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TRIBOCORROSION – INSIGHT INTO MATERIAL DEGRADATION IN SPECIFIC ENVIRONMENTS

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ABSTRACT

Tribocorrosion is an irreversible surface degradation mechanism of a metallic and/or non-metallic material as a result of its physicochemical and mechanical interactions during relative motion (friction, sliding, impact, abrasion, erosion) in corrosive media. It encompasses synergistic effects between mechanical wear and chemical / electrochemical processes which interact with each other. Tribocorrosion processes lead to uneconomical material loss as well as to the decreasing of the following characteristics: durability, reliability, safety, performance, energy efficiency, pollution and health. Recent activity in tribocorrosion research aims at addressing the need to select or design new surfaces for future equipment as well as minimizing the operating costs and extending the life of existing machinery and medical devices. The work presents an overview and some experimental results from tribocorrosion tests of biomaterials and nanocomposite coatings in specific environments from physiological solutions to industrial environments.

KEYWORDS: corrosion, tribocorrosion, nanocomposite coatings, biomaterials, material degradation, specific environments

1. Introduction

Tribocorrosion is regarded as the science of surface transformations as a result of the chemical reactions and mechanical disturbances that occur between the elements of a tribo-system exposed to a corrosive environment.

In the recent years, ***tribocorrosion*** a, research activity that combines the science under focus corrosion and the science of tribology, has been focused by both engineers and scientists from different research areas, contributing to the development of a new topic of research beyond conventional ones.

Tribocorrosion involves mechanical and chemical/electrochemical interactions between surfaces in relative motion between one another, and in the presence of a corrosive environment. The tribocorrosion process is common in many areas where it can cause premature destruction of devices, equipments and even vehicles. It is also found in living systems in case of metal implants in the human body such as artificial joints, orthopedic plates and screws and dental implants. Therefore all of this complex tribocorrosion process is studied and researched in terms of two broad categories of applications [1-10]:

- tribocorrosion in industrial systems;
- tribocorrosion in living systems.

Tribocorrosion applications

The study on tribocorrosion evolves to be an active research area, due to its wide existence in a variety of industries, such as mining, oil, automotive, food, nuclear, offshore marine and biomedical, Figure 1 (a-f). Tribocorrosion is a surface degradation process resulting from simultaneous tribological and electrochemical actions in a corrosive environment [11-14].

The tribocorrosion process cannot be simply predicted from the knowledge of isolated wear and corrosion behaviors of the material, since synergistic effects of these two processes can accelerate the mass loss in the tribocorrosion test. Tribocorrosion can cause material degradation, and affects the friction, wear and lubrication behavior of the tested materials.

In the biomedical applications the tribocorrosion process is increasingly interesting to researchers and is studied under two major aspects: orthopaedic science and surgery and dental implants.

