooling to room temperature the samples were carburized-treated.

Treatment conditions for the fluidized bed carburizing process were heating at 900 °C during 60 min. specimens were then air-cooled to room temperature. The microstructure of the carburized samples was observed by optical microscopy (Olympus BX 50). Photomicrographs were obtained at a magnification of 200X (figure 2). In figure 3 is presented the size distribution of analyzed powders.

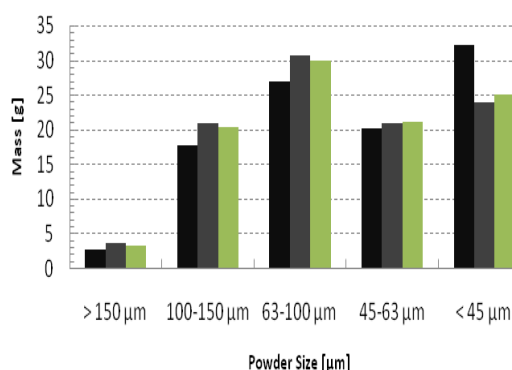


Fig. 3. - Size distribution of analyzed powders

2.2. Mechanical properties

The carburized in fluidized bed samples were analyzed according to their mechanical properties. The microhardness tests were performed by measuring Vickers microhardness, and the test parameters are: the penetrator is a diamond pyramid diameter and load of 100g. The microhardness was the average of three indentations on the top and another on the bottom surfaces of the samples.

2.3. Abrasion wear tests

Abrasive wear is a process of removal and destruction of surface tested material. Is affected by many factors such as, mechanical properties and abrasive

materials, microstructure, loading condition, etc. It is accepted that abrasive wear rate of a surface is inversely proportional to its hardness [2]

Samples subject to fluidized bed carburizing were tested for abrasion wear test (Fig. 4). The SiC particles on the emery papers were the size of 80μm and the load applied was 855g. The distance traversed in each case was limited to 150 cycles corresponding to 76,5 m. The samples were assay to circular motion over the wheel on which the emery papers were stiff.

The abrasion wear process in which the abrasion test was carried out included:

- first, fixing the emery paper on the wheel;
- the samples of known weight were loaded on the machine and applied the load;
- the specimen surface and the emery paper were always in strong contact with each other under the predetermined load, and
- the samples were cleaned and weighed prior to and after each test interval.

The samples were weighed using a precision balance a sensitivity of 10^{-4} before and after each test (Table 3), so it was possible to evaluate the wear suffered by the material.

After the tribological tests, the worn surfaces were examined by optical microscope, in order to identify the dominant wear mechanisms.



Fig. 4. Aspect of worn surface after the abrasion test

3. Results and discussion

3.1. Microstructure

Optical micrographs representative of carburized samples are reported in Figures. 5 a) – c). Microstructural analysis shows uniform structures with specific components of steel depending on diffusion carbon content.

Given that most alloying elements moves S point to the left of the diagram Fe-C, means that powder by increasing the carbon content by applying the thermochemical treatment in fluidized bed carburizing can reach at the surface structures of eutectoid hypereutectoid steel (pearlite and cementite).

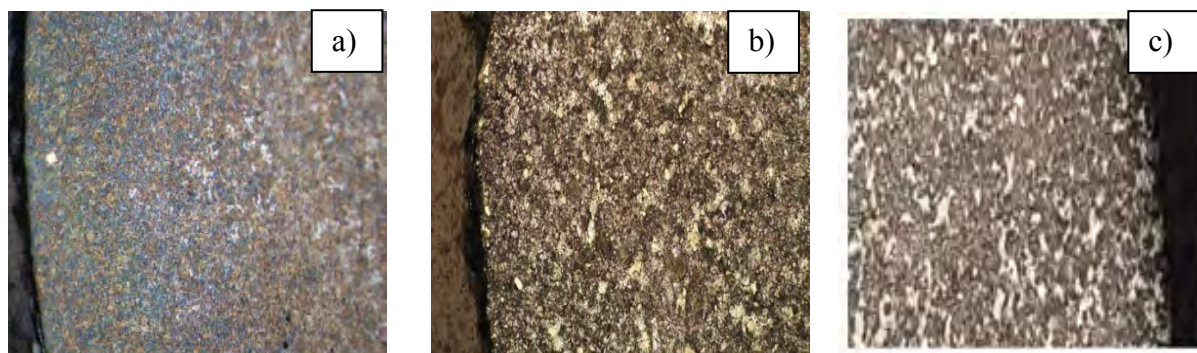


Fig. 5. Microstructure of sintered steel subject to fluidized bed, etching 2% Nital, 200x.

This distribution of structures explains the major hardness of carburized superficial layer. Figure 6 shows a comparison between the values of microhardness of the carburized treated samples studied. It is found that the three type of samples have proximate values of Vickers microhardness.

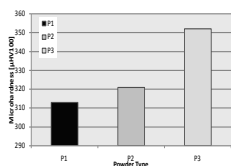


Fig.6. Vickers microhardness values of the carburized samples.

3.2. Tribological tests

The worn surfaces of carburized

samples after abrasion tests were examined in optical microscopes, the typical aspects of abraded surfaces are represented in Figure 8. The depth and width of wear grooves of carburized samples P₁ are greater compared to samples P₂ and P₃.

Figure 7 depicts the weight loss of sintered samples tested to abrasive wear. The wear rate was measured as the weight loss, sample P₃ provided the greatest weight loss.

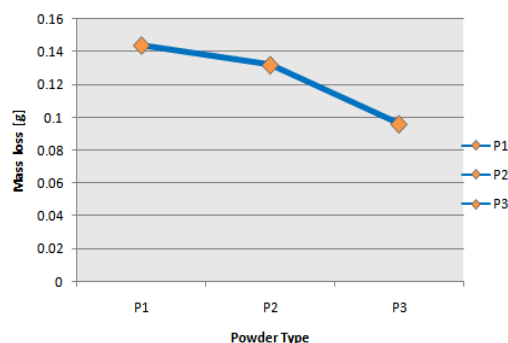


Fig. 7. Weight loss for carburized treated samples.

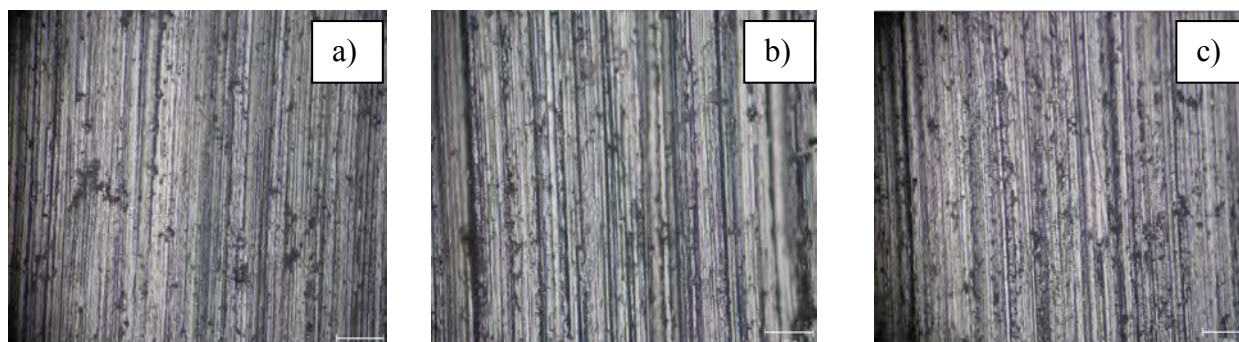


Fig.8. Optical photomicrographs of worn surfaces for carburized samples (x200):
 a) P_1 , b) P_2 and c) P_3

4. Conclusions

According to the experimental results in this study, the following conclusions may be discussed:

-As generally observed, a primary role on the resistance to abrasive wear of PM steels is played by the composition. In this regard, the best behavior was observed for the more hardenable fluidized bed carburized samples with higher Ni and Mo content (P_3).

-Based on the measurements of microhardness, the samples P_2 and P_3 show higher values compare to P_1 (the reference).

-Aspect of the surfaces subjected to abrasive wear for all three types of powders, presents deeper traces in unalloyed samples and finer trace in samples alloyed P_2 and P_3 , as subsequently wear tests giving results in conformity with these aspects of the surface.

-The carburized sample P_1 presents a depth and width of wear grooves greater, thus there is a possibility of less resistance offered.

-The carburized samples P_2 and P_3 present a wear groove width much less, that can assure a good resistance.

-The weight loss is less for the carburized samples P_2 and P_3 .

References

- [1] **K.V. Sudhakar**, *Fatigue behavior of a high density powder metallurgy steel*. Int J Fatigue 2000;22:729–34.
- [2] **G.B. Jang, M.D. Hur, S.S. Kang**, *A study on the development of a substitution process by powder metallurgy in automobile parts*, J Mater Process Technol 2000;110–5.
- [3] **V. B. Akimenko, I. A. Gulyaev, O. Yu. Kalashnikova, M. A. Sekachev**: *The Prospects for Russian Iron Powder*, Central Scientific-Research Institute of Ferrous Metallurgy, Vol. 37, No. 5, p. 472–476, ISSN 0967-0912; 2007.
- [4] **J. Georgiev, T. Pieczonka, M. Stoytchev, D. Teodosiev**, *Wear resistance improvement of sintered structural parts by C_7H_7 surface carburizing*, Surface and Coatings Technology, volumes 180-181, 1 March 2004, Pages 90-96.
- [5] **C. Anayarana C, E. Ivanov, V.V. Boldyrev**, *The science and technology of mechanical alloying*. Mater Sci Eng A 2001;304–306:151–8
- [6] **K.S. Narasimhan**, *Sintering of powder mixtures and the growth of ferrous powder metallurgy*. Mater Chem Phys 2001;67:56–65.
- [7] **Hadrian Djohari, Jorgel Martínez-Herrera, Jeffrey J.Derby**, *Transport mechanisms and densification during sintering: I. Viscous flow versus vacancy diffusion*, Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis MN55455-0132, USA
- [8] **G. Krauss**, *Microstructure residual stress and fatigue of carburized steels*, in: Proceedings of the Quenching and Carburizing (Melbourne), The Institute of Materials, 1991, pp. 205–225.
- [9] **G. Krauss**, *Principles of Heat Treatment of Steels*, American Society for Metals, Vol. 1, pp. 251



[10] **M. Askaria, H. Khorsand S.M. Seyyed Aghamiric**, *Influence of case hardening on wear resistance of asintered low alloy steel*, Journal of Alloys and Compounds Volume 509, Issue 24, 16 June 2011, Pages 6800-6805.

[11] **S. Mansoorzadeh, F. Ashrafizadeh**, *The effect of thermochemical treatments on case properties and impact behaviour of Astaloy CrM*, Surface and Coatings Technology, Volume 192, Issues 2-3, 21 March 2005, Pages 231-238

[12] **J. Kazior, C. Janczur, T. Pieczonka, J. Ploszczak**, *Thermochemical treatment of Fe–Cr–Mo*

alloys, Surface and Coatings Technology, Volumes 151-152, 1 March 2002, Pages 333-337

[13] **I. D. Radomysel'skii, A. F. Zhornyak, N. V. Andreeva, G. P. Negoda**, *The pack carburizing of dense parts from iron powder*, Powder metallurgy and metal ceramics, Volume 3, Number 3, 204-211.

[14] **O. I. Pushkarev, V. F. Berdikov**, *Increasing the wear resistance of equipment in pressing parts from high-hardness powder materials*, Refractories and industrial ceramics, Volume 39, Numbers 9-10, 326-328, DOI: 10.1007/BF02770594

SPECTROMETRY AND SEM ANALYSIS APPLIED OF TiN AND Ti (C, N) THIN FILMS COATED VIA PNCVD

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ABSTRACT

In the Pressure Normal Chemical Vapour Deposition (PNCVD) coating technique, Spectrometry analysis gives the concentration profiles of the compound elements from the superficial coated layer and the layer thickness. Scanning electron microscopy is a good method than can be used in order to estimate the grain sizes of the compounds and to have an impression about the substrate cover uniformity. A minimum roughness value is necessary for the substrate in order to achieve an uniform and efficient covering. The XRD analyses confirm the existing of interstitial compounds like Co₃N and Fe₃N in these zones. After the coating processes, first of all the microhardness of the coating variants HV0,100, HV0.050 have been measured.

KEYWORDS: Spectrometry, PNCVD coating, SEM, thickness, microhardnes

1. Introduction

For tools manufacturing, the improvement of wear resistance has been made using coating technology. Thus, good results have been obtained for TiN, Ti(C,N) layers. In order to achieve these deposition, TiCl₄ as Ti, precursor and N₂, (CH₄) as a nitrogen (carbon) source have been used.

For wear resistant applications, in the case of widia, a minimum deposition temperature is required in order to not disturb the previous hardened and tempered structure.

The pressure normal activation conditions are necessary in these cases, in order to excite the reactants and to be able to break bonds in the precursor or activate the precursor to react with co-reacts. TiCl₄ is frequently used during CVD processes assisted PNCVD for wear resistant applications [1].

The high – strength electric field over the boundary layer between the temperature

and surface causes the acceleration of ions to the surface.

Optical emission spectrometry (OES) can be used to find chemical composition profiles of the coatings in depth. Thus, minimum 60 % titanium has been considered like a inside boundary of the layers thickness.

Scanning Electrons Microscopy (SEM) analysis method has the possibility to provide information about the covering grade of the substrate and the compound crystal sizes too.

2. Methods

2.1. Materials

The constructive and active geometry of the plates types T.P.U.N. 22.04.08 P30 have been tested and dimensions of samples used were:

$$\alpha = 8, \dots \beta = 12, \gamma = 60, \chi = 0$$

For the purpose of the experiments the maximum limit of the cutting speed was taken higher than the usual speeds to obtain a plate durability under the most difficult operation condition which should not excessively increase the time of the experiments and the material consumption [2].

2.2. Deposition Method

The experiments conducted to obtain thin layer of nitride and carbide by the vapor chemical deposition method have followed an original path to make $TiCl_4$ directly in the working room thus avoiding the import of these hazardous substances. The $TiCl_4$ is obtained in the heat treatment chamber by adding chloride acid vapors passed over the incandescent pure titanium. Lab-scale systems have been designed with the possibility of use at industry scale for small production [3]

The thickness of the deposit layer increases with the time of exposure to the working temperature.

The TiN and Ti(C, N) coated plates feature higher endurance capabilities than those uncoated for the same cutting speed both for steel and white cast iron.

2.3. Experimental procedure

The coatings have been made in a PNCVD reactor and these consist in two kind of layers: TiN and Ti(C,N).

For the first variant of deposition – TiN – the parameters of the process were: $T = 1050^\circ C$, $I = 4A$, $p = 1atm.$, time = 4hours for thickness $6\ \mu m$, layer is adherent, uniform and homogeneous throughout its depth.

For the second variant of deposition – Ti(C,N) – the parameters of process were: $T = 1130^\circ C$, $I = 4A$, $p = 1atm.$, time = 6hours for thickness $8\ \mu m$, layer is adherent, uniform and homogeneous throughout its depth [4].

After the coating processes, first of all the microhardness of the coating variants – $HV_{0,100}$, $HV_{0,050}$, $HV_{0,025}$, $HV_{0,010}$ have been measured. The average values of these measurements are presented in Table 1.

Table 1. The average hardness values of the coatings, for different applied loads

Sample (cutting plates)	Layer type	$HV_{0,100}$	$HV_{0,050}$	$HV_{0,025}$	$HV_{0,010}$
		[MPa]			
1	TiN	16512	18880	22560	28100
2	Ti(C, N)	17860	22780	26740	30050

Thus, after each surface Optical Emission Spectrometry (OES) analysis which provide the Ti, N, C concentration profiles, considering some concentration points at different depths) on each profile

provided by the original OES analysis. The figures 1,2, presents the SEM micrographs of TiN, Ti(C,N) coating surface and figure 3 present a cross – section image of TiN coated sample [5,6].

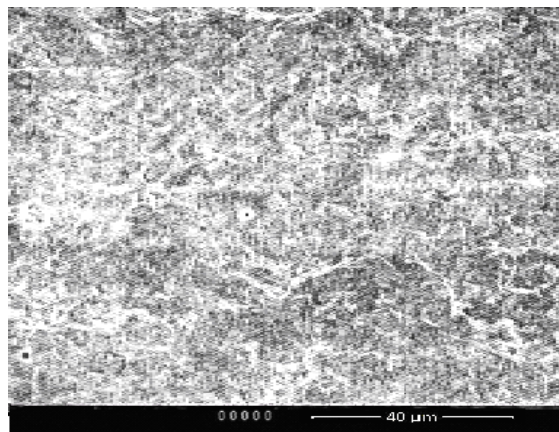


Fig.1. The SEM micrograph of TiN deposition (x2000)

Figures 1 and 2 superficial aspects of the layers are deposited CVD compared to monolayer TiN uncovered a plate appearance, classic, studied by electron microscopy. It is clear difference in size of

crystals of layer size and size uniformity and surface roughness [7].

In figure 3, the metallographic appearance is set for good quality coated plates.

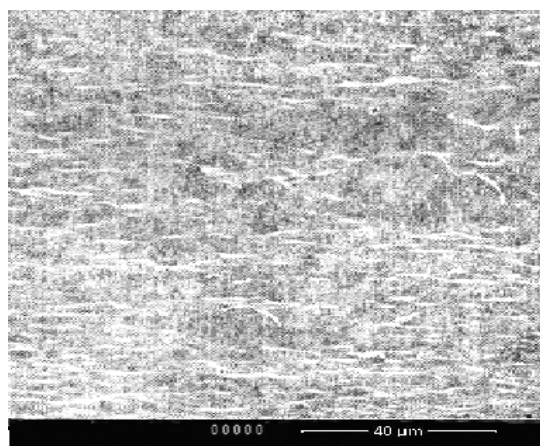


Fig. 2. The SEM micrograph of Ti(C, N) deposition (x2300)

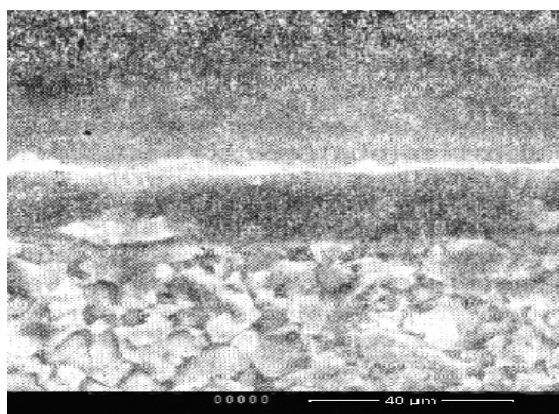
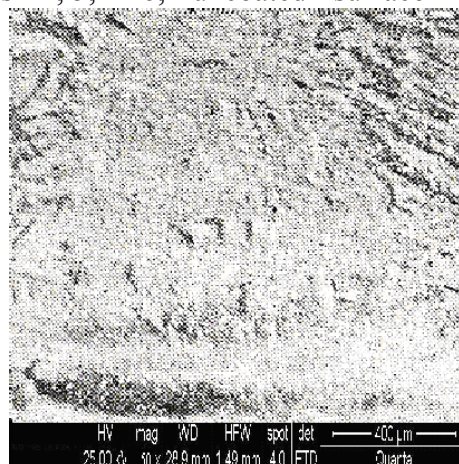


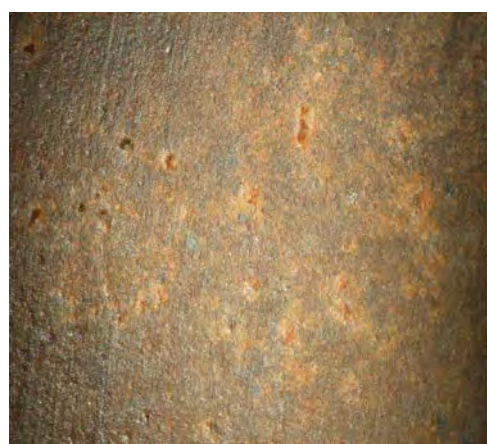
Fig.3. The SEM cross-section of TiN deposition (x2000)

TiN coating is composed of uniform thickness and the grain, having crystal columnar layer. Almost uniform grain isomorphous layer and its purity ensure proper behavior at cutting premises [8]. As seen in figures 4, 5, 6, uncoated surface TiN

samples have surface oxides by 70% if the samples coated with the thickness of $6\mu\text{m}$ TiN has slight traces of surface oxides on 5% non-stick surface and covered with Ti(C,N) samples with thickness of $8\mu\text{m}$ surface shows no oxides.