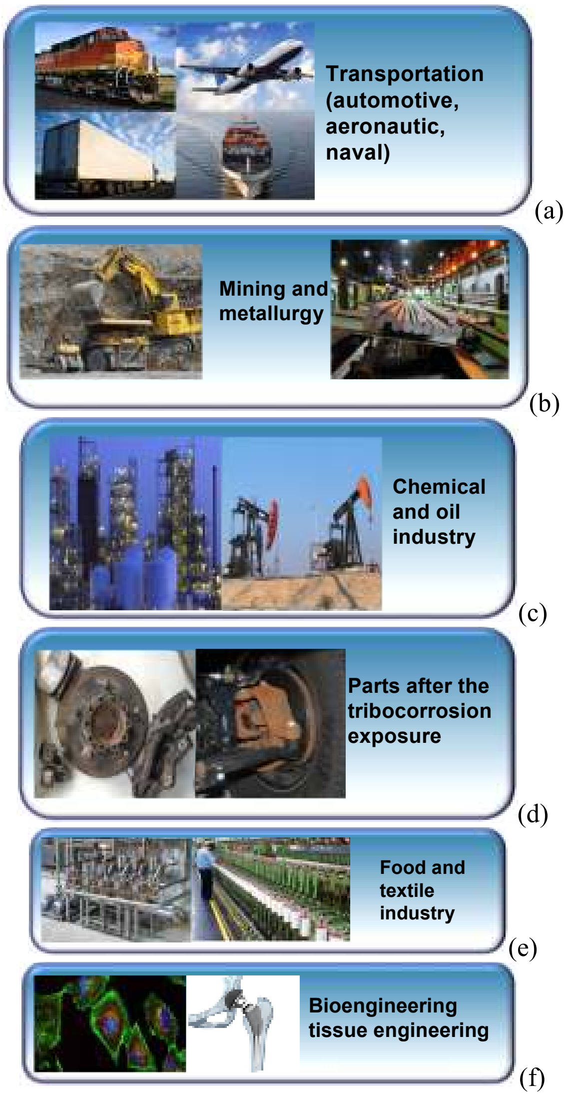


***Fig. 1**. The variety of tribocorrosion process applications and needs of knowledge: (a) - transport; (b) - mining and metallurgy; (c) - chemical and oil industry; (d) - different parts of mechanisms in moving conditions under corrosive environments; (e) - food and textile industry; (f) - bioengineering and biomaterials*

Orthopaedic science and surgery. The tribological aspects of bone implants, particularly hip and knee joints are addressed by many researchers to increase their lifetime and to avoid that patients undergo too often a repair surgery (recovery). However, as the tribological aspects in such implants are influenced by human body fluids at the interface (Periprosthetic fluids), the complex tribocorrosion process must be taken into account. The tribocorrosion process can occur in hip joint implants and many authors already stress the importance of better understanding the electrochemical behavior of metallic implants after mechanical destruction and surface destabilization and the protective passive film stability in the presence of simulated body physiological solutions [1].

Dental implants are another area where tribocorrosion processes have direct applications. In fact, each mastication or biting process is a tribocorrosive cycle, friction taking place between teeth and food particles in the presence of liquid called saliva. The behavior of materials used is strongly influenced by the solutions pH and acidification improves the electrochemical response of the material. Evolution of the material repassivation is strongly influenced by the nature of the electrolyte [1].

The tribocorrosion processes are still poorly understood and explained, the literature being still quite poorly represented. Investigation of the tribocorrosion processes with industrial and biomedical applications involve a multidisciplinary approach to know and understand a system composed of a surface of a material, an environment (electrolyte, solution, human fluid) and a mechanical contact [1].

Integration of researchers from several disciplines such as materials science, mechanical engineering, electrochemistry/chemistry, tribology, biology and medicine may lead in the future to better knowledge and interpretation results.

The ***tribocorrosion*** process can be characterized by its synergy effects resulting from the combination of mechanical and environmental effects, Figure 2.

This synergism leads to degradation, and thus to a loss of material, which is often much greater than the one which we would expect by simply summing the degradation of the two processes separately.

$$W_T \neq W_E + W_M$$

Where: W_t – total volume of the lost material; W_E – volume of material lost by electrochemical corrosion and W_{M-} volume of material lost because of mechanical wear.

There is a synergetic interaction between friction and corrosion. Friction induces tension in materials and plastic deformation, residual stress and in a number of materials can even cause structural modifications.

Also, friction induces local destruction of the layer formed by material surface interaction with the environment. In general, the adsorbed layers are present on surfaces. Passive layers or corrosion products may also be present on surfaces. On the passivable materials, a thin (passive) layer protects material against corrosion. As a result, the reactivity of the surface is deeply modified by the friction on the contact surface and thus it modifies completely the kinetics of corrosion and passivation. On the other hand, corrosion, or electrochemical reactions that occur on the material surface, can strongly influence the tribological conditions and/or mechanical wear.

The surface composition is modified by electrochemical reactions and particularly by corrosion, as a result, the mechanical properties of the surface change too, along with the resistance to mechanical wear.

Fig. 2. *Synergy of friction and corrosion processes occurring simultaneously on the surface of a material*

Corrosion by-products may contribute to the formation of a third body in the process of degradation. They may also lead to changes in the composition and properties of lubricants. Finally corrosion affects geometric characteristics and surface roughness. Consequently the action of corrosion on a tribo-surface can substantially alter the friction coefficient, and the kinetics and mechanism of wear.

First tribologist 2400 B.C.

Tracing back the history, we may find that the understanding of the role of friction in man-made machine certainly goes back to the ancient Egyptians (ca. 2500 BC). Overcoming friction in moving large pieces of stones and statues must have been a great challenge for them.

Some carvings and images of that time tell that the use of water might have given some reduction in the friction and thus less work for the slaves who had to carry out this monumental task of building the Pyramids, Figure 3 (a, b). Also, there is a clear indication of the use of lubricated wooden planks to reduce contact area in moving very large pieces of stones or statues. A situation much closer to that of today's time was faced in the case of the lubrication of the chariot wheel hubs, for war or other usages. Around 1500 BC, the art of chariot building was quite advanced in Egypt and the use of leather and animal fats to lubricate the wheel hub was generally practiced [15].

A more famous Tribologist - 500 years ago or another Leonardo da Vinci revelation?

Modern tribology began some 500 years ago, when Leonardo da Vinci deduced the laws governing the motion of a rectangular block sliding over a planar surface [16, 17]. Leonardo da Vinci (1452-1519) can be named as the father of modern tribology.

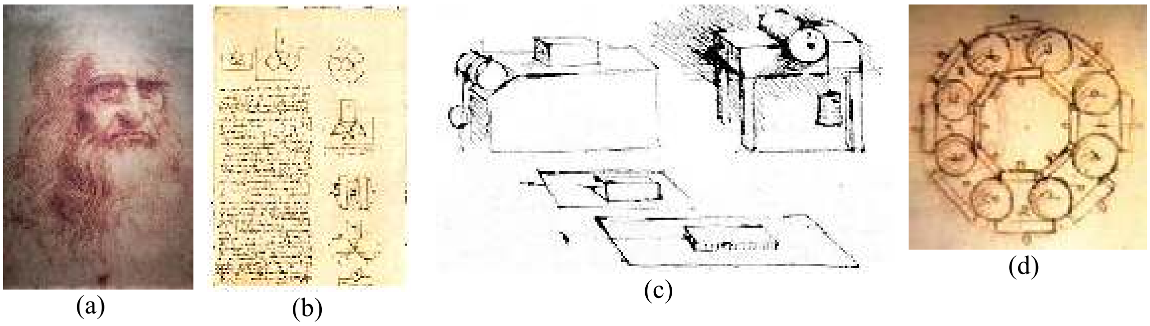
(a)

(b)

Fig. 3. *Indication of the use of tribology in ancient Egypt: (a) - Transporting the statue of Ti – from a tomb at Saqqara, Egypt; (b) - The first recorded tribologist – pouring lubricant (water or oil) in front of the sledge in the transport of the statue of Ti*

He studied an incredible manifold of tribological subtopics such as: friction, wear, bearing materials, plain bearings, lubrication systems, gears, screw-jacks, and rolling-element bearings. 150 years before *Amontons' Laws of Friction* were introduced, he had already recorded them in his manuscripts. Hidden or lost for centuries, Leonardo da Vinci's manuscripts were read in Spain a quarter of a millennium later [16, 17]. In Figure 4 there are presented some aspects of tribological studies from his manuscripts.

Leonardo da Vinci introduced the first concept of friction. He found the dependence of friction on load and the independence of geometrical contact area.



(a) (b) (c) (d)

Fig. 4. *Leonardo da Vinci's Studies of Friction from writings and sketching in the Codex Atlanticus, the Arundel MSS. 263 and the Codex Madrid discovered as recently as 1967 confirm his acute recognition and understanding of many basic features of tribology: (a) Leonardo da Vinci; (b) Ball Test Geometry; (c) - Sled Friction Test Geometry; (d) Leonardo's Ball Bearing with Cage*

Nanotribology

Since the 1990s, new areas of tribology have emerged, including the nanotribology, biotribology, and green tribology. These interdisciplinary areas study friction, wear and lubrication at the nanoscale (including the Atomic force microscopy and micro/nano electromechanical systems, MEMS/NEMS), in biomedical applications (e.g., human joint prosthetics, dental materials), and ecological aspects of friction, lubrication and wear (tribology of clean energy sources, green lubricants, biomimetic tribology).