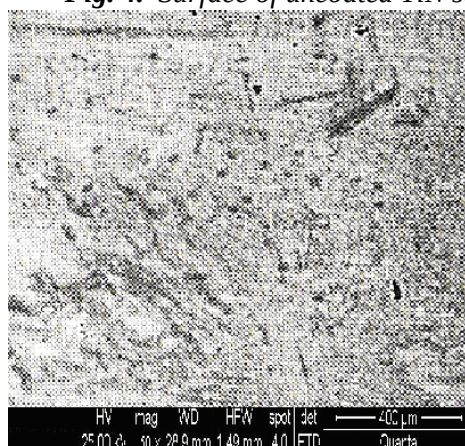


a)

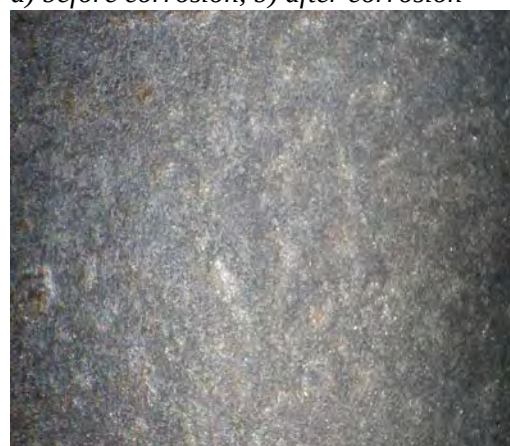


b)

Fig. 4. Surface of uncoated TiN samples: a) before corrosion, b) after corrosion

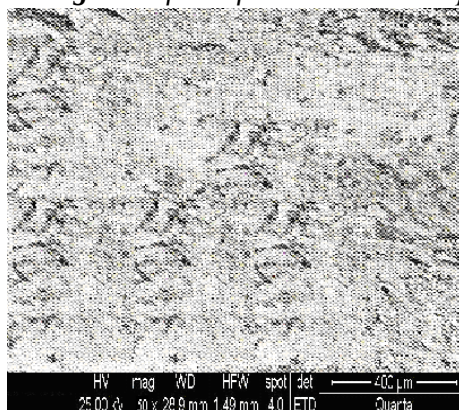


a)

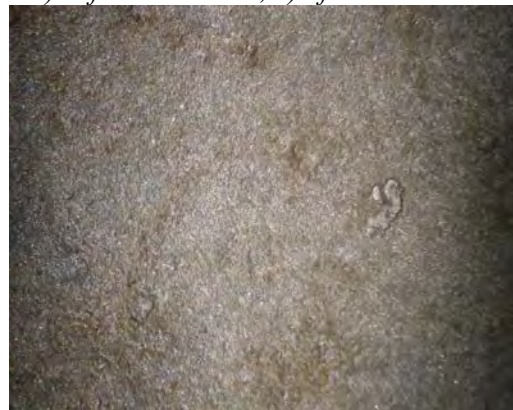


b)

Fig. 5. Surface of covered TiN samples $6\mu\text{m}$: a) before corrosion, b) after corrosion



a)



b)

Fig. 6. Surface of covered Ti(C,N) samples $8\mu\text{m}$:
a) before corrosion, b) after corrosion

It noted that in corrosion test in water samples covered with TiN channel are stronger compared with uncoated samples TiN [9].

The thickness of the thin layer increases with the exposure time at the working temperature, as illustrated in figure 7.

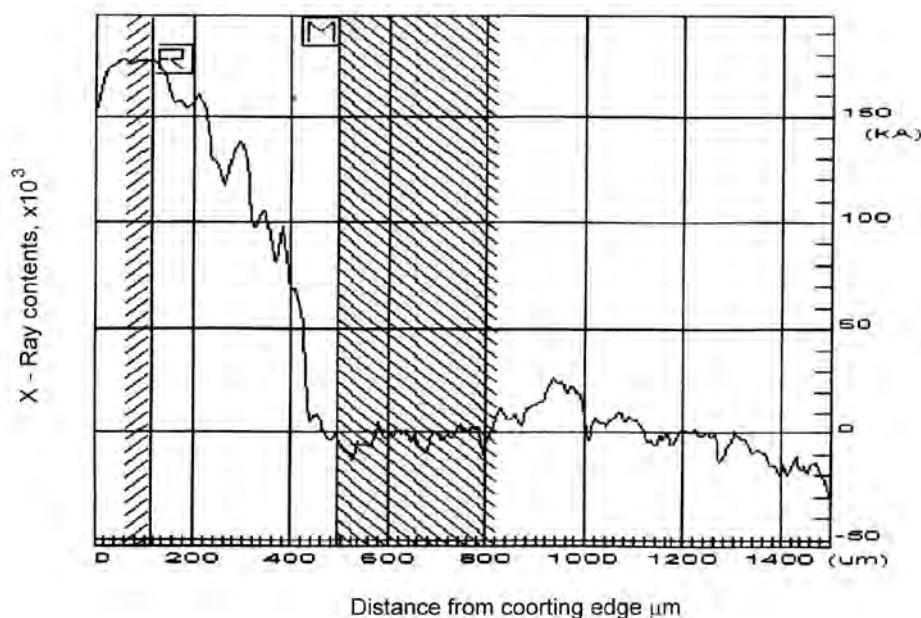


Fig 7. Surface profilometer measurement of the thickness of TiN film for 4 h exposure time at 1050°C

3. Conclusions

These coatings have good wear resistance, abrasion resistance, corrosion resistance and a strong strate -substrate interface. This leads to formation of thick and rough coating. The coating is fine grained, adherent, dense and free from cracks.

In order to SEM analyses, the biggest grain sizes (average values) were obtained for Ti(C,N) layers 8μm and the smallest for TiN layers 6 μm but in this case , on t he surface layer appears colossus grains .

In the same time, SEM analyses confirm that the maximum density of nucleation (and covering uniformity) is characteristic of TiN layers.

For all the variant of layers (see Fig.3), the SEM analyses present different structures bellow the coating, which is characterized by a high density.

Elsewhere, the XRD analyses confirm the existing of interstitial compounds like Co₃N and Fe₃N in these zones.

Corrosion test in water samples covered with TiN and Ti(C,N) channel are stronger compared with uncoated samples TiN.

References

- [1]. O. Mitoșeriu, S. Constantinescu, T.Radu. ș.a. - *Modern methods to perform the properties of metal materials*, University „Dunărea de Jos,, of Galați, 1998;
- [2]. S.Constantinescu, T.Radu - *Modern methods to perform thin layers*, Romanian Metallurgical Foundation Scientific. Publishing House, București, 2003;
- [3]. S.Constantinescu - *Metals properties and physical control methods*, Didact și Pedag. Publishing House, București, 2004;
- [4]. S. Constantinescu - *Distructive and nondestructive tests of metals*, Evrika Publishing House, Galați, 2000;
- [5]. S. Constantinescu, E. Drugescu - *Studies on Mechanism and Kinetics of Phase Transformation in*



Superficial Layers Using Unconventional Procedures. Research Contract no. 5005, Galati, 1995, p. 53 ;

[6]. C. Ciocardia and others - *Hard Alloys Sintered from Metallic Carbides*, Bucharest, Editura Tehnica (1984), p. 103.

[7]. S. Constantinescu. - *Influence of manufacturing process on chemical and structural homogeneity of welded pipe sheets for tanks and vessels working under pressure*, Proceeding of the International

Conference on Advances in Materials and Processing Technologies, september 18 – 21 , Leganes, Madrid, Spain, 2001 , p.57 ;

[8]. S.Constantinescu, E.Drugescu, T.Radu. - *The coating on the steel support* , 2003European Congress and Exhibition on Advanced Materials and Processes, 1-5 sept., Lausanne, Switzerland, 2003 , p. 59, paper F4-456 . 2003

[9]. C., E. Morosanu.- *Chemical vapour deposition thin layers*, Ed.Tehnică, Bucuresti, 1981.

OBTAINING AND CHARACTERIZING TIN-LEAD COATINGS ON STEEL BAND

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ABSTRACT

The experimental research was at the basis of the hot immersion coating technology with Sn-Pb alloy of the steel bands presented in the study. The characterisation of these layers was achieved through microscopic analyses and the analysis of resistance to corrosion. Coatings with four tin-lead alloys were carried out. The micro-structural aspect of the tin-lead alloys, the aspect of the covered band surface, the micro-structure of the layers, the layer thickness variation according to the duration of the immersion and the chemical composition of the layers are presented. The resistance to corrosion was assessed through the gravimetric index. The samples were exposed in sea water for five weeks. The corrosion speed was determined for every type of coating, according to the period of exposure to the corrosive environment and the kinetic process for the time intervals studied.

KEYWORD: tin lead coatings, structure, corrosion

1. Introduction

The tin alloys are important in the production of coatings through hot immersion.

The most important of these are the tin-zinc, tin-nickel, tin-cobalt, tin-copper and tin-lead alloys.

The tin-lead coatings are mainly used for protection against corrosion and for preparing the surfaces for soldering.

The protective layer made of Pb-Sn alloys gives the steel plate a good resistance to corrosion, a very good capacity for welding and soldering, and improves deformability.

The coating presents a high resistance to corrosion in the atmosphere which contains sulphur agents, in environments with oil products, in sulphuric and phosphoric acids.

In the case of corrosion resistance of the plate covered in Pb-Sn alloys, a very

important role is played by the Fe-Sn transition layer, formed at the separation limit of the steel-coating.

According to the iron-tin equilibrium diagram, the inter-metallic compound FeSn_2 is formed with 80.95% tin, stable up to 496°C . Like tin, this material presents a crystalline tetragonal structure.

The FeSn_2 layer gives a good coating adherence to the steel support but, because of its fragility, it is not recommended to go beyond a certain thickness.

The reduction of the tin content during the coating, through its replacement with lead, influences the FeSn_2 layer by reducing it and worsens its adherence properties.

In order to compensate this shortcoming, modifications were made in the fabrication technology of the lead plate with a low content of tin, respectively applying a more intense capping process, using new fluxing etc., to activate the surface.

2. Experimental research

For obtaining Sn-Pb alloy coatings, the following technological steps were followed:

- preparing the surfaces of the steel bands;
- development of tin alloys with different lead concentrations;
- achievement of deposits through immersion in melt;
- cooling of the samples

Preparing the steel surface in view of coating is a very important stage, because

the perfect cleaning of the surface determines the obtaining of an adherent layer, uniform and without flows. The surface of the samples was chemically degreased and then degreased in organic solvents (acetone), etched in hydrochloric acid (17% concentration) and covered in zinc chloride flux and ammonium chloride dried at 150 °C.

The sample steel bands on which the deposit was achieved were 0.18mm thick; their chemical composition is shown in Table 1.

Table1. Chemical composition of the support steel bands, in %

C	Si	Mn	P	S	Al	As	Ti	V	Cu	Ni	Cr	Mo
0.025	0.015	0.210	0.013	0.010	0.046	0.004	0.002	0.001	0.005	0.008	0.025	0.001

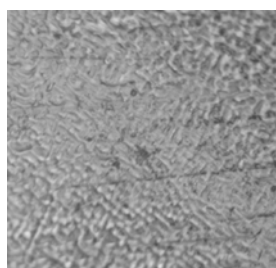
Table 2. Elaborated Sn-Pb alloy chemical composition

Alloy code	Composition		Alloy Melting Temperature [°C]
	Sn	Pb	
1	80	20	180
2	70%	30%	185
3	50%	50%	220
4	32%	68%	260

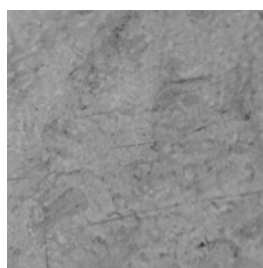
The immersion temperature was 30-50°C above that of the alloy melting temperature, and the immersion duration varied between 3 and 12 seconds.

A first observation is that a growth in the alloy lead concentration influences the aspect of the surface. The aspect of the surface varies from silver in the case of coating with an alloy with a high content of tin (80%Sn-20%Pb), to opaque dark grey in the case of the layers obtained in alloy code

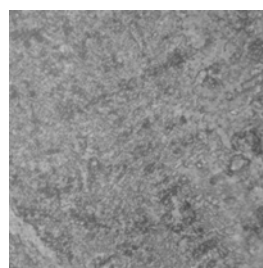
4 (32%Sn-68%Pb). The surface analysis through optical microscopy shows a difference in the solidification process, respectively a structure with fine dendrites for alloy code 1 compared to the other alloys, as can be observed in the micrographs in Figure 1. The increase of the dendrite dimension is influenced by the increasing of the solidification interval [1] of the alloy codes 2 and 3, as compared to 1 and 4.



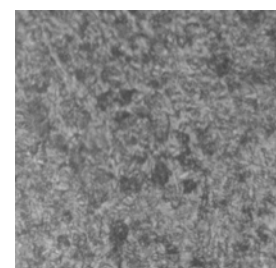
a) 80%Sn-20%Pb



b) 70%Sn-30%Pb



c) 50%Sn-50%Pb



d) 32%Sn-68%Pb

Fig. 1. The aspect of the probe surfaces covered with lead alloys (immersion duration 9 seconds), X100

Figure 2 presents the microstructural aspect of the lead-tin alloys, elaborated in view of coating the steel bands. According to the phasic equilibrium diagram [2], depending on the lead content, what may be

observed is an increase in the eutectic quantity, with the solid solution α in the case of hypoeutectic alloys [3,4] codes 2 and 3 and with the solid solution β in alloy code 4.

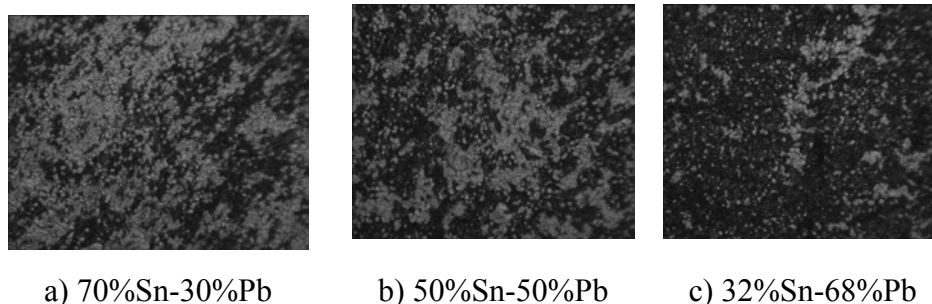


Fig.2. Microstructural aspect of the tin-lead alloy, X100

During the research carried out, the determination of the alloy layer thickness deposited on the steel bands was achieved metallographically as the average of three measurements in different areas. As can be observed from the data presented in Figure 3, the layer thickness depends on the immersion duration, as well as on the chemical composition of the alloy deposited. What may be observed is that, at an increase

of the lead concentration and of the immersion duration (over 6 seconds), the alloy layer thickness increases considerably (the alloy coating codes 3 and 4).

In the case of alloys with a low content of lead (20-30% Pb), the immersion duration does not influence the layer thickness significantly. This can be explained due to the much better flow of the alloys which are rich in tin [5,6].

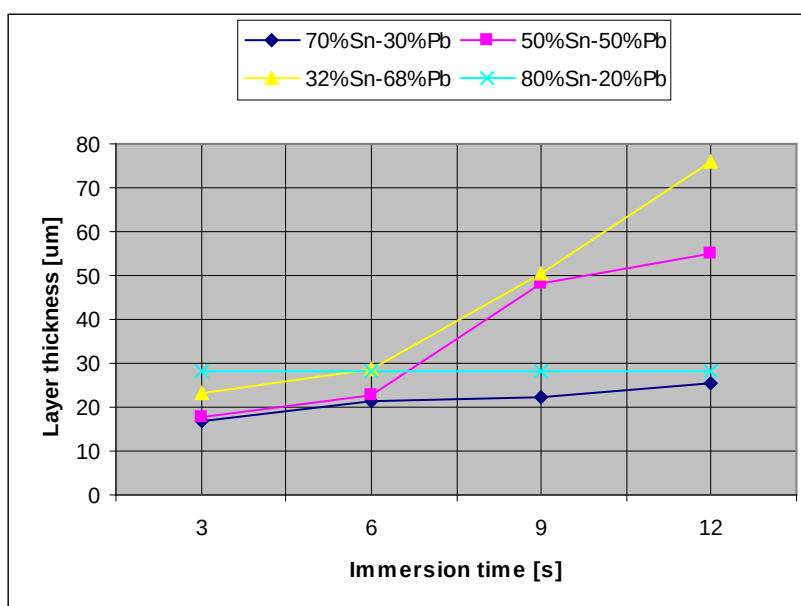


Fig.3. Thickness variation of the Sn-Pb alloy layers according to the immersion duration

The analysis of the microstructures deposited shows that these are uniform and present a structure similar to that of the alloys, thickness varying according to the

immersion duration. Figures 4 and 5 show the microstructural aspects of the coatings, with the layer thickness specified.

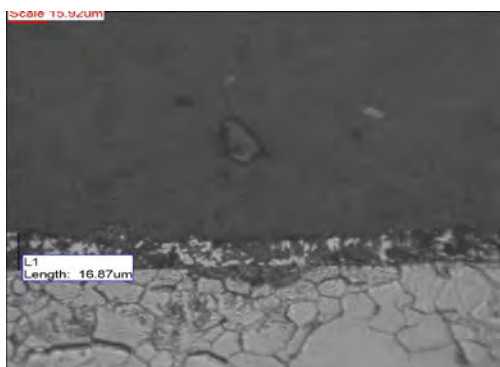


Fig. 4. The 70% Sn 30% Pb alloy coating microstructure, immersion duration: 6 seconds, temperature

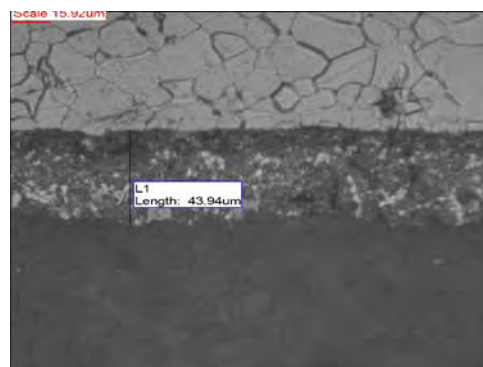


Fig.5. The 32%Sn-68%Pb alloy coating microstructure, immersion duration: 9 seconds, temperature

In order to determine the corrosion speed, some samples were extracted from each type of coating resulting from a 6 second immersion, where the layer thickness was approximately equal. The corrosive environment used was a 3% NaCl solution. The study was carried out for five weeks. The samples were weighed at 7 days intervals, after they were washed in water and then dried.

In order to determine the corrosion speed, the gravimetric method was used. The corrosion speed was determined using the relation:

$$v_{cor} = \frac{m_{cor}}{S \cdot t} \quad (1)$$

where:

v_{cor} - gravimetric index [$\text{g}/\text{m}^2 \cdot \text{h}$]

m_{cor} - mass loss through corrosion [g];

S - / surface area, [m^2];

t - corrosion duration [h]

Both the corrosion speed at different time intervals and the speed during the intervals were determined; the variation curves were also drawn. The corrosion speed

depends on the chemical composition of the alloy deposited on the steel bands, on the thickness of the deposited layer and on the exposure duration of the samples to the corrosive environment [7,8].

Figure 6 shows the behaviour to corrosion of the analysed layers, according to the duration exposure to the corrosive environment.

Analysing the corrosion test results, we may observe a similar behaviour of the alloy coatings 2 and 3. This represents a continuous decrease of the corrosion speed after the first three weeks (504 hours). The alloy layers with a lower content of alloying elements (codes 1 and 4) have a lower corrosion speed after 168 hours of exposure, but an increased corrosion speed after two weeks and a decreased one after 504, with larger values however as compared to alloy codes 2 and 3. The behaviour after 672 hours and after 840 hours respectively becomes the same for all types of alloy, in the sense of a strong increase of the corrosion speed. The best behaviour is at 32% Sn and 68% Pb. The increase of the lead content in the coating alloy improves the resistance to corrosion in the studied conditions.

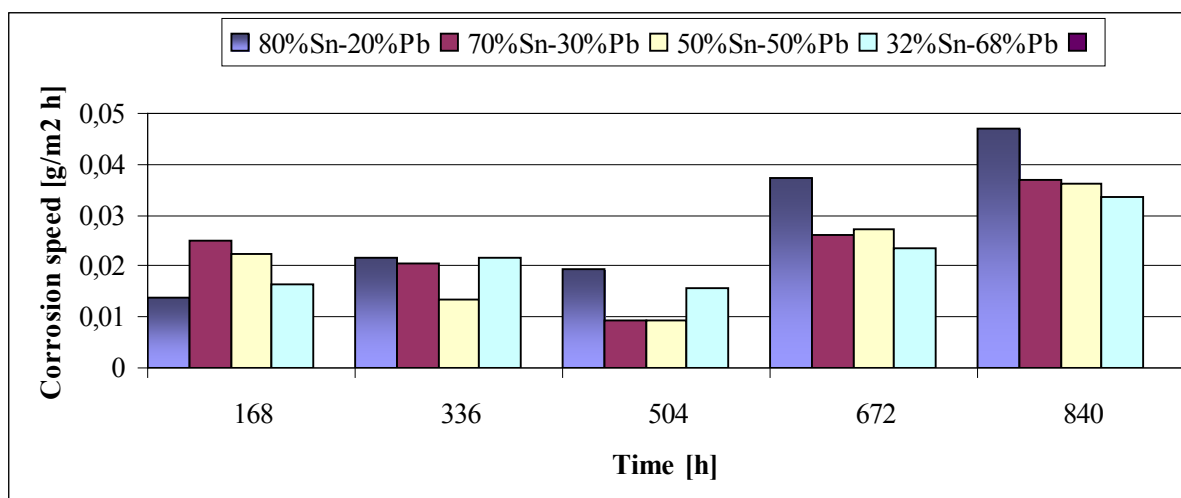


Fig.6. Corrosion behaviour of the analysed layers according to the exposure to the corrosive environment

Analysing the kinetic corrosion process for each alloy presented in Figure 7, we may also observe the similar behaviour at

corrosion of the alloy layer codes 1 and 4, and of those in code 2 and 3 respectively.

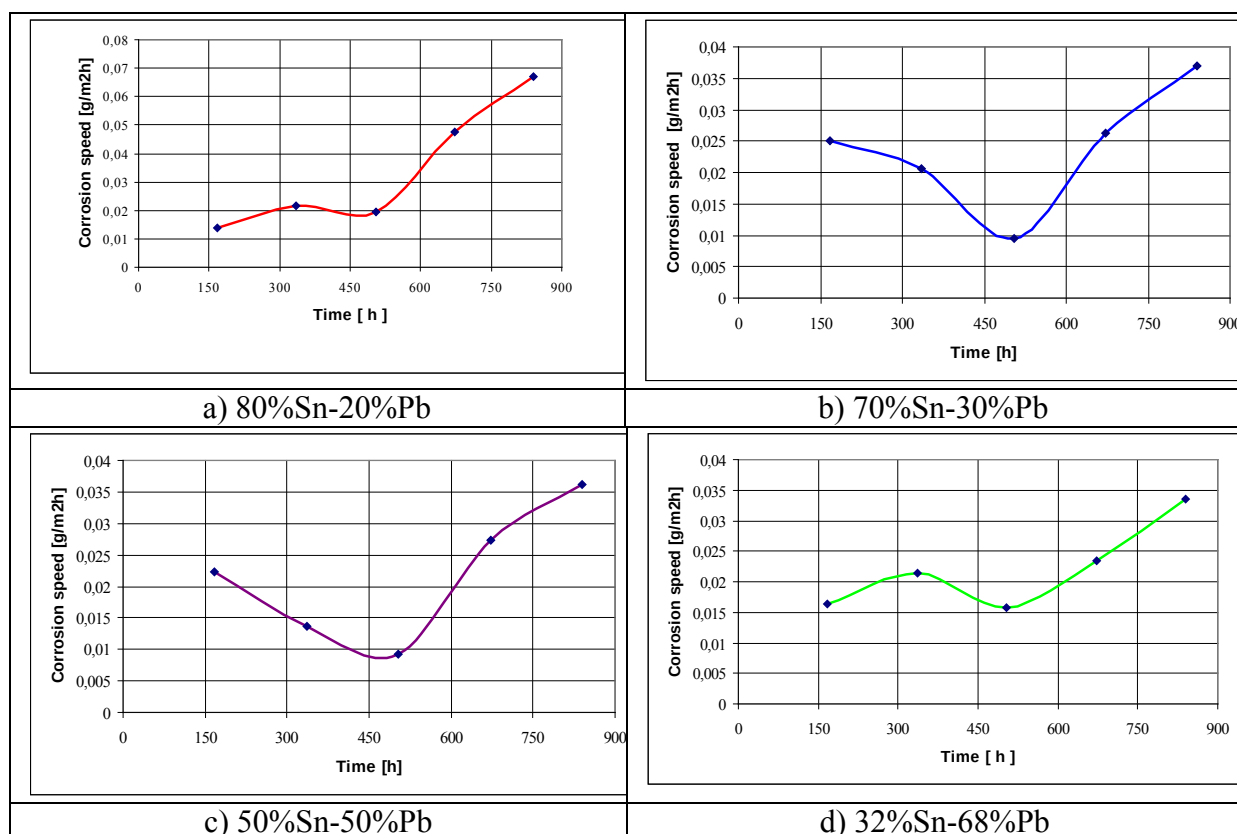


Fig. 7. The kinetics of the corrosion process on the studied time intervals

3. Conclusions

- The increase in the alloy's lead concentration influences the aspect of the surface, which varies from silver in the case of a coating made from alloys with high tin content (80%Sn-20%Pb) to opaque dark grey in the case of the layers obtained from alloys with 32% Sn and 68% Pb;
- The increase of the immersion duration above 6 seconds leads to a significant increase of the layer thickness, in the case of alloys which are rich in lead;
- The microscopic aspect of the surface also shows a difference in the solidification process of the layer, a structure with fine dendrites in the case of alloy with 80 % Sn – 20 % Pb respectively, as compared to the other alloys, due to the increase of the solidification interval of the alloys;
- The tin-lead alloy microstructure shows an increase in the eutectic content, along with the solid solution α (in the case of hypoeutectic alloys) and along with small quantities of solid solution β in the hypereutectic alloy.
- The analysis of the microstructures of the deposited layers shows that these are uniform and present a similar structure to that of the alloys;

- The corrosion test shows good deposit behaviour at corrosion; analysed, they present values close to the corrosion speed in time.
- The kinetics of the corrosion process shows a significant increase of the corrosion speed in weeks 4 and 5 for all the studied layers;
- The increase of the lead content in the coating has a positive influence on the resistance to corrosion.

References

- [1]. **Alexandru H.V., Berbecaru C.**, *Știința materialelor - Creșterea cristalelor*, Ed. Universității din București, 2003.
- [2]. **Yancy W. Riddle**, *Metals Conservation*, Summer Institute, 2006, Alloys & Their Phase Diagrams, University of California.
- [3]. **William D. Callister**, *Binary Phase Diagrams*, 2nd ed., Vol. 3,
- [4]. **Harsh Menon**, *Lab.Report on Lead-Tin Phase Equilibrium*, 2006.
- [5]. **W. E. Hoare, E. S. Hedges & B. T.K. Barry**, *The Technology of Tinplate* Ed. Arnold (Publishes) Ltd., London, 2004.
- [6]. **Silviu Crăciun**, *Cositorirea la cald a materialelor metalice*, 1976.
- [7]. **Tamara Radu, Stela Constantinescu, Lucica Balint**, *Materiale metalice rezistente la coroziune*. Editura Științifică F.M.R., 2004
- [8]. **Opre Flore, Florentina Ionescu, Tamara Radu**, *Coroziune materialelor metalice*, Editura Științifică F.M.R., 2000

MORPHOLOGY OF NICKEL MATRIX COMPOSITE COATINGS WITH NANO- SILICON DISPERSION PHASE

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ABSTRACT

In this paper is presented the morphology of nickel metal layers, nickel matrix composite and particles dispersed phase, obtained by electrodeposition on steel based, using nickel sulphate as electrolyte. Nickel anodes used were 99.9% purity. Experimental investigations were carried out at the temperature of 293 K and various current densities for 1h, with different stirring rates of electrolyte and silicon powder concentrations. The coatings were deposited on a carbon steel substrate which was kept vertically in the solution.

The inclusion of silicon particles about 50 nm led to significant hardening of nickel composite matrix.

KEYWORDS: nickel, silicon, nano, composite coatings, electrodeposition, microhardness

1. Introduction

In recent years there has been an increasing interest in the field of advanced materials in developing composite coatings obtain by electrodeposition. The necessity for coatings with improved resistance to aggressive environments is high, as a result of a growing consumption for safe service life of industrial objects [1, 2].

Composite coatings are used in various fields, from high-tech industries such as electronic components and computers, to more traditional industries such as general mechanics and automobiles, paper mills, textiles and food industries. During the last decades, the main work carried out in this field is aimed almost entirely to the production of wear and corrosion-resistant coatings, self-lubricating systems and dispersion-strengthened coatings [3–6].

With the increasing availability of nano-particles, the interest of the low-cost and low-temperature composite electroplating is

continuously growing, with major challenge being the achievement of high codeposition rates and homogenous distribution of the particles in the metallic matrix. A recent review on the electrodeposition of metal matrix composite coatings containing nano-particles can be found in literature [7].

The production of composite coatings can be achieved through electrochemical deposition of the matrix material from a solution containing suspended particles such as: oxides, carbides, nitrides, metal powder. The usual dimensions of particles in such applications are in the range of micrometers.

The objective of the present experimental work is the extension of these researches when nano-silicon powder (mean diameter 50 nm) is codeposited. The inclusion of nanosized particles can give an increased in microhardness [8]. Many operating parameters influence the quantity of incorporated particles, including current density, bath agitation and electrolyte composition. High incorporation rates of the

dispersed particles have been achieved using a high nanoparticle concentration in the electrolyte solution and smaller sized nanoparticles. It was proved that the uniform dispersion of the codeposited particles leads to the improvement of the mechanical, tribological, anti-corrosion and anti-oxidation properties of the coatings [9, 10].

2. Experimental procedure

Two types of samples were prepared. Samples coated with pure nickel coating and samples coated with Ni-Si coating. Ni coating was deposited at a current density of 2A/dm^2 , while Ni-Si composite coatings were deposited at a current densities of 2A/dm^2 and 3A/dm^2 . The process of deposition was carried out at the temperature of 293 K and the stirring rate was 500 rpm. The layers were deposited on a carbon steel substrate.

The Ni - Si coatings were electrodeposited from a suspension of Si nanoparticles (50 nm) in nickel sulphate electrolyte. Suspensions were prepared by adding 10 g/L of Si nanoparticles and they were stirred for 1 h before the deposition. The substrate was steel and the anode pure nickel. Study of the surface morphology, microhardness measurements were carried

out for the characterization of the composite coatings of this work.

Investigation of morphological appearance of coatings was performed with an optical microscope Olympus BX 51M.

Measurements of the Vickers microhardness of pure nickel and Ni-Si composite deposits were performed on their surface by using a 20 g load for a period of 10 s and the corresponding final values were determined as the average of 3 measurements.

3. Results and discussion

3.1. Morphology

In Fig. 1 is presented the macrostructure of metallic support, without nickel coating.

A macrography of a pure nickel coating obtained by eletrolitic deposition is shown in Fig. 2 while Ni - Si coatings are shown in Fig. 3 a nd Fig. 4. Both coatings were electrodeposited at a current density of 2A/dm^2 .

As it can be observed from Fig. 3 (dark field and bright field illumination), the composite coatings are more compact than the pure one. As a consequence better mechanical and anticorrosive properties of the composite coating should be expected.



Fig. 1. Metallic support (without Ni coating, X200)

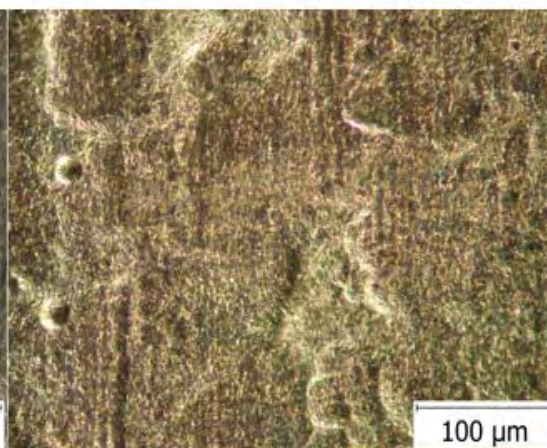


Fig. 2. Ni coating, 2A/dm^2 , 500 rpm (X400)

Surface appearance of metal deposition (Ni) reveal a uniform and compact layer without pores or other defects, which faithfully follows the steel support. In figure

3 is presented the macrostructure of Ni-Si coatings (10 g/L Si 50 nm) for operating conditions: current density – 2A/dm^2 , time – 60 min, stirring rate – 500rpm.

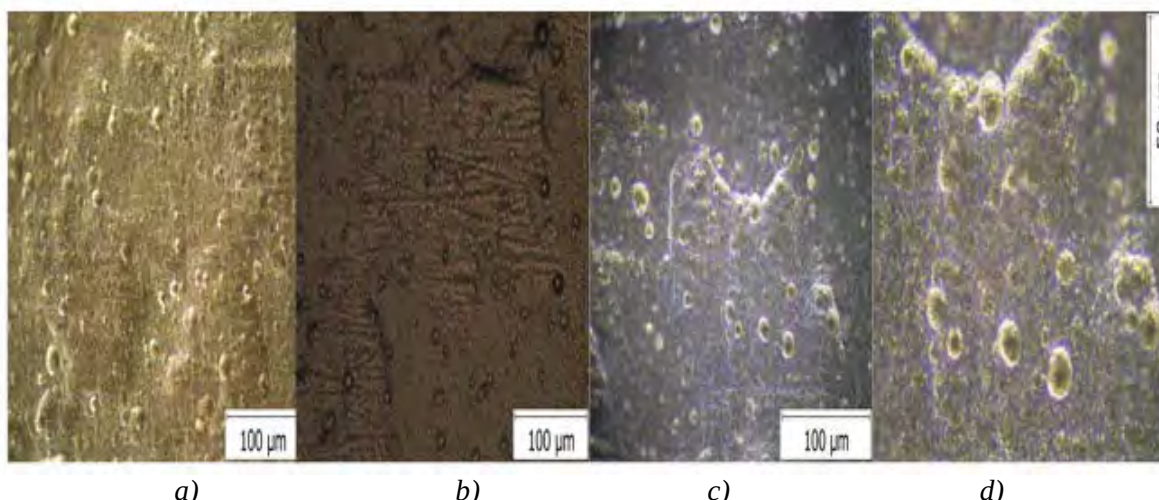


Fig. 3. Macrostructure of Ni-Si coating (10g/L Si 50 nm), 2A/dm^2 , 60 min, 500rpm:

- a) X400 dark field illumination, b) X400 bright field;
 c) X500 dark field; d) X1000 dark field.

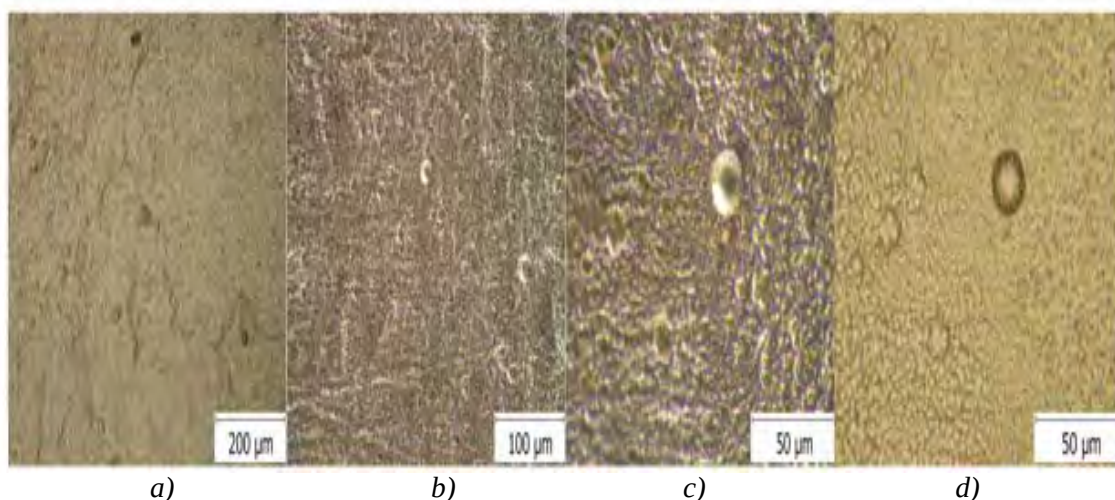


Fig. 4. Macrostructure of Ni-Si coating (10g/L Si 50 nm), 3A/dm^2 , 60 min, 500rpm:

- a) X200 dark field illumination, b) X400 dark field;
 c) X1000 dark field; d) X1000 bright field.

In figure 4 is presented the macrostructure of Ni-Si coatings (10 g/L Si nm) for operating conditions: current density – 3A/dm^2 , time – 60 min, stirring rate – 500 rpm.

3.2. Mechanical properties

Vickers microhardness measurements were performed on pure nickel and on Ni -

Si coatings. Microhardness measurements were carried out using a Vickers microhardness tester, applying 20 g load for 10 s time.

The mean value of Vickers microhardness of pure nickel coatings has been found of about $300\text{HV}_{0.02}$ while composite coatings is about $505\text{HV}_{0.02}$. This result shows that the codeposition of Si

nanoparticles ameliorates the mechanical properties by 70% microhardness increase.

Fig. 5 and 6 depict the microhardness of the nanocomposite coatings prepared as a function of electrolyte stirring rate.

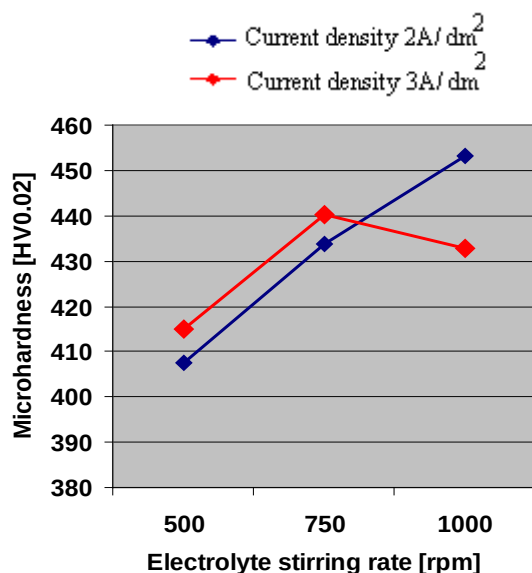


Fig. 5. Microhardness as a function of electrolyte stirring rate (10 g/L Si 50nm)

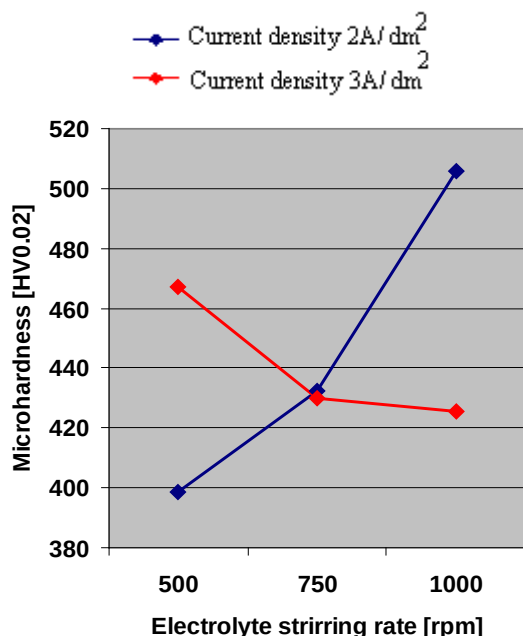


Fig. 6. Microhardness as a function of electrolyte stirring rate (20 g/L Si 50nm)

Silicon particles dispersion lead to hardening of nickel matrix, so the nickel metallic coating had a mean value of 300

HV_{0.02} comparing to value of 505 HV_{0.02} for Ni-Si composite coating (2A/dm², 1000 rpm, 1h, dispersion phase 20g / L Si (50nm)). Amelioration of the mechanical properties of the composite coating results in a 70% increase of the coating microhardness.

4. Conclusions

The experimental results led to the identification of electrodeposition parameters that provide a very good adhesion to metallic support, the metal layers are compact without pores or other defects, almost flat, with relatively constant thickness.

Significant increase in composite coatings hardness versus nickel coatings certifies that nano-silicon particles were included and their presence induces a strong hardening in the metal matrix.