Micro/nanotribology as a field is concerned with experimental and theoretical investigations of processes ranging from atomic and molecular scales to the microscale, occurring during adhesion, friction, wear, and thin-film lubrication at sliding surfaces [18-20].

This involves determination of the chemical, physical and mechanical properties of the surfaces undergoing relative motion at length scales of the order of nanometers. Interaction between rubbing surfaces occurs at asperities [roughness of surfaces] at which the local pressure and temperatures can be very high.

These conditions can lead to formation of tribochemical films with the unusual properties necessary for efficient wear protection. The nanomechanical properties of these films are being investigated by interfacial force microscopy (IFM) which is capable of determining the elastic constants and unelastic behavior of the films in boundary layer lubrication [18-20].

The potential for nanotechnology to transform civilization as we know it is breathtaking and the nanomechanical systems of the future will all require new atomic lubrication schemes to overcome the debilitating effects of friction. In order for this impending revolution to be fully realized, we need a fundamental understanding of friction and corrosion at the atomic to meso-scale.

Electrodeposition, nanocomposite coatings (layers) and tribocorrosion systems

Electrodeposition of new and advanced nanocomposite coatings is a process of low energy consumption, and therefore very convenient for the surface modification of various types. Published research works in tribocorrosion (wear - corrosion) behaviour of electrodepositd nanocomposite coatings are also in the attention of our researchers starting from 2001. One example is the starting work dealing with electrodeposition and characterisation of Ni-SiC nanocomposite coatings, which since its publication (2001) has generated over 186 citations in ISI international journals [21, 22].

Tribocorrosion process and damage effects

As it is reflected in Figure 5, corrosion ***leads to***: material loss, reduced reliability, reduced durability, reduced energy efficiency, reduced safety performance, increased health hazards, increased pollution, etc.

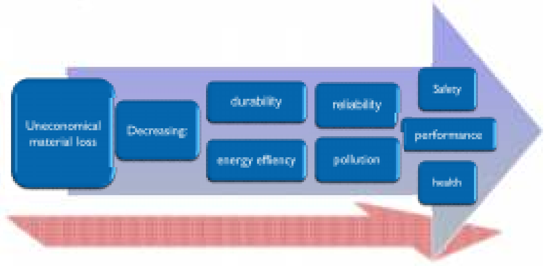


Fig. 5. *Damage effects of tribocorrosion processes*

2. Experimental set-up for tribocorrosion study

Electrochemical Cell

Uni-directional or bidirectional pin-on-disk contact geometry can be used and an electrochemical cell connected to a tribometer. Schematic set-ups for tribocorrosion studies are given in Figure 6.

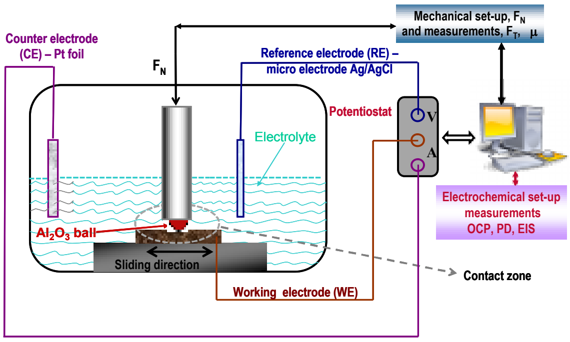


Fig. 6. *Description of the pin-on-disc set-up used to study the tribocorrosion behavior of materials and coating in aqueous solution: the electrochemical cell connected to potentiostat reference electrode (RE), counter electrode (CE), working electrode (WE) is the sample with the material or coating on the top of a cylinder or a plate, the mechanical set-up with counterbody (pin), made by corundum (Al_2O_3), wear track on the surface of the sample. The experiment is controlled by PC for imposed mechanical - electrochemical parameters and mechanical - electrochemical data*

The counter body (pin) is usually a hard ceramic like alumina (Al_2O_3) or zirconia (ZrO_2) cylinder (7 mm in diameter), mounted vertically on a rotating head, above the sample. The lower spherical end (radius = 100 mm) of the pin is then applied against the material surface (disc) with an adjustable normal force, correlated with the real application. When rotation is applied, the end of the pin draws a circular wear track (16 mm in diameter) on the working surface (for the uni-directional contact geometry) or a wear track with an amplitude of about 200 µm (for bi-directional contact geometry).