References

- [1]. I. Gurrappa, L. Binder, *Electrodeposition of nanostructured coatings and their characterization - a review*, Sci. Technol. Adv. Mater. 9, 043001, 2008.
- [2]. R. C. Agarwal, Vijaya Agarwal, *Electroless alloy/composite coatings: A review*, [Sadhana](#), volume 28, issue 3-4, pages 475-493, 2001.
- [3]. J. Kubisztal, A. Budniok, *Electrolytical production of Ni + Mo + Si composite coatings with enhanced content of Si*, Applied Surface Science, volume 252, pages 8605-8610, 2006.
- [4]. C. Kerr, D. Barker, F. Walsh, J. Archer, *The electrodeposition of composite coatings based on metal matrix-included particle deposits*, Transactions of the Institute of Metal Finishing A., vol. 78, issue 5, pages 171-178, 2000.
- [5]. M. Musiani, *Electrodeposition of composites: an expanding subject in electrochemical materials science*, [Electrochimica Acta](#), volume 45, pages 3397-3402, 2000.
- [6]. M. Srivastava, V.K.W. Grips, A. Jain and K.S. Rajam, *Influence of SiC particle size on the structure and tribological properties of Ni-Co composites*, [Surface and Coatings Technology](#), volume 202, issue 2, pages 310-318, 2007.
- [7]. C.T.J. Low, R.G.A. Wills, F.C. Walsh, *Electrodeposition of composite coatings containing nanoparticles in a metal deposit*, Surface and Coatings Technology, volume 201, pages 371-383, 2006.



[8]. **S.T. Aruna, V.K. William Grips, K.S. Rajam**, *Ni-based electrodeposited composite coating exhibiting improved microhardness, corrosion and wear resistance properties*, Journal of Alloys and Compounds volume 468, pages 546–552, 2009.

[9]. **T. Borkara, S. Harimkar**, *Effect of electrodeposition conditions and reinforcement content on microstructure and tribological properties*

of nickel composite coatings, Surface and coatings Technology, volume 205, issues 17-18, pages 4124-4134, 2011.

[10]. **I Garcia, J.-P Celis**, *Electrodeposition and sliding wear resistance of nickel composite coatings containing micron and submicron SiC particles*, [Surface and Coatings Technology](#), volume [148](#), issue [2-3](#), pages 171-178, 2000.

DETERMINATION OF FRICTION COEFFICIENT AT SLIDING INDENTATION OF LASER CLADDING WITH Ni – Cr – B – Fe – Al ALLOY

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ABSTRACT

To increase resistance to wear of the surface layers made from 0.45% C steel, multilayer deposit by powder injection with the chemical composition Cr 8.9%, 4.5% Fe, 5.1% B, 2, 4% Al, 0.6% Cu, and Ni was tested in a molten bath with a continuous wave of CO₂ laser, coupled to a table within x-y-z coordinates. The layers were characterized by microstructural analysis, qualitative analysis of phase with the radiation diffractometry X and EDX microanalysis. It was determined the friction coefficient developed during sliding indentation in dry friction conditions.

KEYWORDS: laser cladding, powder injection, sliding indentation

1. Introduction

The sliding indentation test is today widely used, especially by the coating industry and coating development laboratories, as well as in research for evaluating the tribological properties of coatings and other hard surfaces. Different standards were elaborated in Europe and USA [1, 5].

In the sliding indentation test, an indenter (in this case a ball bearing) is pressed by a normal force on the workpiece surface, while being pushed by a force tangential to it.

Under static or quasi – static load application, maintaining the contact operating conditions requires limiting the plastic deformation in the contact area.

For the development of plastic deformation in a hertzian contact, the steps below are followed [1, 2, 3].

- ❖ smoothing the contacting roughness, with the total deformation less than 0.1 μm;

- ❖ plastic deformation of surface roughness until formation of continuous

contact surface with deformations of 0,1 to 10 μm;

- ❖ plastic volume deformation when exceeding the limit of elasticity, as a result of the material flowing beneath the contact surface, the plastic deformation exceeds 10 μm, and the material moves from the contact zone without dislodging the base material;

- ❖ seizing, which occurs at increasing deformation and implies adhesion, detachment and accumulation of material on the contact surfaces.

A material behaviour within an elasto-plastic range depends on: construction parameters (shape, dimensions) and operating parameters (kinematics, energy, environmental) of the contact; the surface layer parameters - microgeometry, metallurgical characteristics (chemical composition, purity, microstructure) and mechanical parameters (hardness, tension) [6].

It was found [1, 2, 3, 4, 6] that the value of the hertzian stress at which plastic deformation occurs in contact increases with the surface hardness. Also, the larger the frictional forces, the lower the plastic

deformation where the seizing tendency occurs.

The choice of surface hardening processes, suitable to a certain material, is an important way to increase the bearing capacity of the contacting surface and reduce the tendency of seizing. Thus laser cladding with alloy Ni - Cr - B - Fe - Al constitutes an effective way to increase the surface hardness that directly affects their behavior to plastic deformation.

Characterization of the surface layers can be highlighted by an installation with a point contact sphere-plane which provides a sliding indentation in dry friction conditions. The evolution of the plastic deformation of the material tested when applying various normal forces led to the determination of the friction coefficients as an indicator of the seizing tendency:

According to the literature [1, 2, 3, 4, 6] with the surface hardened materials transition from elastic to plastic deformation is continuous, so that the strain at the beginning of the plastic deformation ($\delta_p = 0.1$ to $10 \mu\text{m}$) can be expressed with an acceptable approximation by Hertz's equations.

For the point contact sphere-plane, the features are:

- Hertzian pressure:

$$P_{\max} = \left(\frac{6F \cdot E^*}{\pi^3 \cdot R^2} \right)^{1/3} \quad (1)$$

where: F – normal force, E^* - reduced elasticity module, R – indenter radius, $P_{\max}$ max pressure at Hertzian contact.

$$\frac{1}{E^*} = \frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2} \quad (2)$$

where: ν_1, ν_2 - Poisson coefficients, E_1, E_2 elasticity modules of the indenter and surface being tested.

There is a linear relation between the

material yielding point and hardness [7, 8, 9].

Thus: for non hardened material,

$$HV = (2,9 - 3) \cdot \sigma_c \quad (3)$$

and for isotropic hardened materials, acc.to [10], $HV = 2,475 \cdot \sigma_c$ (4)

Calculation of the friction coefficient developed during the testing was carried out using the formula:

$$\mu_{med} = \frac{F_{fmed}}{F_{nmed}} \quad (5),$$

where: F_{fmed} : the average friction force

F_{nmed} : the average normal force the friction forces being recorded by means of a force transducer.

This paper presents a study of the elasto – plastic behavior of some laser cladded samples with alloys of Ni - Cr - B - Fe - Al (code A and B) and the base material (code Mb) made from steel improved 1C45, SR EN 10083-1 : 2007.

The samples obtained were examined by metallographically, qualitative analysis of phase with the radiation diffractometry X and EDX microanalysis. There were determined the friction coefficients developed.

2. Experimental conditions

For cladding purpose it was used the powder „Alliages Speciaux 7569 A Iliajes Frittes, Franța” with the chemical composition: 8,9%Cr; 4,5%Fe; 5,1%B; 2,4%Al; 0,6%Cu; and Ni.

Cladding was made on samples from improved steel 1C45, SR EN 10083-1:2007.

It was used a continuous wave CO2 system, type Laser GT 1400W (Romania), with working table within x-y-z coordinate system and computer programmed working regime, provided with a powder injection laser on the melted surface.

The working regime used to form laser cladding with nickel-based alloy is presented in Table 1.

Table 1. Working regime used in laser cladding

Added material rate [mg/s]	No. of overlapping runs	Working regime					
		P	v	d _s	p _{av}	g	Hardness HV ₅
		[W]	[mm/s]	[mm]			[MPa]
105	4	1150	7.5	1.8	1.5	2.07	11450

NOTE: P - laser radiation power, v - scanning speed of the laser beam on the processed surface, d_s - diameter of the laser beam; p_{av} - transversal advance step, g - thickness of clad layers; m_p - flow rate of added material.

The sliding indentation rig is illustrated in Figure 1.

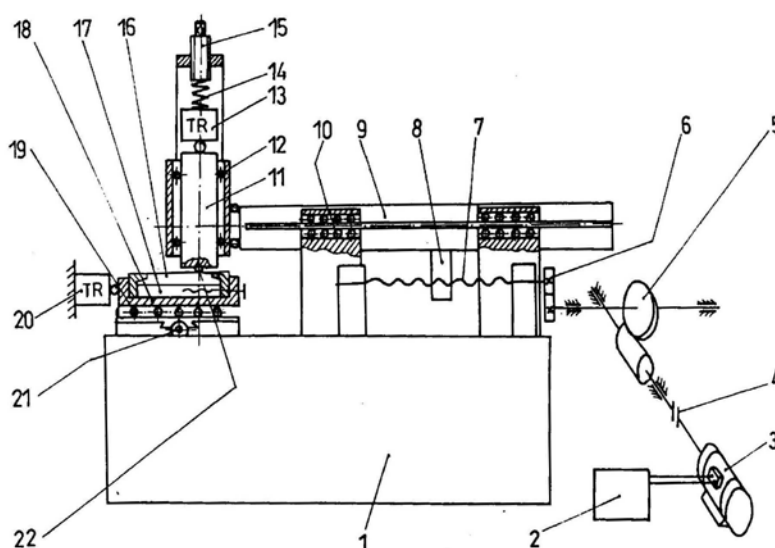


Fig. 1. The components of the rig for sliding indentation tests

1-frame, 2-ABB frequency converter, 3-electric engine, 4-elastic coupling, 5, 6, 7, 8-mechanical transmission, 9-horizontal column, 10-balls guiding, 11-vertical column, 12-balls guiding, 13-force transducer, 14-elastic system, 15-loading screw, 16- specimen, 17-sustenance surface, 18- specimen fixing device, 19-balls guiding, 20-force transducer, 21-screw for transversal movement, 22- indenter

The mechanical composition of the kinematic chain and the presence of the frequency converter cause the feed speed of the horizontal column 9 to take very low values, being adjustable within the range from 0 to 0.172 mm / s. Under these speed conditions the sample strain can be considered quasi-static [9].

The measuring system consists of two identical force transducers (Fig. 1), which determine the normal force and tangential force, and a data acquisition and processing system.

The force transducers are resistive full bridge type HOTTINGER BALDWIN MESSTECHNIK GmbH, C9A with measurement range 0 ... 50 kN.

The sample 16 and indenter 22 (Fig. 1) materialize the tribo-model considered in the study of deformations [5]. The tribo-model will therefore contain a point contact between a ball and a plan. The indenter (ball – mobile tribo-element) is held firmly in a mount, solitary to the vertical column 11 (Fig. 1), the only possible

movement being sliding onto the sample, at the speed of the horizontal column 9 [9].

The fixed tribo-element consists of the

samples to be analyzed (samples).

The samples have rectangular shape and the dimensions of Table 2.

Table 2. Characteristics of the fixed tribo-element

Sample code	Sample length	Sample width	Sample thickness	Hardness HV5
	[mm]		[MPa]	
MB	92	16	15	3400
A	92	24	15	9270
B	92	24	15	9385

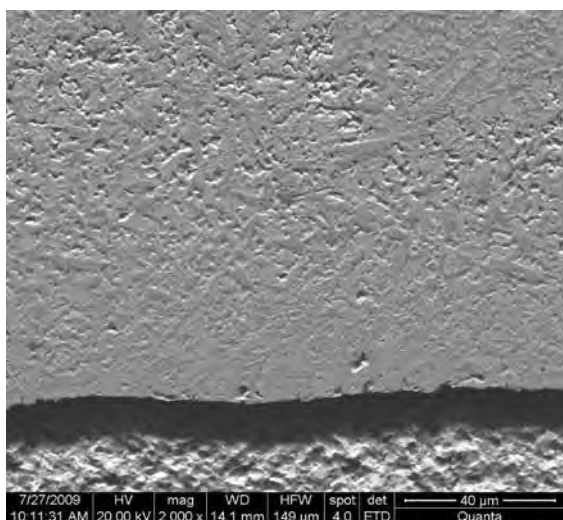
Series of traces on each specimen were made, using a fixed ball mount. For this type of testing, the mobile tribo-element (ball) is subject to two forces: one normal on the fixed tribo-element and one tangential to its surface. Initially the normal force is applied, the ball making a plastic deformation, and then the tangential one resulting a trace in the form of an elongated groove.

The indenter speed is 0.15 mm/s, diameter ϕ 12.675 mm, is made from Rul 1 (SR EN ISO 683-17:2002), hardened and annealing steel. After each test, the ball bearing has been replaced with a new one that was degreased further. Before carrying out any test, the sample surfaces have been degreased with alcohol, to provide conditions for dry friction. The normal

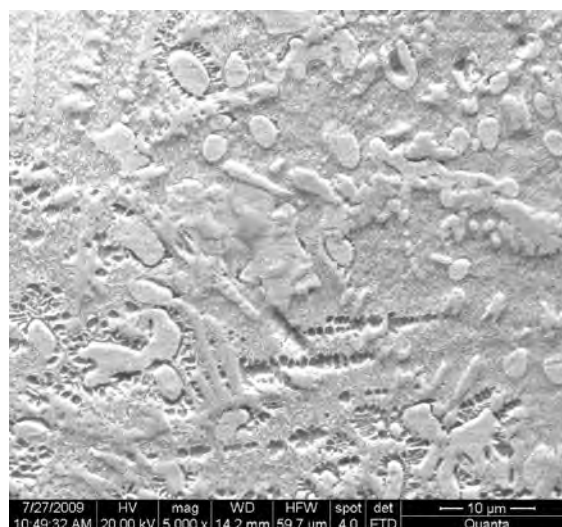
forces F_N , used for indentation were: $F1 = 2.886$ kN; $F2 = 4.330$ kN; $F3 = 5.773$ kN; $F4 = 7.216$ kN. Roughness R_a , as measured by a roughness gauge Surtronic 3+, is $R_a \approx 0.210 \mu\text{m}$ for all surfaces.

3. Experimental results and discussion

The microstructure of the nickel-based alloy laser cladded layer is presented in Figure 2, the attack being electrolytic. According to phase qualitative analysis (fig. 3) the columnar dendritic fine structure of the deposit contains nickel-based solid solution and eutectic colonies of borides (Ni_3B , CrB), CrB being the main hardening phase.



a.



b.

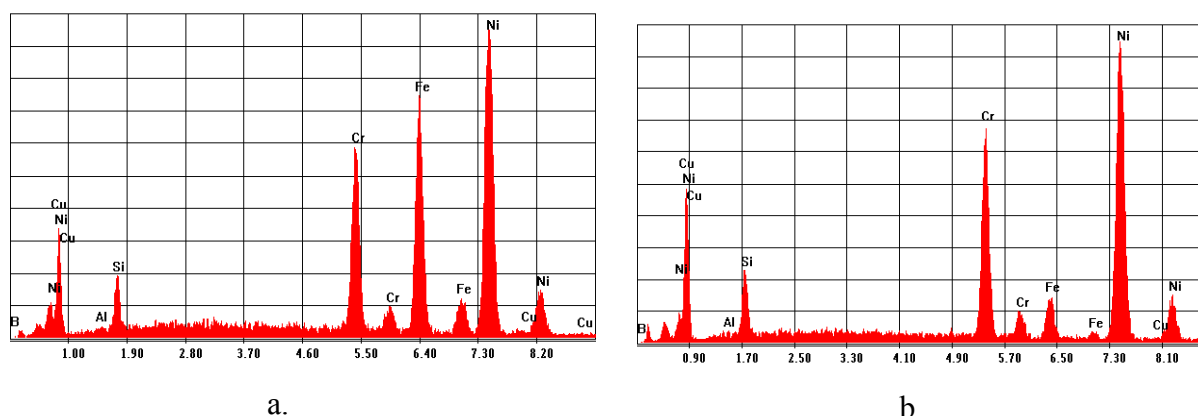


Fig. 2. Microstructure of nickel – based alloy and EDX results: a) base of layer deposited; b) layer surface(x1000). Electrolyte attack, solution 50% HNO_3

Table 3. The EDX results

EDX results for base of layer deposited			EDX results for layer surface		
Element	Wt %	At %	Element	Wt %	At %
B K	0	0	B K	0	0
AlK	0.62	1.24	AlK	0.72	1.4
SiK	4.67	8.97	SiK	7.33	13.71
CrK	14.47	15.01	CrK	21.24	21.46
FeK	23.69	22.89	FeK	5.45	5.13
NiK	55.18	50.72	NiK	63.97	57.24
CuK	1.36	1.16	CuK	1.28	1.06

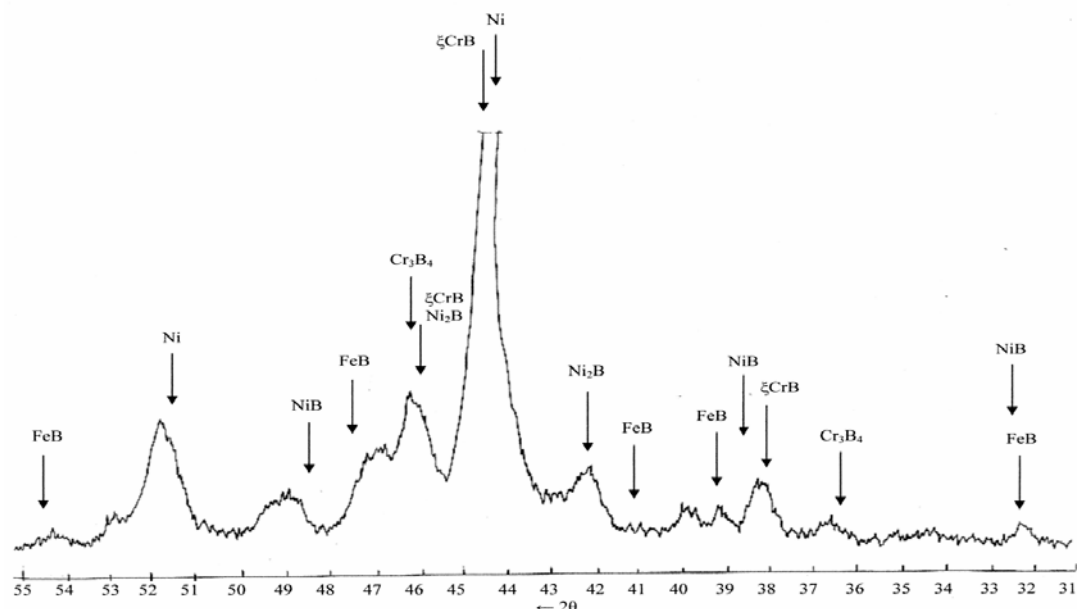


Fig. 3. Diffractogram for the layer cladded on the nickel base alloy

At the bottom of the layer there is a narrow area of nickel-iron dilution without eutectic carbides, which makes the transition to the material support. Good adhesion of

the deposited layer to the substrate is visible. In the presence of aluminum, the nickel can form intermetallic compounds having a hardening effect: Ni_3Al , Ni_2Al_3 [11, 12]. Table 3 shows the EDX results. If we analyze the EDX results we found that: the iron concentration decreases, and the

chromium, nickel, aluminium concentration increases from base to surface.

Traces obtained from sliding indentation for the basic material are presented in Figure 4. Max. pressures, obtained by relation (1), for the normal forces used are given in Table 4.

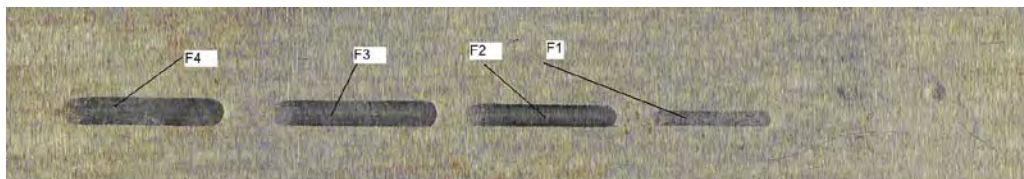


Fig. 4. Picture of specimen MB with the sliding indentation tracks

Table 4. Maximum pressure obtained for the normal strains applied

Pmax [MPa]	Normal force, F_N [kN]
5773.529	2.886
6609.550	4.330
7274.611	5.773
7836.247	7.216

The variation of the friction coefficient with the normal force for the three samples is presented in figure 5 and table 5. The different values can be accounted for by the

presence of intermetallic compounds (borides and carbides) which results in inhibition of adhesion.