In – situ electrochemical measurements

In-situ applied electrochemical methods are: the open circuit potential measurements (OCP), the potentiodynamic polarization measurements (PD), the potential step from active to passive state and the electrochemical impedance spectroscopy (EIS).

Open circuit potential measurements

The measurement of open circuit potential gives information on the electrochemical state of a material, for example active or passive state in the case of passivable materials. However, open circuit potential measurements provide limited information on the kinetics of surface reactions. The open circuit potential recorded during uni-directional pin-on-disk sliding tests, in which the disk is the material under investigation, is a mixed potential reflecting the combined state of the unworn disk material and the material in the wear track. One must be aware that a galvanic coupling between worn and unworn parts on the disc surface may take place. The measured open circuit potential is an average value depending on current density distribution over the disk surface.

In - situ mechanical measurements

During the sliding tests, the normal force, tangential force, coefficient of friction, number of cycles, displacement amplitude as well as the open circuit potential are recorded.

Ex-situ wear track investigations

All samples with wear track can be examined ex-situ by SEM and high surface microtopography to evaluate the damages provoked and to estimate the mass, track depth or volume loss.

3. Experimental results for Ni/nano-WC layers used in industrial applications

Working on developing environmentally friendly materials with high corrosion and wear resistance by electrodeposited coatings were obtained ***Ni/nano-WC layers*** on 304L steel support. In this way it could be offered to the industry improved materials for longer and more efficient use in the cooling system of the nuclear power plants.

The Ni/WC nanocomposite coatings obtained by electro-codeposition of WC nanoparticles (60 nm mean diameter) with nickel from a dispersing nickel plating bath were characterized comparatively with pure nickel coatings for tribocorrosion behaviour.

Reciprocating sliding wear tests (as in the set-up presented in Figure 6) were performed in solution containing LiOH and H_3BO_3 on the sample sliding against corundum balls (10 mm diameter) for 10000 cycles. Al_2O_3 ball was selected as a counter body due to its high wear resistance, high chemical inertness and high electrical resistance. Tests were done at normal load of 5 N displacement amplitude of 200µm and the sliding frequencies of 1 Hz.

The coefficients of friction performed during wear tests in wet conditions is shown in Figure 7. During friction in the wet environment the coefficient of friction oscillates between values. As an average it was appreciated 0.20 for Ni/nano-WC and 0.37 in the case of pure Ni at the normal applied force of 5N (Figure 7).

The open circuit potential (OCP) data recorded on the Ni/nano-WC and pure Ni coatings before, during and after fretting tests in the solution, are shown in Figure 8. The sliding tests were done at the normal forces of 5 N (Fig. 8), at 1 Hz fretting frequency with displacement amplitude of 200 µm, for 10000 cycles.

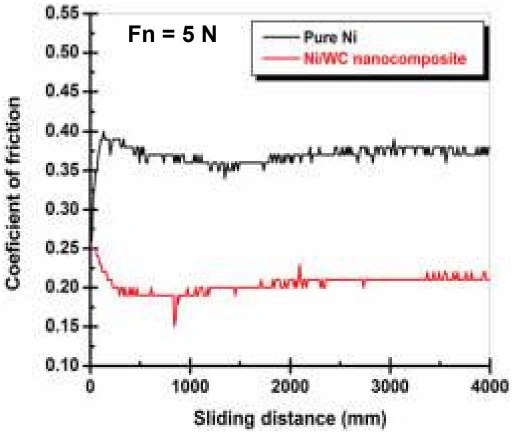


Fig. 7. *Evolution of the friction coefficient of Ni/nano-WC composite and pure Ni coatings during fretting wear tests performed in wet conditions (solution with LiOH and H_3BO_3) at 1 Hz, 200 µm, 10000 cycles for the normal force of 5 N [L. Benea and group - unbublished work]*

In the time interval preceding the starting of corrosion-wear fretting, a large increase of the open circuit potential for both Ni/nano-WC composite and pure Ni coatings is noticed. It can be observed also that before the start of the sliding tests, the potential of the samples is quite stable. Also it should be mentioned that the potential measured before sliding tests of Ni/nano-WC nanocomposite coatings is more ennobled as compared to pure Ni coatings, thus leading to a significant increase of anticorrosion effect. This means that an ennoblement of the coating surface occurs when WC nanoparticles are incorporated into the electrodeposited nickel layer.