Table 5. Friction coefficient determined

Sample code	Normal force [kN]	Friction coefficient, μ_{med}
MB	2.886	0.068
	4.330	0.079
	5.773	0.082
	7.216	0.093
A	2.886	0.079
	4.330	0.071
	5.773	0.049
	7.216	0.063
B	2.886	0.153
	4.330	0.055
	5.773	0.039
	7.216	0.040

Their amount increases from the base material containing cementite precipitates in sample A with a larger amount of borides in particular, reaching its maximum with sample B which has the highest hardness.

From Figure 5 we can see that for the base material (sample code MB) the friction coefficient takes the highest value, which increases with increasing normal force. This can mean a larger plastic deformation. As a result the friction surface is higher and so is the adhesion tendency.

Analyzing the behavior of sample A it can be seen an intermediate value of the friction coefficient (between those of samples MB and B). The explanation is on account of lower plastic deformation, due to a higher quantity of intermetallic compounds. This leads to reduced indenter penetration and less friction surface associated with a reduced adhesion tendency. This increase of friction coefficient occurs at a normal force greater than 5.65 kN.

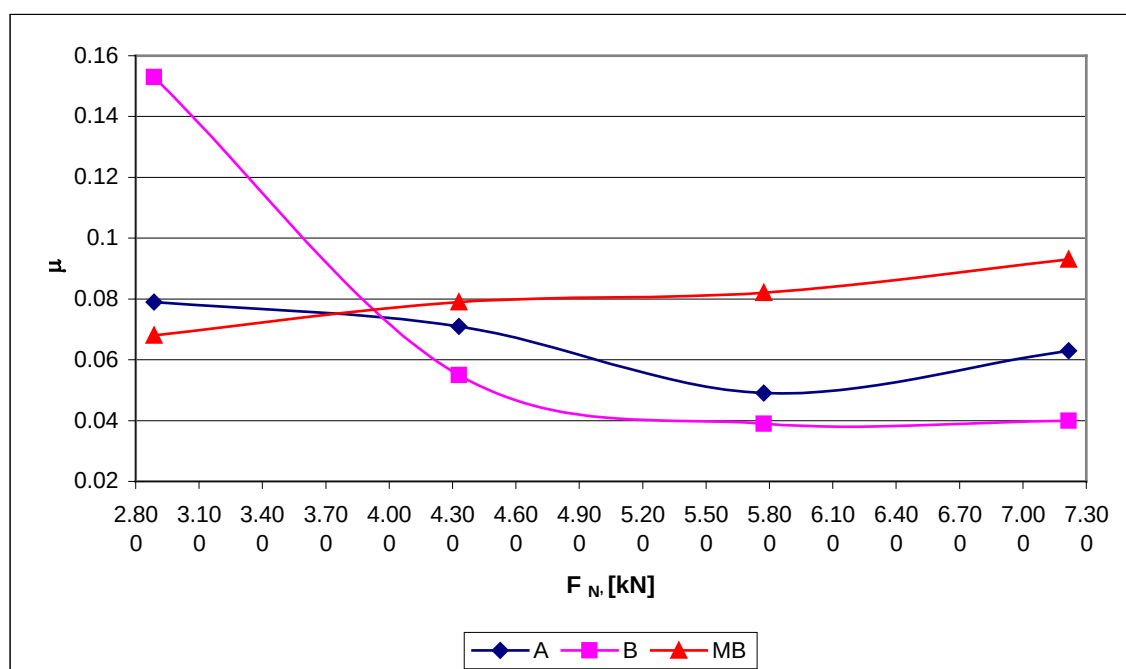


Fig. 5. Variation of the friction coefficient with the normal force for the three samples MB, A, B

Analysing the behaviour of the sample code B it is found that high hardness due to the large amount of borides makes plastic deformation to be minimal. The indenter penetration into material penetration is the lowest of the three cases, the low-friction surface associated with minimum adhesion has led to an extensive range of strains in

which the friction coefficient is minimal. Therefore in the range of forces concerned there is no tendency of adhesion and increasing friction coefficient.

Figure 6 presents track depth variation with normal force and figure 7 presents track width variation with normal force.

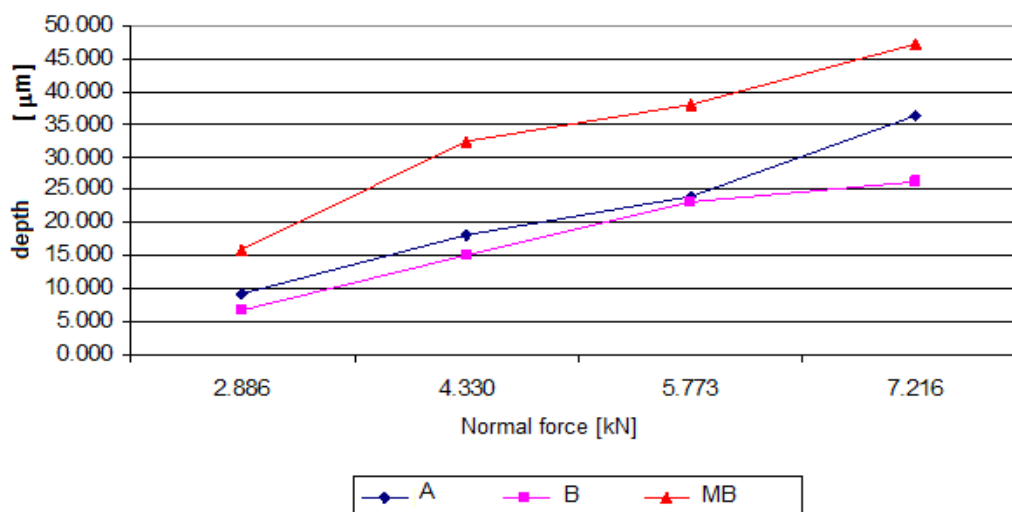


Fig. 6. Track depth variation versus normal force

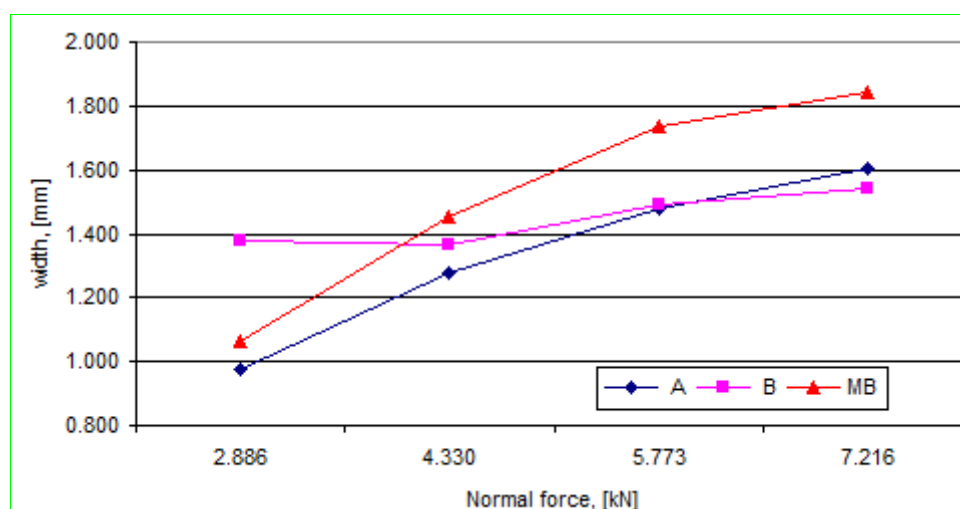


Fig. 7. Track width variation versus normal force

Form figure 6 it could be notice that for small normal forces the deformation depth of specimen code B is reduced but the zones near to the track begin to participate at the deformation process, recording a maximum width.

With the increasing of the normal force, in depth deformation becomes prevalent and for the force F4 the width for specimen B get less than the width of the specimen A.

Analysing the track width variation with the normal force (fig. 7), it appears that trace depth growth occurs, due to normal force increasing and to the arising of plastic

deformation, fact more visible for the substrat material.

4. Conclusions

The experimental research led to the following conclusions:

- ❖ Laser cladding is an efficient way to move the elasto-plastic transition at higher contact pressures;
- ❖ with increased layer hardness and normal force, the friction coefficient decreases, and the material can be used at higher pressures;

- ❖ with increase layer hardness the trace depth is reduced;
- ❖ the comparisons of the geometrical characteristics of the different digital depth profiles confirm the better behaviour of the laser cladding layers.

References

- [1]. **Kragelskii I.V.** – *Trenie i iznos*, MAŠGIZ, Moskova, 1962.
- [2]. **Popinceanu N, Gafițanu C, Diaconescu E, Crețu S, Mocanu D.R.** - *Fundamental problems of rolling contact*, Ed. Tehnică, București, 1985.
- [3]. **Levcovici S. M.** – *Contributions to the laser surface treatment of tool steel*, Doctoral thesis, Galați 1997.
- [4]. **Z. Liu, J. Sun, W. Shen**, *Study of plowing and friction at the surfaces of plastic deformed metals*, Tribology International 35 (2002) 511–522.
- [5]. **DIN 50320** - Verschleiß. Begriffe, Systemanalyse von Verschleißvorgängen, Gliederung des Verschleißgebietes.
- [6]. **Crudu I** – *Contributions to the study of the influence of normal stress on static destruction by pitting of the point contacts*, Doctoral thesis, Iași, 1969.
- [7]. **A.E. Tekkaya** – *An improved relationship between Vickers hardness and yield stress for cold formed materials and its experimental verification*, Annals of the CIRP, vol. 49/1, pg. 205 – 208.
- [8]. **D.A. Hills** – *Mechanics of elastic contacts*, Butterworth – Heinemann, Oxford, 1993.
- [9]. **C.Spănu** – *Studies and researches on tribomodels as regards surface layer plastic deformation under rolling and sliding*, Doctoral thesis, Galați 2002.
- [10]. **K. Komvopoulos** – *Three – dimensional contact analysis of elastic – plastic layered media with fractal surface topographies*, Journal of Tribology, pg. 632 – 640, 2001.
- [11]. **Boiciuc S** – *Research regarding laser cladding with injected powder*, Doctoral thesis, Galați 2010.
- [12]. **Levcovici S, Levcovici D.T., Gheorghies C., S. Boiciuc** – *Laser Cladding of Ni-Cr-B-Fe-Al Alloy on a Steel Support*, The International Thermal Spray Conference and Exposition (ITSC 2006) May 15th–17th, 2006, Seattle, Washington, U.S.A, Proceedings on CD, pp.1339-1344.

STRUCTURAL STUDY OF EXTRUDED $\text{CuAl}_{13}\text{Ni}_4$ SHAPE MEMORY ALLOY

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ABSTRACT

This paper presents a structural study for a copper based shape memory alloy. The behavior of $\text{CuAl}_{13}\text{Ni}_4$ alloy, is evaluated by X-ray diffraction. On cooling, the martensitic transformation takes place from the ordered structures to long period two layered structure. The crystalline phase transformations of those alloys are very sensitive to the heat treatments, deformation degrees and also to the undesired aging effects. In particular, the study has been made on the $\text{CuAl}_{13}\text{Ni}_4$ shape memory alloy samples after hot extrusion, quenching and aging in martensitic state

KEYWORDS: Shape Memory Alloy Cu - Al - Ni, martensitic transformation, XRD, ER, DSC

1. Introduction

The studies of Cu- based ternary SMAs have been generally on single crystals but only few publications on polycrystalline alloys were found. [1]. This paper presents a structural study for a Cu-based SMA. The behaviour of $\text{CuAl}_{13}\text{Ni}_4$ alloy is evaluated by XRD. On cooling, the martensitic transformation takes place from the ordered structures to long period two layered structure. The crystalline phase transformations of these alloys are very sensitive to the heat treatments, deformation degrees and also to the undesired aging effects. In particular, the study has been made on the $\text{CuAl}_{13}\text{Ni}_4$ SMA samples after hot extrusion, quenching and aging in martensitic state.

Polycrystalline Cu-Al-Ni SMA's are a considerable cheaper alternative to classical Ti-Ni alloys. They are more resistant to degradation of functional properties due to undesired aging effects than Cu-Zn-Al

SMA's [2] and may work at a higher temperature (near 473 K).

The characteristic temperatures of martensitic transformation Cu-Al-Ni alloys are in the range from 73K to 473K and depend on aluminum and nickel content. The following empirical equation shows the stronger influence of Al content and estimates the M_s temperature [4]:

$$M_s \text{ (K)} = 2293 - 45 \times (\text{wt\% Ni}) - 134 \times (\text{wt\% Al}) \quad (1)$$

Depending on alloy composition and heat treatment, Cu-Al-Ni SMA's may transform from high temperature parent phase β_1 (DO3) to two types of thermal induced martensite at low temperature: β_1' (18R), for 11%-13 % Al, or γ_1' (2H), for more than 13%Al. In alloy compositions near 13%Al, two martensites can coexist [4].

The investigated alloy in this paper Cu-13Al-4Ni (wt %) lies in the region of the phase diagram where β_1' and γ_1' thermal

induced martensites may coexist. The effect of nine months aging in extruded state, annealing time and temperature, thermal cycling of transformation temperatures was studied on a polycrystalline sample with 13 %wt Al, by differential scanning calorimetry (DSC), electrical resistivity (ER), X ray diffraction (XRD), scanning electron microscopy (SEM).

2. Experimental procedures

The polycrystalline Cu-13 Al-4Ni (wt %) alloy was elaborated by classic melting in a tilting induction furnace from Dunărea de Jos University of Galati. The samples were extracted from 9 months aged hot extruded wires 4 mm diameter and 145 mm length. The samples were machined with different geometries for following tests. For each test we studied the same samples after extrusion and a subsequent quenching.

The experiments for quenched samples comprised heat treatment using a vertical furnace (air environment) holding at 1123 K, 1173 K, 1203 K during 30 minutes.

The samples were cut from wires (4mm diameter) and were introduced in the furnace at the holding temperature for annealing. After solubilization, the specimens were immediately quenched in ice water.

2.1. DSC

For DSC measurement were used small pieces weighting less than 0.100g. The calorimetric experiments were performed by using SETARAM 92 instrument in the temperature range between 223 K and 523K (cooling by liquid nitrogen) with a heating and cooling rates of 0.25K/s. Endothermic and exothermic peaks on DSC profiles were taken from two sets of experiments:

- One thermal cycle was performed for each condition of heat treatment;
- Ten thermal cycles were performed for sample annealed at 1123K for 30 minutes and rapidly quenched in ice water.

2.2. XRD analysis

The XRD analysis was run on a RIGAKU (Cu sealed tube) at room temperature using 20 mm x 2 mm x 1 mm dimension samples. The peaks were observed between 10° and 90° value for 2θ . The acquisition time was 1s/point. The radiation used was Cu-K α . The divergence, anti-scatter and receiving slits were set at 0.40, 0.40, and 0.15 mm, respectively.

2.3. Electrical resistivity

Electrical resistance was measured using a home made four-point probe based connected with a power supply, Thermo Electron COOP DC 50-K40. Samples of 71.25mm x 1.15mm x 1.2mm were used to analyze the transformation temperatures and the hysteresis involved. Thermal cycles were performed between room temperature (below M_f) and 423K (above A_f) on heating, and between 423K and 253K on cooling, for all quenched samples. These thermal cycles were applied to 9 months aged, as well as 1123K, 1173K, and 1203K annealed/quenched specimens.

Prior to the DSC, ER and XRD experiments all the samples were submitted to the chemical etching (1:1 HNO₃ in H₂O) for 13 minutes in order to remove the layer deformed by the cutting operation as well as the oxide.

2.4. SEM

SEM micrographs were carried out in a ZEISS DSM 962 Scanning Microscope. The surfaces of the samples were first mechanically polished using conventional procedures and etched with FeCl₃. Also SEM images were observed in cross sections from tensile test specimens.

3. Results

3.1 DSC analysis

Figure 1 shows the transformation temperatures (A_f , A_s , M_s and M_f) as a function of annealing temperature for one cycle performed in each condition of heat treatment.

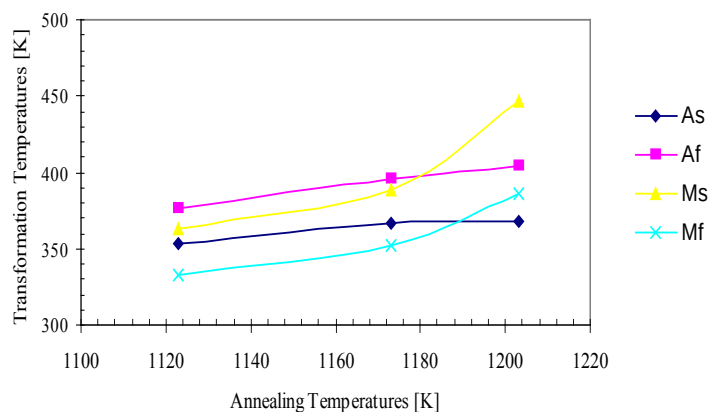


Fig.1. The transformation temperatures at Cu-13 Al-4Ni (wt %) for different annealing temperatures

Figures 2-3 show the DSC curves plotted and the transformation temperatures (Af, As, Ms and Mf) for ten thermal cycles performed on a sample annealed at 1123K using 0.25K/s cooling and heating rate.

The transformation temperatures were calculated from the DSC curves associating

the start and finish temperatures to 1% and 99%, respectively.

3.2. XRD analysis

Figure 4 compares the XRD patterns for a sample aged for 9 months at room temperature after extrusion of a sample annealed at 1123K for 1.8ks

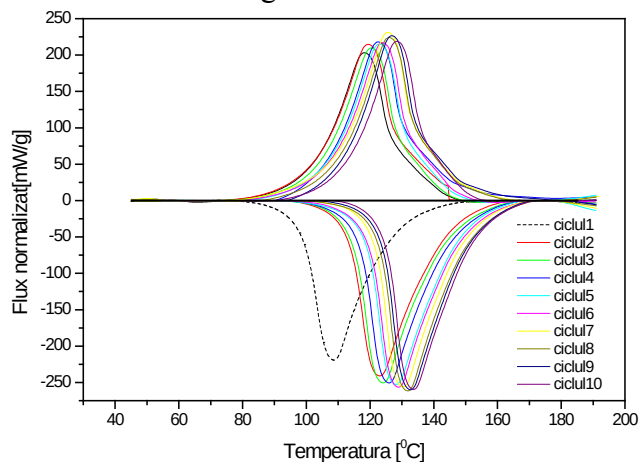


Fig.2. The DSC curves plotted for ten thermal cycles performed on a sample annealed at 1123K

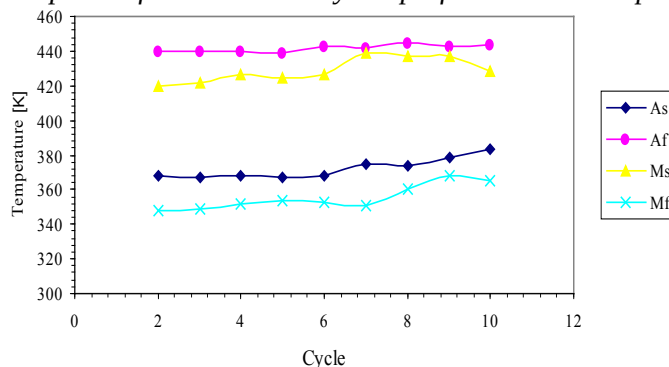


Fig.3. The transformation temperatures of the sample annealed at 1123K (cooling and heating rate 4.8K/s) vs. thermal cycles number

3.3. Electrical resistivity analysis

Figure 5 show electrical resistivity on plate shaped samples solubilised at 1123K and 1153K.

3.4. Tensile tests

Mechanical behavior was studied for tensile test until fracture on the samples annealed at 1123K, 1173K and 1223K all of them immediately quenched in iced water (Fig. 6).