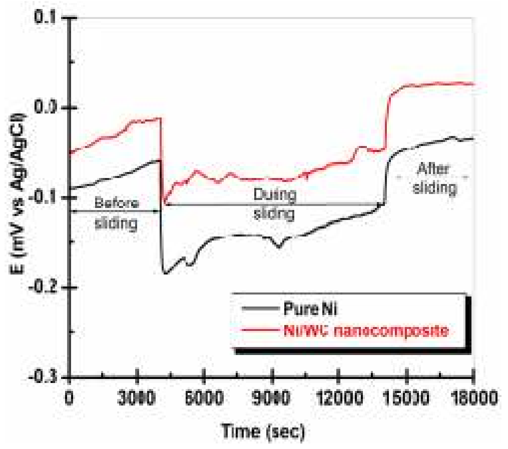


Fig. 8. *Evolution of the open circuit potential recorded before, during and after sliding tests of Ni/nano-WC composite and pure Ni coatings in the boric acid and lithium hydroxide solution at 1 Hz, 200 µm, 10000 cycles for the normal force of: 5 N [L. Benea and group - unbublished work]*

4. Experimental results for surface modified Ti-6Al-4V alloy used in biomedical applications

Working on enhancing corrosion and tribocorrosion properties of biomaterials in simulated body fluids solution, two electrochemical methods for surface modification of Ti-6Al-4V were applied. in this way it could be offered to biomedical applications improved biomaterials surfaces for longer and more efficient use.

The evolution of the friction coefficient versus sliding distance (mm) measured on untreated and surface modified Ti-6Al-4V alloy by nanoporous TiO_2 film growth and hydroxyapatite electrodeposited into nanpores is shown in Figure 9.

The fretting corrosion sliding test was performed against corundum counterbody in Fusayama - Mayer artificial saliva solution at a normal load of 800 mN, sliding frequency of 1 Hz for sliding cycles of 1000.

From Figure 9, it appears that for each separate surface the lowest coefficient of friction was recorded for hydroxyapatite electrodeposited into nanoporous TiO_2 layer surface formed on Ti-6Al-4V alloy. The coefficient of friction for untreated Ti-6Al-4V alloy exhibits strong oscillations during the sliding test compared to the anodized one and electrodeposited hydroxyapatite films. These oscillations could be attributed to the formation, accumulation and ejection of third - body particles (wear debris) [3].

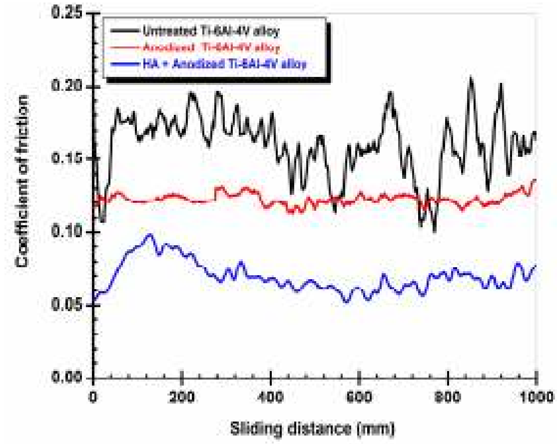
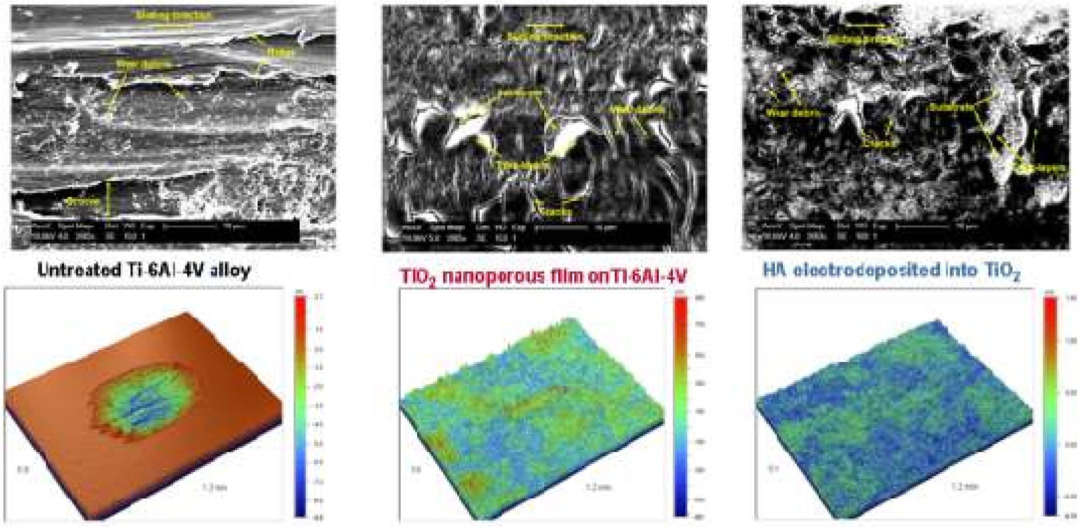


Fig. 9. *Evolution of the friction coefficients versus sliding distance for (▬) Untreated Ti-6Al-4V alloy surface; (▬) Anodic nanoporous TiO_2 film surface and (▬) hydroxyapatite electrodeposited into nanoporous TiO_2 layer, at normal forces of 800 mN, sliding frequency - 1 Hz and sliding cycles - 1000*

The corresponding scanning electron micrographs of the wear tracks and the 3D views obtained by non-contact profilometry of the wear tracks generated after reciprocating sliding tests (F_N=800 mN, displacement amplitude 500 µm, 1 Hz and 1800 sliding cycles) in Fusayama - Mayer saliva solution are shown in Figure 10 for (a) untreated Ti-6Al-4V surface, (b) nanoporous TiO_2 film surface and (c) HA electrodeposited layer into nanoporous TiO_2 film formed on titanium alloy.

The 3D morphologies of the wear tracks, the were track depth profiles and the volumetric material loss in the wear tracks was further investigated by non-contact white light profilometry.

The wear track of untreated Ti-6Al-4V sample reveals that it has suffered a major damage due to the plastic deformation and worn of wear debris provided by the fretting action of the alumina ball. For untreated Ti-6Al-4V alloy, wear debris are found spread out over the entire wear track surface [3]. The third bodies are obtained by the accumulation of wear debris particles detached because of the mechanical action between the first (metallic substrate) and second (hard inert counter piece) bodies. The third body particles which are not ejected from the contact can adhere to both first and second bodies and so contributing to the formation of a transfer film or can be fragmented in smaller particles being spread on the first body [3]. These third bodies trapped at the interface contribute to an enlarged real contact area.



(a) (b) (c)

Fig. 10. *SEM images of the wear tracks in the central region and 3D views obtained by non-contact profilometry of the wear tracks after reciprocating sliding tests (F_N=800 mN, displacement amplitude 500 µm, 1 Hz and 1800 sliding cycles) performed in artificial saliva for: (a) untreated Ti-6Al-4V alloy surface; (b) Anodic nanoporous TiO_2 film surface and (c) hydroxyapatite electrodeposited into nanoporous TiO_2 layer surface*

Since anodic nanoporous TiO_2 film surface and hydroxyapatite electrodeposited into nanoporous TiO_2 layer surface do not reveal wear debris in a significant amount, the dimension of the wear tracks corresponding to these surfaces is less than the dimensions of the untreated Ti-6Al-4V sample. As shown in Figure 10, untreated Ti-6Al-4V is characterized by a very high wear rate, which is in good agreement with the morphology of the worn surface. The irregular surface profile of the wear track in case of untreated surface points out the presence of adhered wear debris in the track indicating again the abrasive wear mechanism, observation also supported by SEM micrographs of the wear tracks developed on the same surface. The wear tracks of the anodic formed nanoporous TiO_2 film surface and hydroxyapatite electrodeposited into nanoporous TiO_2 are very shallow in depth and narrow in width compared to the untreated Ti-6Al-4V surface. Electrochemical methods applied for surface modification of Ti-6Al-4V alloy led to the lowering of wear depth and hence improved wear resistance compared to the untreated Ti-6Al-4V surface.