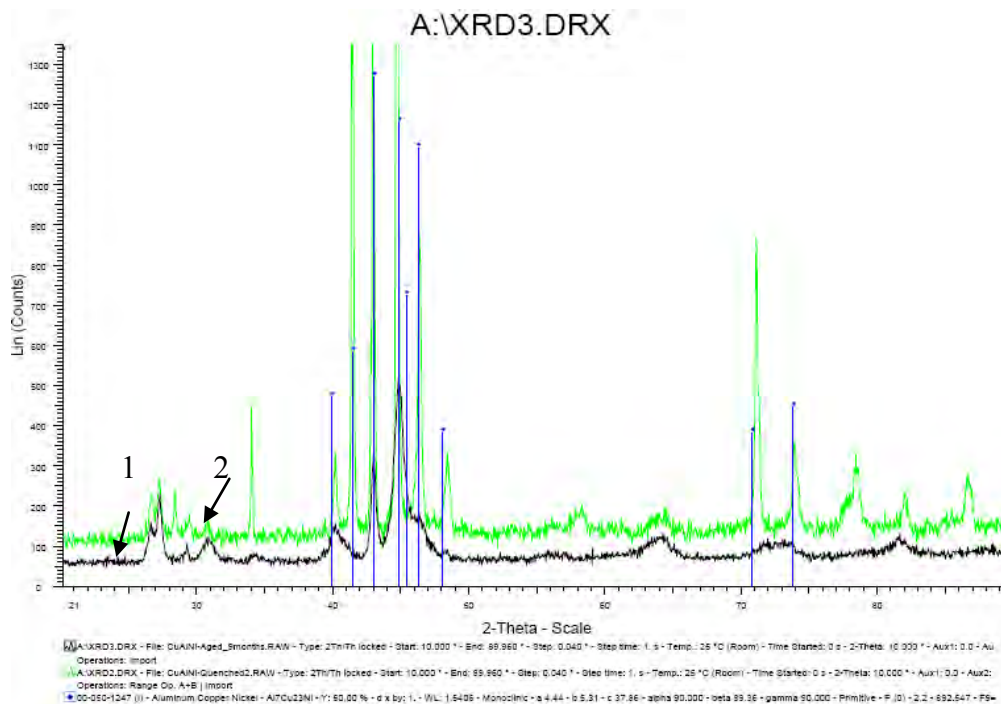


Fig.4. The room temperature XRD patterns of plate samples: aged (1), quenched (2)

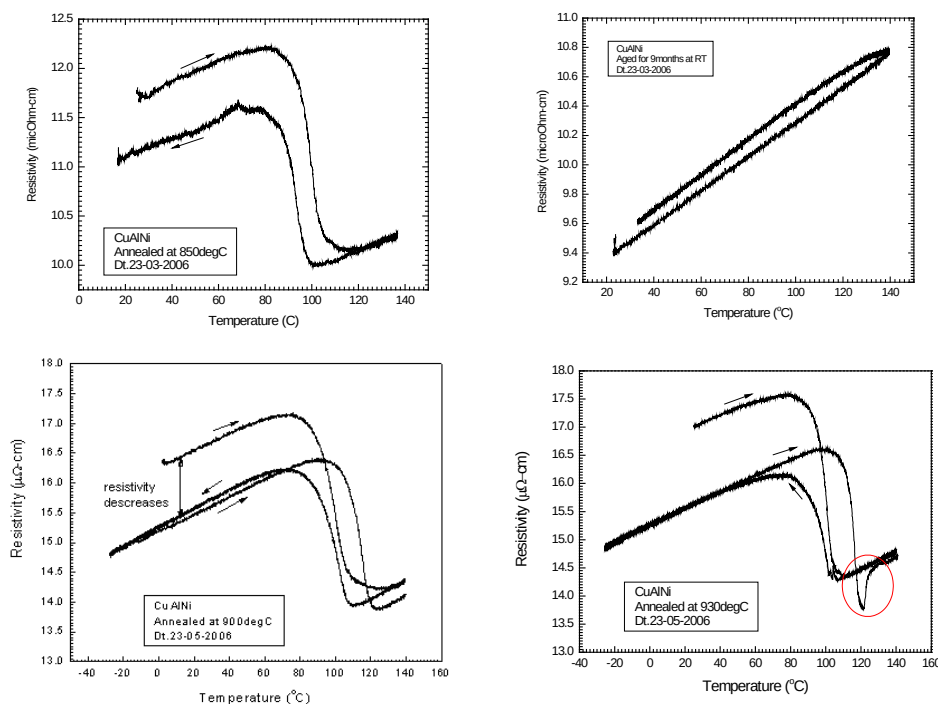


Fig. 5. ER curves at different annealing temperatures

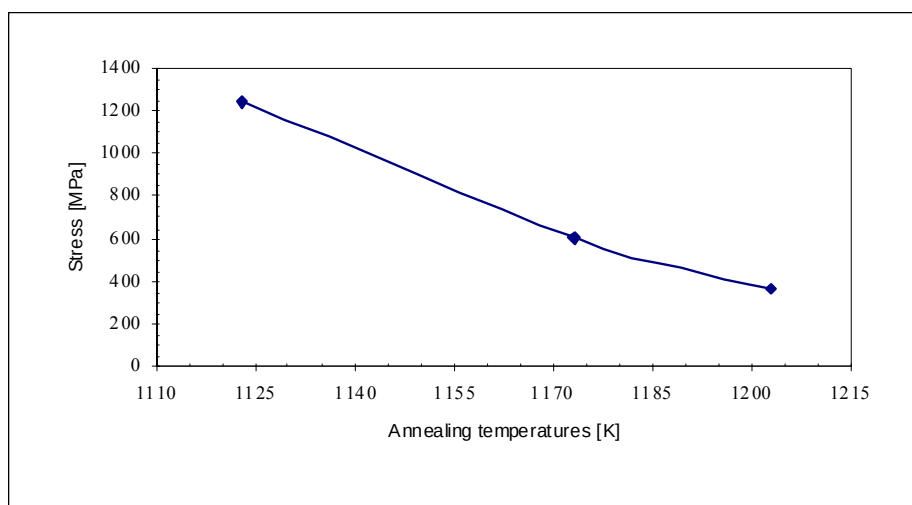


Fig.6. Ultimate stress vs. annealing temperature

3.5. SEM micrographs

Figures 7- 8 present the SEM images

on aged and quenched alloy (failure surface and etched surface)

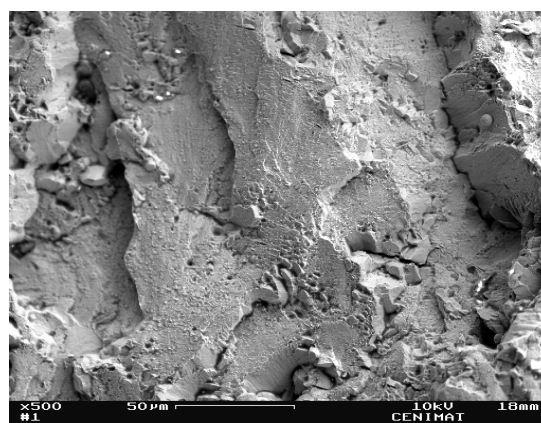
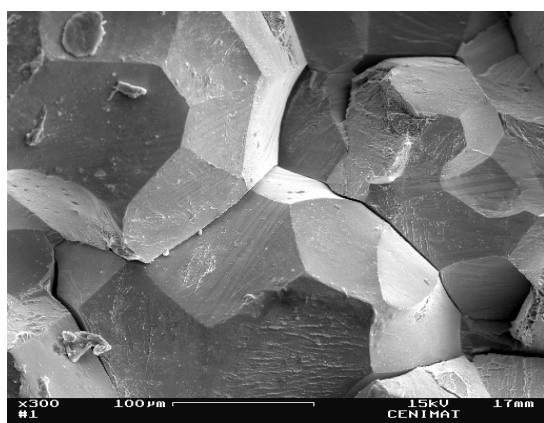
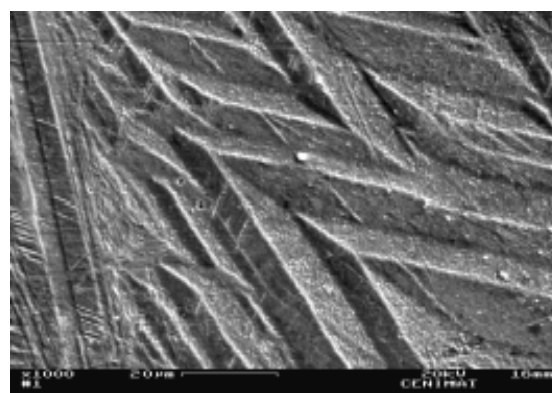
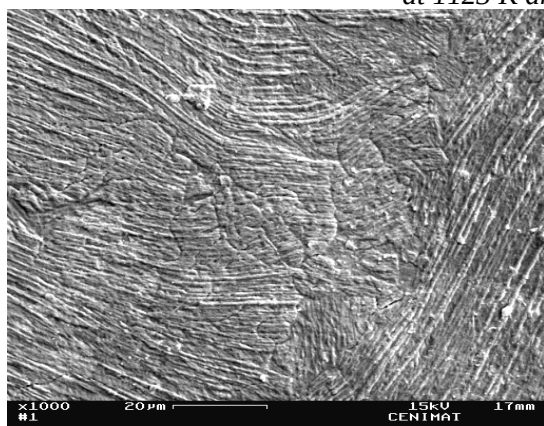


Fig.7. SEM micrographs of Cu-13 Al-4Ni (wt %) in fracture surface, aged (a) and annealed at 1123 K and quenched (b)



a

b

Fig. 8. SEM micrographs of Cu-13 Al-4Ni (wt %) mechanically polished and etched with $FeCl_3$ aged (a) and quenched from 1123K (b)

4. Discussion

4.1. Phase transformation and critical points

The DSC plot of aged hot extruded alloy shows no phase transformation. After quenching, the samples showed typical characteristics of thermoelastic martensitic transformation.

Concerning the influence of annealing temperature on critical points position (figure 1), A_s and A_f temperatures remain almost constant for the three annealing temperatures studied (1123, 1173 and 1203 K), M_s and M_f increases with increasing annealing temperature, reaching 473 K for annealing at 1203 K. This observation is important because one strong point for this polycrystalline Cu-13 Al-4Ni alloy is the high service temperature (near 473 K [10]) inaccessible for Ni Ti alloys.

Figure 2 shows of 10 DSC cycles (heating / cooling between 223 K and 523 K). Endothermic and exothermic thermal flux peaks values are approximately constant, from 225 W /g to 250 W /g, showing a relatively good thermal stability of the alloy on repeated heating / cooling cycles.

When thermal cycling is complete (direct and reverse martensitic transformation) a large number of dislocations in martensitic phases are produced. That results in an increase of both M_s and A_f temperatures in parallel.

The transformation temperatures do not change significantly during the successive 10 thermal cycles tested: A_f increased only 4 K and M_f increased 12 K. The DO3 parent phase order, in fact, generate a much lower density of dislocations than B2 ordered structure does in Ni-Ti SMAs, giving a relatively good stability during thermal cycling. Electrical resistivity reveals how M_s temperature is affected by precipitation and ordering upon aging the parent phase of Cu-Al-Ni SMAs. The SMAs with lower Ni content are susceptible to decomposition and

thus the precipitation from the β phase proceeds upon aging, as seen from the increase of electrical resistivity. For the 9 months aged sample, the ER increases linearly within the temperature range tested, showing that there is no phase transformation.

At 1123K solubilized sample there is a phase transformation that starts around 358K, the resistivity starts to decrease until 376K when the phase is finished and the resistivity has the tendency to increase. On cooling a reverse phase transformation takes place. For the specimens solubilized at 1173K and 1203K we observed phase transformation on heating and on cooling only that on 503 K. A decrease of resistivity appears between the first cycle and the other two (fig.5).

4.2. Structural constituents and morphologies

The XRD patterns performed at room temperature show the presence of α -CuAl, $Al_7Cu_{23}Ni$, Cu_9Al_4 , NiAl. All constituents detected in the 2 θ range from 10° to 90° belong to the ternary system Cu-Al-Ni.

The tensile test was performed at room temperature on 4 mm diameter extruded wires for aged state and machined samples for annealed and quenched state. In the case of the 9 months aged sample, the ultimate tensile stress (UTS) value is 579 MPa. This mechanical parameter increases significantly for the sample annealed at 1123 K (1238.4 MPa) due to the high mechanical strength of the martensitic phases. On the other hand figure 6 shows that the UTS decreases with increasing annealing temperature. This fact is explained by the coarse grained structure. In this alloy, high annealing temperatures give rise to an accentuated grain growth and, finally, brittleness. Mechanical failure of polycrystalline Cu-Al-Ni alloys is normally caused by high shear stress concentrations at grain boundaries resulting in a brittle intergranular cracking. High shear stress concentrations appear because of high elastic

anisotropy and consequently incompatible deformations of adjacent grains [11].

4.3. Mechanical Behavior

The fracture surface after tensile tests showed a considerable difference between the aged and the annealed/quenched samples (figure.7). The aged hot extruded samples with a large grain size, well defined contribute to the stress concentration. SEM micrographs present the same difference between aged and quenched alloy in microstructure after etching with FeCl_3 .

The aged structure is a distorted one. In the annealed/quenched states the samples usually transform into two typical martensites configuration, 18R (β_1) and 2H (γ_1) long period stacking order (LPSO). Figure 8 b confirm the coexistence of all types of martensite structures in the investigated samples.

The structure of 18R martensite variants is a monoclinic formed typical zig - zag morphology. These results are coherent with ones obtained from the XRD patterns. The 2H martensite appears as coarse variants [2].

5. Conclusions

Aged and annealed/quenched Cu-13 Al-4Ni (wt %) SMA samples were investigated by DSC, XRD, ER, tensile test, and SEM, techniques. The results are summarized as follows:

1. After solubilization followed by quenching the Cu-Al-Ni showed phase transformations that are typical of the Shape Memory Effect.
2. The investigated samples showed a good stability of the transformation temperatures after thermal cycling (up to 10 cycles).
3. During tensile testing, the fracture occurred very early, most probably due to the porosity of the material.
4. The electrical resistivity (thermal cycling) tests have shown that there is a

gradual structural evolution during heating up to 413K that results in a gradual decrease of the electrical resistivity.

5. SEM and XRD observations have shown simultaneous presence of two martensite types phases in the same specimen, 18R (β_1) and 2H (γ_1) LPSO.

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References

- [1]. R. Zengin, S. Ozgen, M. Ceylan, *Oxidation behavior and kinetic properties of shape memory CuAl_xNi_4 ($x=13.0$ and 13.5) alloys*, TCA 414 (2004) 79-84
- [2]. G. Logen, I. Anzel, A. Krizman, E. Unterwegwr, zB. Kosec, M. Bizjak, *Microstructure of rapidly solidified Cu-Al-Ni shape memory alloy ribbons*, Mater. Proc. Tech., 162/163 (2005) 220
- [3]. K.Sugimoto, *Jpn.Ist.Met.* 24 (1985) 45.
- [4]. U. Sari, I. Aksoy, *Electron microscopy study of 2H and 18R martensites in Cu-11.92 wt% Al- 3.78 wt%Ni shape memory alloy*, JALCOM- 13173, 2005
- [5]. V. Recarte, J.I. Perez-Landazabal, A. Ibarra, *High temperature β phase decomposition process in a Cu-Al-Ni shape memory alloy*, Mater. Sci.Eng. A378 (2004) 238
- [6]. R. Gastien, C.E. Corbellani, M. Sade, F.C. Lovey, *Thermal and pseudoelastic cycling Cu-14.1Al-4.2 Ni (wt%) single crystals*, acta Mat. 53 (2005), 1685
- [7]. W. Huang, *On the selection of shape memory alloys for actuators*, Mat and Design, 23 (2002), 11
- [8]. H. Morawiec, J. Lelatko, D. Stroz, M. Gila, *Structure and properties of melt-spun Cu-Al-Ni shape memory alloys*, Mat.Sci. Eng. A273 (1999) 708
- [9]. K. Otsuka, C.M. Wayman, *Shape memory Materials*, Cambridge University press, 1998
- [10]. J.I. Perez-Landazabal, V. Recarte M.L. No, J. San Juan, *Determination of the order in γ_1 phase in Cu-Al-Ni shape memory alloys*, Intermetallics 11(2003) 927-930
- [11]. J.Gui, W.H.Zon, D.Zang, *X-RAY diffraction study of the reverse martensitic transformation in Cu-Al-Ni-Ti shape memory alloy*.
- [12]. C.Tar R. Zeghin, *The effects of γ - irradiation on some physical properties of Cu13.5 wt%Al-4wt.%Ni shape memory alloy*
- [13]. J.Font, E.Cesari, J. Muntasell, J.Pons, *Thermomechanical cycling in Cu-Al-Ni-based melt-spun shape memory ribbons*

A POSSIBILITY TO DECREASE THE SINTERING TEMPERATURE OF CORUNDUM CERAMICS

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ABSTRACT

The ceramics consisting of more than 95 % Al_2O_3 is called corundum ceramics. The name comes from the name of the α -crystalline form of the aluminum oxide - corundum.

The basic technological process influencing the properties of this ceramic is the temperature and the duration of the sintering process. Sintering aids are used to improve sintering and to control grain size.

The possibility to use $CaTiO_3$ as sintering aid is investigated. This substance lowers the sintering temperature with more than $100^\circ C$ and at the same time the mechanical properties are preserved. The compressive strength is more than 2000 MPa and the flexural strength is more than 200 MPa.

KEYWORDS: alumina, sintering temperature, corundum, calcium titanate

1. Introduction

The ceramics consisting mainly of Al_2O_3 is called corundum ceramics after the name of the α -form of alumina - corundum. This ceramics must contain more than 95 % Al_2O_3 and the main crystalline phase has to be corundum [1]. The corundum ceramics possesses series of valuable properties and for this reason it is widely applied.

The sintering of the corundum ceramics is the basic technological process influencing its properties. The sintering is carried out at relatively high temperatures – $1600-1750^\circ C$. Corundum is difficult to sinter. The diffusion mechanism as well as the recrystallization process depends on temperature and time of exposure at high temperature, the grain size and crystalline condition of the raw material, the initial density of the sample [2]. The presence of

especially introduced additives shows particular influence on the sintering temperature and the grain size and from there on the properties of the final product.

2. Results and Discussion

The alumina ceramic must have fine grain polycrystalline structure consisting mainly of $\alpha-Al_2O_3$ (corundum). This microstructure is essential for the mechanical properties of the ceramic components. The increase of the grain size decreases the strength of the material. Sintering aids are used to improve sintering and to control grain size. The possibilities to use $CaTiO_3$ as sintering aid are investigated.

$CaTiO_3$ is added to Al_2O_3 micron powder in quantity 3, 6 and 9 weight %. Samples are fabricated by pressing and sintering at different temperatures. The

apparent density, the compressive and flexural strength in relation with the sintering temperature are determined.

It is interesting to evaluate whether high content (up to 10 %) of CaTiO_3 will lower considerably the sintering temperature and at the same time preserve the high mechanical

properties of the corundum ceramics. The mechanical properties versus the sintering temperature and the quantity of the sintering aid are studied. The average values of the compressive strength depending on the CaTiO_3 content and the temperature of the heat treatment are given in table 1

Table 1. Compressive strength in MPa of samples with different CaTiO_3 content and sintered at different temperatures

Sintering temperature, °C	CaTiO_3 3 wt %	CaTiO_3 6 wt %	CaTiO_3 9 wt %
1580	1932.4	906.5	475.0
1630	1456.6	743.5	392.1
1680	1134.1	557.6	321.1

An increase of the CaTiO_3 content and the sintering temperature is detrimental for the mechanical characteristics of the

composite material on Al_2O_3 basis (fig.1 and fig.2).

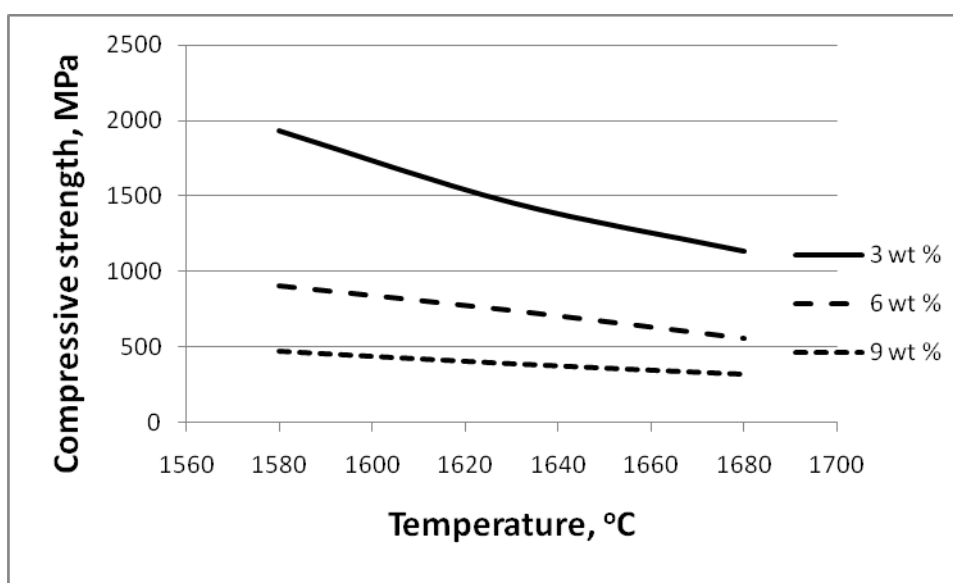


Fig.1. The compressive strength in relation with the sintering temperature

As per our previous research [3] part of the calcium titanate reacts with the alumina and is converted into $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$ – β -alumina. The higher the temperature and the CaTiO_3 content more β -alumina is obtained.

According to Buchvarov [2] the presence of β -alumina is not favourable for the mechanical characteristics of the ceramic on Al_2O_3 basis.

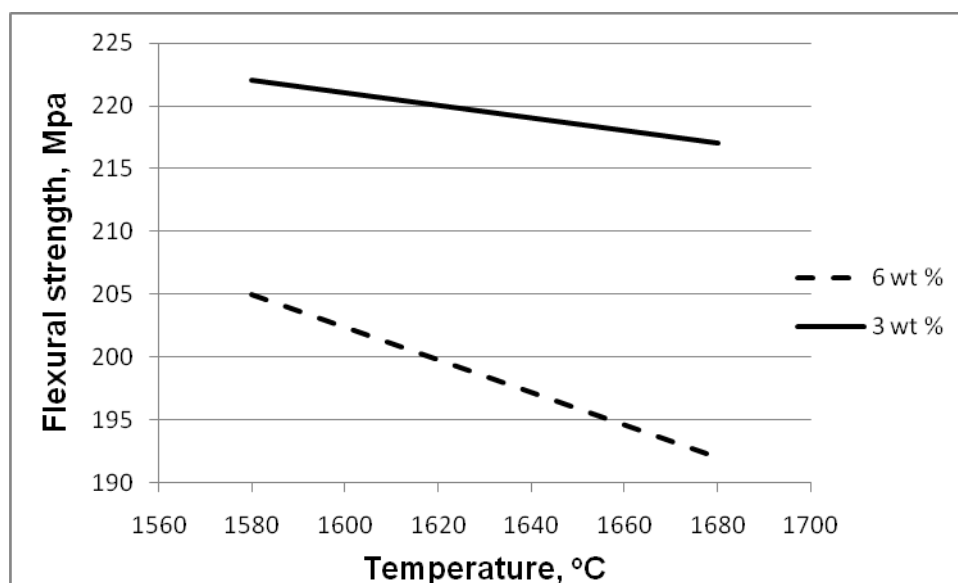


Fig.2. The flexural strength in relation with the sintering temperature

The maximum quantity of CaTiO_3 which has to be added as sintering aid is 3 %. We made a detailed study on the

sintering temperature (fig. 3). The maximum density of 3930 kg/m^3 is achieved with sintering temperature 1600°C .

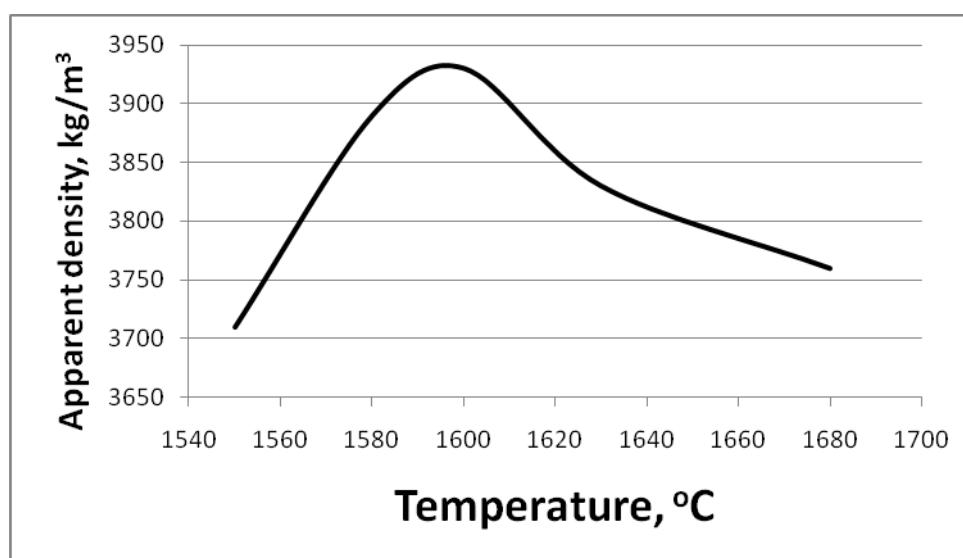


Fig.3. The apparent density in relation with the sintering temperature (CaTiO_3 – 3 wt.%)

When the compressive strength at different sintering temperatures is

determined a similar relation is achieved (fig. 4).

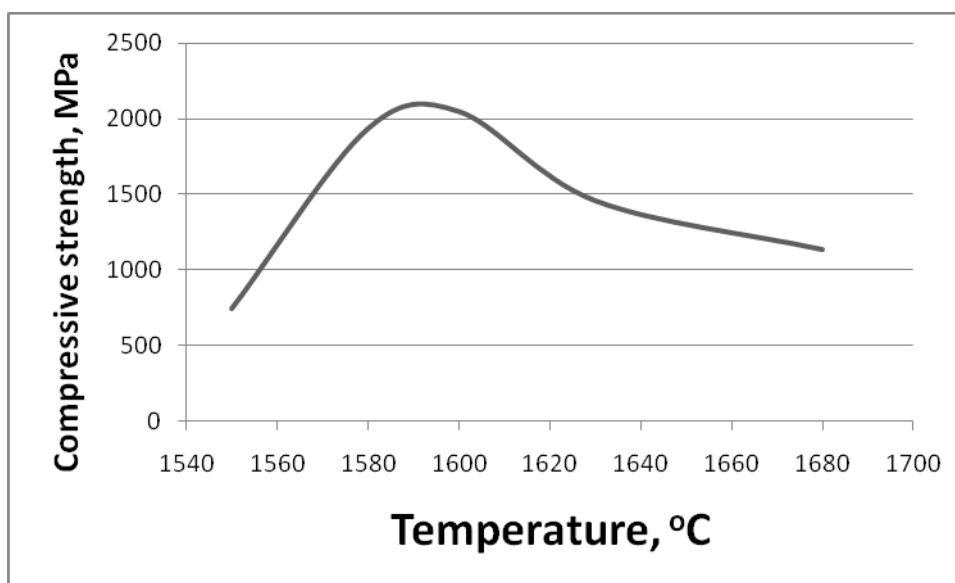


Fig.4. The compressive strength in relation with the sintering temperature
 ($\text{CaTiO}_3 - 3 \text{ wt.}\%$)

3. Conclusions

Calcium titanate can be used as sintering aid for ceramic on Al_2O_3 basis.

During the temperature treatment part of the CaTiO_3 reacts with the alumina and is converted into $\text{CaO} \cdot 6\text{Al}_2\text{O}_3 - \beta\text{-alumina}$. The presence of $\beta\text{-alumina}$ is not favourable for the mechanical characteristics of ceramic on Al_2O_3 basis. The content of CaTiO_3 must not exceed 3 weight % in alumina based ceramic.

The sintering temperature of ceramic on Al_2O_3 basis containing CaTiO_3 should not be higher than 1600°C . Samples with 3 wt. % CaTiO_3 as sintering aid and sintered at 1600°C possess compressive strength 2100 MPa and flexural strength 220 MPa.

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References

- [1]. Kingery W.D., H.K. Bowen, D.R. Uhlmann - Introduction to Ceramics, 2nd ed., NY, Wiley and Sons, 1976.
- [2]. Buchvarov S. - Ceramic Technology, Sofia, 2003, 865 (in Bulgarian).
- [3]. D. Teodossiev, V. Petkov, R. Valov, J. Georgiev, M. Selecka S. Stefanov - Composite Material on Al_2O_3 Basis Coated With Vitreous Carbon for Medical Needs, Powder Metallurgy Progress, 2011, (to be published)

RESEARCHES ON WASTE PROCESSING CELLULOSIC MATERIALS BY PYROLYSIS PROCESS

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In this paper experiments were performed on the processing laboratory by pyrolysis process of urban waste components (wood, paper, textiles). He used an own construction and installation were applied several operating modes in terms of temperature and plant maintenance time. The analysis of physical and chemical properties of products obtained was found that pyrolysis process can be an effective alternative treatment of urban waste to reduce their quantity and environmental protection.

KEYWORDS: pyrolysis process, urban waste, environment

1. Introduction

Currently, the global volume of waste increased. This is due, on the one hand, global population growth and increasing urbanization process and on the other hand, high rate of industrialization. They helped to increase quantity and diversification of types of solid waste, not only in developed countries but also in developing countries. Waste concentration is much higher in cities than in rural areas, urban population because of the tendency to consume more than the rural..Therefore, currently, there is the more acute the problem of waste reduction, recycling and recovery either part thereof, or by destruction, by various methods, those that can not be recovered.[1]

By recycling and recovery of the global aims of urban waste is currently working on their part as advanced (and therefore decrease the amount) and on the other hand, pollution reduction and environmental protection. By-products from these processes can be used in other industries. The largest amount of urban waste is organic in nature (biomass): wood products, plastics, paper, cardboard, textiles, food waste, rubber, leather, etc..

The main substances contained in municipal solid waste: cellulosic substances, albuminoidal and protein, fat, minerals, etc.

Processing methods of these types of waste are diverse: biological, mechanical, thermal, etc.. Among the most commonly used heating methods are drying, incineration, pyrolysis and co-incineration.

Pyrolysis is a thermal process that takes place in the absence of oxygen and consists of successive decomposition of the main constituents (cellulose, lignin, hemicellulose), which have different thermal stability.

The process of breaking and rearrangement of bonds in polymers (constituents) that form the biomass, leading to a large number of products, grouped into three fractions:

- *solid fractions* (coal) is the solid residue formed mostly of carbon;

- *fraction liquid* (bio-oil, tar, steam): a mixture of compounds, volatile pyrolysis temperature, which then condenses at ambient temperature. Are high molecular weight components;

- *fraction gas*: CO, CO₂, H₂, hydrocarbons. Are low molecular weight components.

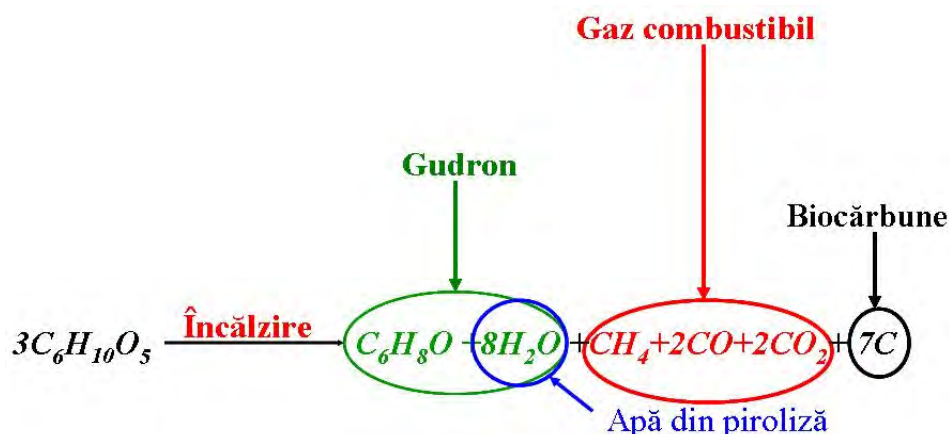


Fig.1 Cellulose pyrolysis

Considering that biomass has the basic component of cellulose, we can say that the pyrolysis (thermal decomposition) is governed by the following scheme (Figure 1) [2].

In terms of energy, pyrolysis reactions are endothermic and have a whole multiple effects:

- removal and transformation (neutralization) of waste and other waste, taking into account the environmental conditions
- reducing waste volume and weight to be treated
- obtaining liquid and gaseous fuels

Composition and quality of products from pyrolysis depend on the quality of processed waste, but also operating conditions and working facilities operating. With adequate facilities, some products can be separated and recovered completely as a fuel or raw material for chemical industry

Pyrolysis can be applied in several ways, depending on conditions: [3]

- low temperature pyrolysis (400 ... 600 ° C) and medium (600 ... 1000 ° C);
- high temperature pyrolysis (2000 ° C);
- pyrolysis in molten metal bath salts or;
- vacuum pyrolysis.

2. Materials used and method of working

To achieve the laboratory experiments were used as household waste sawdust,

paper packaging (cardboard) and yarns [4]. All these materials have approximately the same composition:

- Cellulose ($C_6H_{10}O_5$) x, the proportion of 40 ... 50%;
- Similar hemicellulose xylan ($C_5H_8O_4$) m, the proportion of 15 ... 25%;
- Lignin [$C_9 H_{10} .3 (OCH 3) 0.9$ to 1.7] n about. 20 ... 30% (characteristic of the wood - is found in stems, foliage and bark)
- Organic substances: polysaccharide, pentozani, hexozani, resins, tannins, dyes, waxes, alkaloids.

Optimal conditions for carrying out the pyrolysis process is necessary that the materials are composed of particles as fine, so they chose wood waste as sawdust, cardboard was cut into very fine strips and textile were chose cotton waste.

Experiments were conducted in the University "Dunarea de Jos" of Galati, Faculty of Metallurgy in the Laboratory, Materials Science and Environment and Department of Chemistry. To make pyrolysis technology has been established based on the following steps (Fig. 2).

To this end was made an installation consisting of a furnace automation, with forced bars in which to enter an air-tight enclosure for protection treatment. To completely remove the resulting gas, nitrogen was introduced on site that circulated throughout the deployment process at a pressure $1,2 \cdot 10^5$ Pa.

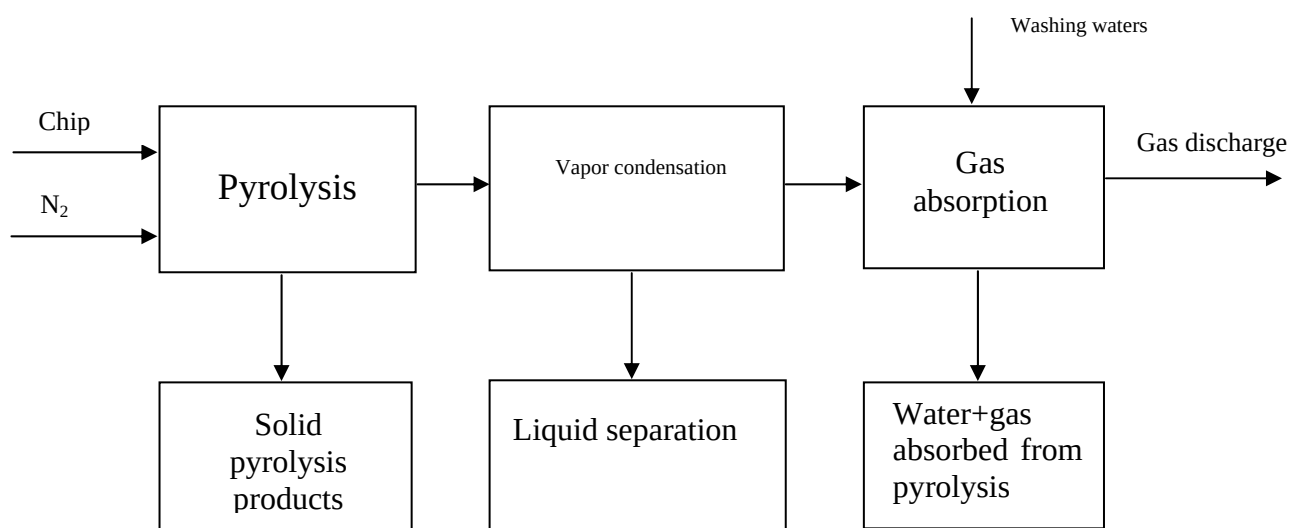


Fig.2. Scheme of the technological process of pyrolysis of wood waste

Gas capture two vessels were used for washing plastic (PET) which was introduced in distilled water and were linked with pyrolysis chamber. Any gas dissolved in

water, the liquid can be analyzed. The third plastic container was left empty, to capture the last amounts of gas were not dissolved in water. (Fig.3).



Fig.3 Scheme pyrolysis plant

Pyrolysis process was carried out by the following:

- *sample preparation.* Waste samples were dried in the oven, placed in two metal tanks and electronic weighing on a balance, then placed inside the oven work;
- *the process of pyrolysis.* We have chosen several temperatures: 600°C, 400°C, 300°C, 200°C.

Maintenance times: 4 hours, 1 hour, ½ hours. Nitrogen while working continuously circulated through the plant.

- *completion of the process.* Installation stops after the time established by the cooling furnace, nitrogen flows through the site still to be captured as fully as any gas.

- *sampling and laboratory analysis.*
Finally pyrolysis products are presented as three fractions:

- solid fractions consisting of small particles (wires) of coal with waste initially about the size and shape (fig. 4);



- liquid fraction, collected in a coil of silicone rubber, connected to the first tank of gas capture;

- gaseous fraction, dissolved in distilled water in containers. We used this method to determine the physical properties of gases results.



Fig.4 Solid fraction resulting from the pyrolysis
a - sawdust, b – paper

3. Experimental results

In the process of pyrolysis were analyzed resulting three fractions as follows:

Solid fraction. Coal obtained was weighed and compared with the initial sample in terms of mass, after which he

analyzed the chemical composition. In tables 1,2,3 are presented the main parameters of the process and table samples, initial and final mass loss after thermal processing.

The diagrams in Figure 5 is shown the variation of mass loss depending on process parameters and material evidence.

Table 1. Applied thermal regime and mass loss of samples analyzed Sawdust

Sample	Thermal regime		Solid mass fraction (g)		Weight loss (ΔG)	
	Temperature ($^{\circ}\text{C}$)	time (hours)	initial G_0	final G_1	(g)	%
B1	600	4	20	5.30	14.70	73.5
B2	600	1	20	6.40	13.60	68.0
B3	400	1	20	6.59	13.41	67.07
B4	300	1	20	8.10	11.90	59.5
B5	200	1/2	20	8.70	11.30	56.5

Table 2. Waste paper

Sample	Regime		Solid mass fraction (g)		Weight loss (ΔG)	
	Temperature ($^{\circ}\text{C}$)	Time (hours)	initial G_0	final G_1	(g)	(%)
H1	300	1	20	6.90	13.10	65.50
H2	300	1/2	20	7.49	12.51	62.55
H3	200	1	20	9.23	10.77	53.85
H4	200	1/2	20	11.17	8.83	44.15

Table 3. Textile waste

Sample	Thermal regime		Solid mass fraction(g)		Weight loss (ΔG)	
	Temperature ($^{\circ}\text{C}$)	time (hours)	initial G_0	final G_1	(g)	%
T1	600	1	20	3.95	16.05	80.25
T2	400	1	20	7.49	12.51	62.55
T3	300	1	20	9.07	10.93	54.65

ΔG mass loss is determined by the relationship: $\Delta G = G_0 - G_1$

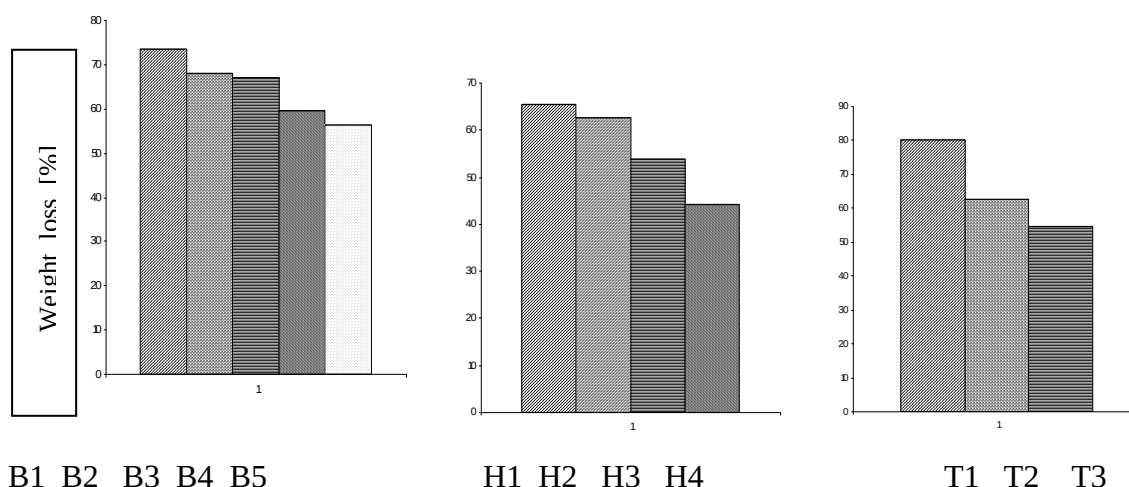


Fig.5. Mass loss resulting from pyrolysis

Mass loss increases with increasing temperature and working time is quite important even at low temperatures (200 ... 300 $^{\circ}\text{C}$). On a coal plant was analyzed LECO

result of pyrolysis of waste wood and cardboard. Efficiency shows the percentage of carbon recovery process and the possibilities of solid fraction (Table 4).

Table 4. Carbon and sulfur content of the samples analyzed

Material	Sample	Thermal regime		Carbon (%)	Sulf (%)
		Temperature ($^{\circ}\text{C}$)	Time (hours)		
Rumeguș	B4	300	1	73.24	0.30
Rumeguș	B5	200	1/2	71.90	0.32
Rumeguș	B6*	300	1	70.95	0.34
Carton	H1	300	1	57.33	0.18
Carton	H2	300	1/2	56.89	0.17
Carton	H3	200	1	53.44	0.18

*B6 sample was obtained by pyrolysis of wood waste in the absence of nitrogen.

Carbon content is high, so the thermal decomposition is advanced even at low temperatures. For identification of other

elements present in the solid fraction was used XRF spectrometer. The results are presented in Table 5.

Table 5. The content of the main elements present in the material pyrolysis

Proba	Zn	Fe	Mn	Cr	Ca	K
H1 (Carton)	31.61	353.93	41.91	386.01	15728.2	28552.15
B4 (Rumegus)	26.29	321.09	39.62	335.07	15310.34	27698.71
T3 (Textil)	442.91	362.89	-	396.46	12162.84	3033.41

Analyzed samples were subjected to the same work (temp = 300°C, time = 1 hour). Liquid fraction as a result of strong smelling tar, dark brown color and consistency of oil. Because very small amount obtained could not make a full analysis of this material.

Gas resulting from pyrolysis were dissolved in distilled water determining the

physicochemical properties of the resulting liquid, multifunctional analyzer with Consort C862.

At each sample were determined pH, electrical potential (V), conductivity (λ), resistivity (ρ) and total dissolved salts (TDS). The results are shown in Table 6.

Table 6. Physical properties of gases dissolved

Parametrul	Unități de măsură	Cod probă		
		Rumeguș (B4)	Carton (H1)	Textil (T3)
pH	upH	3.74	4.44	3.67
V	eV	164	116	185
λ	$\mu\text{S}/\text{cm}$	62.5	24.9	141
ρ	$\text{k}\Omega \cdot \text{cm}^{-1}$	15.99	47.5	7.09
TDS	mg/L	37.1	11.2	83.6

All liquid samples analyzed have low acid pH. Acidity of the samples is given by the content of organic acids and carbon dioxide, retained as a result of distilled water barbotage of the gas resulting from the pyrolysis process.

Liquid samples have variable conductivity, the highest values occurring in those from the textile waste. The total

content of dissolved salts recorded higher values throughout the textile waste. Gas fraction. Gas analysis was conducted for the pyrolysis of wood waste at a temperature of 300°C for one hour.

Gases were captured in two plastic containers no longer use distilled water. He used a combustion gas analyzer type MSI. Results are shown in Table 7.

Table 7. The composition of the pyrolysis gas fraction of wood waste

Recipientul	O ₂ (% vol)	SO ₂ (ppm)	NO (ppm)	CO (ppm)	CO ₂ (% vol)
1	10.8	281	509.5	853.6	9.8
2	19.4	35	412.3	543.8	1.5

The pyrolysis conditions applied resulted in a high content of NO and CO.

4. Conclusions

Research has led to the following observations:

- decomposition of organic matter by pyrolysis process was carried out in a simple

installation, with low consumption of energy;

- low temperature process was long and low;

- solid fractions remaining after pyrolysis is a small amount, ranging between 27 ...

56% of initial mass, according to the rules and working conditions

- coal result called "biological coal" has a high mineral content, which can do useful as fertilizer in agriculture.

- captured gases contain a high percentage of NO and CO. In an industrial gas plant output can be used as fuel in the pyrolysis process, thereby eliminating and carbon monoxide

From observations made during experiments it can be concluded that in an urban area, depending on how waste storage and processing possibilities, pyrolysis may be preferred to other waste treatment processes through the advantages presents:

- consumption of waste;

- the use of charcoal as a solid material for wastewater treatment, including those resulting from the pyrolysis;

- the possibility of energy recovery products;

- possibility of a wide variety of organic waste;

- low environmental impact.

References

[1]. **Ndiaye F.T.** *Pyrolyse de la biomasse en reacteur cyclone-recherche des conditions optimales de fonctionnement* – I.N.P. Lorraine, 2008

[2]. **Ion V. Ion-** *Energia biomasei – Energie nr.7(38) – 2006, p14-30*

[3]. **G.I.E. PROCEDIS** – *Pyrolyse – gazeification de dechets solides – Etude ADEME/ Procedis -2004*

[4]. **G.Finqueneisel** – *Les mecanismes primaires de pyrolyse de la biomasse- Universite de Metz - 2009*

STUDY ON CHARACTERIZATION AND SPA TOURISM POTENTIAL THE RESORT SARATA MONTEORU BUZAU COUNTY

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This paper presents an overview of the area Sarata-Monteoru and characterization in terms of tourism and spas. In the field investigations were samples of mineral water from several springs and therapeutic properties of sludge and laboratory testing of physical-chemical terms. It has the characteristics of rehabilitation and reintroduction in the tourism resort and spa nationally and internationally, as was its beginnings in the late nineteenth century and the beginning sec. XX.

KEYWORDS: tourism, resort, spa, mineral water

History

Sarata-Monteoru is a resort town located 20 km from Buzau, in a hilly valley between hills Istritei, crossed the river Sarat. Towards the end of the nineteenth century, the town and surrounding land were bought by the Greek Monteoru Gregory, who gave the name of the settlement after Monteoru massif located in the south of the mountains Siriu at the foot of which have an estate. Successfully exploit oil deposits in the area, establishing here the first oil mine in Europe.

In 1871 a distillery opens and oil, apply the most modern processing technologies, which provide not only an immense fortune, and even a real celebrity "beyond the borders of his country."

In 1885 established joint consists of the villages Monteoru yards, Sărata Nenciulesti (Bugheni) and bottom Sărății. In 1888 the arboretum building a house, a school and hall. It is said that the park was done in the style of English gardens, a paradise for that time (fig.1).



Fig.1. Sarata -Monteoru baths - Park

Also built a hospital with 20 beds for the poor, ensuring maintenance and annual rent. [1]

Knowing the therapeutic value of mineral springs in the area, locals used empirically, but certified by chemical analysis since 1884, Gregory Monteoru using German architect Edward Honzik, founded a resort from the more modern "en suite" of Europe, equipped with hotels, a beach, a casino and a family chapel. The inauguration takes place on 1 July 1895. Intended to build a tram line (decauville) until all of his high station in 1871 but died of septicemia in 1898.

The resort has its peak before World War II, was destroyed after the establishment of the communist regime and the confiscation of property. In the 1970s, the communist state began to make some small investments in new resort, completed after the regime fell, the other private initiatives in tourism, not to reaching the brilliance of the past.

Characterization of climatic spa resort of Sarata Monteoru

Climate

Sarata Monteoru resort benefits from a continental climate of the hill was defended by northwest winds of depression due to the shape of the relief. The average annual temperature is 10⁰C, the average during the month of January as the -2⁰C and 21⁰C in July. General characteristics of the climate is a factor Sarata Monteoru suitable for performing spa treatment in all seasons.

Station operating continuously since 1895, is recommended to treat rumatisme, those traumatic, peripheral neurological, gynecological, etc..

Mineral waters

Sarata Monteoru spa, mineral water have concentrated salt, sodium, iodine, bromine, calcium, magnesium, some sulfur, high concentration (188.5g/l), sulfide mineral mud, all derived from groundwater,

especially recommended the cure external and internal treatment less. Water temperature is 8...16⁰C are classified as water athermic.

Some of the sources of those areas are characterized by the presence of hydrogen sulphide or sulphate. Shallow water infiltration of dissolved gypsum rocks, which are partially reduced, in turn, under the action of hydrocarbons. The 19 natural springs, mostly undeveloped, are occasionally used by locals or those who come to clean the spa. The resort, although rich in mineral springs, has little concrete pools or wells capture the stone (mineral reserves estimated at 2.5 million m³) [2].

Research on the characterization of mineral waters and mud of the resort Sarata Monteoru

Although the resort has a large number of mineral springs, now the only resource that can be used according to regulations in force is extracted from deep salt water through wells. So far, this individual water baths it with exceptional effects on a wide enough range of musculoskeletal disorders, circulatory disorders, or peripheral and central neurological diseases. Water rich in sodium chloride, bromine and iodine salts have very strong effects in these diseases, especially combined with electrotherapy and physical therapy procedures. Used as aerosol inhalations, salt water has exceptional effects in treating respiratory disease, chronic bronchitis, and certain forms of asthma. Saltwater aerosol procedures have a beneficial effect for allergic diseases with respiratory symptoms.

One of the few sources arranged captured and used for internal treatment (stomach). Water-sodium chloride stimulates digestion, prevents bloating, improve or cure gastric and duodenal ulcer, gastritis, gall stones, enterocolitis, pancreatitis, acute indigestion. It is a source of powerful

effects, which should be used only under medical guidance as it may have unpleasant effects in certain conditions.

A source is much appreciated by locals "the source to the eye" with salt water but with lower salinity than water for baths. According to local views, but others who have used this water, it would have strong anti-inflammatory and anti-infective eye, is beneficial in treating conjunctivitis, blefarites and as an aid to eye infections. According to the people who used it, this water may also have effects to prevent aging and degeneration of the eye tissue. Spring is arranged and was not ever considered by specialists. Many springs are located in the woods, including local houses, without signs, their healing properties are known only approximate information, scientifically unfounded. Number of sources is not known precisely, the first documentary attestation

dates from 1837. The first tests were conducted in 1890 in Paris at his request after the doctor's Monteoru Guyenot Gr. Analysing the water compared to Sarata Monteoru with foreign waters concluded that these sources are superior to those of Hall (Upper Austria), Kreuznach (Germany), La Motte (France).

The first chemical analysis made in Romania are published in "Guide to spas in Romania" in 1896. A new series of chemical tests were performed in 1952: "Spring ferruginous" on top of mud and "Spring No.6." (Table 1, 2)

- The analysis made that water is iodides, chlorides, sodium, concentrated. (Table 1) - Water chloride, sulphate, bicarbonate sodium, calcium, magnesium. (Table 2) Indications: can be used in digestive diseases and hepato-biliary diseases and in the airways.

Table 1. Ferruginous source analysis

Content at 1 L water		1	2	3	4	5
		mg	m.moli	m.echiv.	mg %	m.echiv %
A N I O N I	Clor	52394.8	1477.990	1477.990	60.811	99.632
	Brom	25	0.312	0.312	0.029	0.022
	Iod	18.1	0.142	0.142	0.021	0.008
	Bicarbonic	305	4.999	4.999	0.354	0.338
						100.000
C A T I O N I	Sodium÷potasiu calculated as sodium	30103.5	1308.850	1308.850	34.938	88.230
	Amoniu	72.7	4.021	4.021	0.084	0.272
	Calciu	2952.3	73.660	147.320	3.426	9.930
	Magneziu	276.8	11.381	22.762	0.321	1.534
	Fier	13.7	0.245	0.490	0.016	0.034
	Mineralizare	86161.9	2881.600	2966.886	100.000	100.000

Table 2. No.6 source analysis

Content at 1 L water		1	2	3 4 5		
		mg	m.moli	m.echiv.	mg. %	m.echiv. %
A N I O N I	Clor	2964.1	83.597	83.597	42.820	73.674
	Brom	3.4	0.042	0.042	0.049	0.038
	Iod	0.5	0.004	0.004	0.007	0.004
	Nitric	9.4	0.151	0.151	0.136	0.136
	Nitros	urme				
	Sulfuric	853.2	0.001	17.763	12.326	16.080
	Bicarbonic	543.7	8.912	8.912	7.854	8.068
						100.000
C A T I O N I	Sodiu	1786.6	77.690	77.690	25.810	70.328
	Potasiu	40.3	1.030	1.030	0.582	0.932
	Amoniu	abs.				
	Litiu	0.14	0.020	0.020	0.002	0.018
	Calciu	511.2	12.779	25.558	7.385	23.136
	Magneziu	74	3.043	6.086	1.069	3.310
	Fier	2.4	0.042	0.085	0.034	0.076
	Mangan	urme				
	Aluminiu	urme				
		6788.94	196.191	220.938		100.000
	Acid Metasilicic	20.6	0.263		0.298	
	Acid Metaboric	81.3	1.855		1.174	
	Amidogen	Urme				
		6890.84	198.309			
	CO ₂	31.4	0.713		0.454	
Mineralizare		6922.24	199.022		100.000	

The following chemical tests were conducted in 2005 on demand for SC MONTERU S.A. by National Institute of Rehabilitation, Physical Medicine and Balneoclimatology Bucharest. It was considered a single source, the salt water from the hill Murătoarea. (Table 3) Water

analysis can be used in external cure the following diseases: state preartrozice (prophylactic treatment in high risk professions) degenerative rheumatism, rheumatism abarticular peripheral nervous system disorders, musculo-articular sequelae after trauma.

Table 3. Analysis of salty spring

		1 l of water content results				
		mg	m.moli	m.echiv.	mg %	m.echiv. %
ANIONI	Clor	134 736.6	3800	3800	61.060	99.871
	Brom	26.9	0.337	0.337	0.226	0.173
	Iod	18.4	0.145	0.145	0.008	0.004
	Nitric	3.70	0.060	0.060	0.02	0.002
	Nitros	Nedoz.				
	Sulfuric	36.6	0.381	0.762	0.017	0.020
	Bicarbonic	219.6	3.599	3.599	0.100	0.095
	Carbonic					
	Fosforic	abs.				
	Arsenic	abs.				
				3804.902		100.165
CATIONI	Sodiu	76071.5	3309.038	3309.038	34.479	86.958
	Potasiu	718	18.362	18.362	0.325	0.483
	Litiu					
	Amoniu	5.2	0.288	0.288	0.002	0.008
	Calciu	7156.6	178.558	357.116	3.244	9.386
	Magneziu	1458.5	59.971	119.942	0.661	3.152
	Fier	8.7	0.078	0.156	0.004	0.004
	Mangan	-	-	-	-	-
	Cobalt	-	-	-	-	-
	Nichel	-	-	-	-	-
	Cupru	-	-	-	-	-
	Zinc	-	-	-	-	-
	Vanadiu	-	-	-	--	-
	Molibden	-	-	-	-	-
	Crom	-	-	-	-	-
	Aluminiu	-	-	-	-	-
				3804.902		100
	Acid Metasilicic	4.7	0.060		0.002	
	Acid Metatitanic	-	-	-	-	-
	Acid Metaboric	104.2	3.746		0.074	
	Amidogen	1.8	0.112		0.001	
	Subst. Organice	2.3	0.144		0.001	
		220633.3	7374.879	7609.805	100.214	
	Dioxid de Carbon	-	-	-	-	-
	Hidrogen Sulfurat	3.5	0.103			
	MINERALIZARE	220633.3	7374.879		100.214	

In a study at the Faculty of Metallurgy, Materials Science and Environment, in 2011 we looked at several mineral waters and mud springs resort Sarata

Monteoru. Analyses were conducted in laboratories of faculty and Environment Agency Galati spectrophotometric methods. The results are presented in Table 4.

Table 4. Results analysis

Analyze indicators	U.M.				
		Drinking water	Izvorul "pentru ochi"	Izvorul sărat	Izvorul feruginos
0	1	2	3	4	5
pH	upH	7.35	7.46	6.16	6.94
Cloruri (Cl ⁻)	mg/l	66	2265	54368	49107
Sulfați (SO ₄ ²⁻)	mg/l	106	0	0	0
Amoniu (NH ₄ ⁺)	mg/l	0.064	0.361	6.70	3.72
Fier	mg/l	0.274	4.24	6.53	6.10
Zinc	mg/l	0.027	0.675	9.05	15.4
Conductivitate	μS/cm	1561	9390	124 300	122 200
Calciu	mg/l	48	64	280	240
Magneziu	mg/l	38.8	43.7	72.9	24.3
Produse petroliere	mg/l	-	0.6195	-	-

Sludge from Sarata Monteoru

Sludge treatment is found in some small Balti, undeveloped, wooded slopes of one of the surrounding resort. The place is called "Peak sludge". Mud is a mineral consisting of clay, salt water, the mix and quantity of oil. It is a resource that has never been scientifically researched, but the locals and people from neighboring villages or even use it permanently Buzau. Characteristic is that, after treatment, sludge is not removed from the skin than salt water source nearby. This treatment effects in a wide range of diseases, from chronic rheumatism and degenerative lombosciatica, muscle aches rebel sequelae after fractures, sprains, and chronic sinusitis and rhinitis.

They took samples of the sludge and were analyzed in terms of mineralogical. For a comparative study were sampled and the

mud from Salt Lake - Braila, performed the same analysis. The results are presented in Table 5. It appears that the two are very similar sludge in terms of mineral content.

Table 9. Results mud Sarata Monteoru

Chemical element	Sludge origin	
	Sărata – Monteoru (ppm)	Lacu Sărat (ppm)
Titan	3494.25	3907.75
Mangan	224.5	401.25
Fier	26511.5	17373.25
Zinc	58.75	68.5
Plumb	17.66	24.5
Rubidiu	120.25	59.25
Strontiu	621	315.75
Zirconiu	116	327.75

Tourist attractions

Sarata Monteoru resort enjoys near tourist attractions of great value, including virtually all aspects: geographical, geological, historical, art, architecture, and a priceless treasure of Popular Traditions:

- Salt mine oil from Monteoru is unique in Europe and second in the world. It is situated at a distance of about 2 km from the resort and is only in operation in the world.

- West of the village on the banks Sărății were discovered dating from Neolithic settlements and cemeteries. Here Citadel Hill were discovered traces of a

culture called Carpathian Culture Monteoru suggestive.

- About 50 km from the resort is Vulcanii Noroiosi, a geological nature reserve type, on an area of 30 ha. Like volcanic cones forms were born of the earth due to gas eruptions giving rise to the surface mud and water, an extremely rare phenomenon on Earth.

- 82 km away from Colti Amber Museum, the only collection of amber from Romania, one of the world's most beautiful and unique due to the variety of colors and shades of the specimens exposed: from black to bright yellow opaque.



Fig.2 Vulcanii Noroiosi



Fig.3. Amber Museum in Colti



- 25 km is Ciolanu Monastery, one of the monastic settlement of Buzau county

sec.al documented since XVI. Here there is a museum where you can admire icons, some

painted by George Tattarescu by 1886, religious objects and religious vestments

- Traditional folk festivals and fairs taking place in almost every town in the county, in all seasons.



Fig.4. Ciolanu Monastery

Conclusions

- Sarata Monteoru resort area has a great tourism potential, covering most branches of existing tourism: health tourism, cultural, mountain, etc. ecumenical. Through proper management could offer tourists a wide range of possibilities for treatment, rest and entertainment.

- The resort has all the features Sarata Monteoru needed to develop a natural spa center of national and even international, as it was in the past.

- The first aspect is the need for infrastructure according to European standards - To develop the resort requires a large study conducted by specialized institutions on the characterization of mineral waters and mud in the area and their therapeutic properties.

- A European resort requires conducting a systematic project which includes restoring the historical area and highlighting the exceptional

- Near the monastery is the Magura sculpture camp.



Fig. 5. Magura sculpture camp

personality of Gr Monteoru, imposing a traditional architectural style, according to the area, stopping deforestation and chaotic construction occurring in increasing numbers .

- Rehabilitation of sewerage network and water supply and adequate waste management, issues which are currently totally ignored.

- A well-designed advertising program for the enhancement of the area and description of all targets of interest for tourists

- The development of spa treatment.

References

- [1]. **Marin M.** *Luminile cetatuiei* – Ed. ALPHA MDN – Buzău 2010
- [2]. **Marin M, Marin I.** – *La Poalele Istritei* – Ed. VEGA – Buzău 2008