5. Conclusions

► Tribocorrosion process of materials degradation is present in many fields of materials, biomaterials, nanomaterials or coatings applications.

► New knowledge about tribocorrosion process and its synergy is needed in order to develop improved materials/coatings for industrial and biomedical applications.

► Accelerated tribocorrosion tests are possible for industrial problems based on mechanistic understanding, and determination of rational criteria for materials selection.

► New advanced nanocomposite coatings could be developed by electrochemical methods to improve the friction coefficients and wear-corrosion resistance in specific environments.

► Successful electrochemical methods could be applied to improve surface properties and biocompatibility of biomaterials for longer and more efficient use.

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CHARACTERIZATION OF THE RED MUD RESULTED FROM THE ALUMINA BAYER PROCESS PRODUCTION FOR THE FUTURE USE IN GEOPOLYMERS SYNTHESIS

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ABSTRACT

This paper presents the results of analyses on the chemical, structural and morphological processing of bauxite red mud resulting from alkaline wet Bayer technology. The characterization of the material considered as waste from alumina production industry aims at obtaining geopolymeric materilas. The results obtained were compared to literature data and support further research for the synthesis of inorganic polymers (geopolymers) intended for the manufacture of construction materials, starting from red mud as base material.

KEYWORDS: red mud, geopolymers, property, building materials

1. Introduction

The solid and semi-solid industrial waste is generated in large quantities in many production processes, which involve real problems with treating and storage. Geopolymerization as a recycling or reuse of waste technique, has become attractive both because of the need to resolve environmental issues and sustainability and stability of the material while geopolymeric materilas are obtained. By geopolymerization, a rich source of aluminosilicate is activated in a strongly alkaline solution to yield a solid, compact polymer structure due to the typical network of three-dimensional arrangement of atoms [1]. Because the reactions that occur are running in parallel and can not clearly distinguish the mechanism of the geopolymerization, in literature, there have been proposed four stages, namely: the first stage corresponds to the dissolution of Al and Si atoms in aluminosilicate materials in strongly alkaline solution; the second stage is the formation of oligomers in the aqueous phase of Si-Si and/or Al-Si; the third stage is the stage of polycondensation of the oligomers and the formation of three-dimensional aluminosilicate grid and the fourth stage is the formation of a solid geopolymeric structure [2].

Inorganic polymers, and hence the geopolymers, have outstanding chemical and physical properties, a chemical composition similar to that of zeolite even though their structure is amorphous, not crystalline. Wastes that are used most often as a source of aluminosilicate to obtain geopolymers are: fly ash [3-5] clay resulting from the production of pig iron [6-8] demolition waste [9] metakaolin result by kaolin calcination [10-12] and red mud resulting from the production of alumina by the Bayer process [13-16]. In this regard, the paper presents the results of analyses on the chemical, structural and morphological characteristics of red mud resulted from bauxite processing, using the wet alkaline Bayer technology. The characterization of this material aims at obtaining subsequent realization of geopolymeric materials. The results were compared to data from the literature and support further research to obtain inorganic polymer types (geopolymers) intended for the manufacture of construction materials, starting from red mud as base material.

2. The red mud

Red mud (RM) is the most important industry waste product from the alumina production by the Bayer process bauxite ore. In this process it is used a sodium hydroxide concentrated solution to solubilize the aluminum from bauxite ore in the condition of pressure and high temperature (150-250 °C) depending on the nature of the ore, respectively, gibbsitic, diasporic or bohemitic [17]. After completing the steps in the process red mud will result in the main-product and by-product aluminum hydroxide. The by-product is highly alkaline (pH = 10.5-13), has a high content of water [18], and a big content of heavy metals which make its re-use to be limited. Figure 1 shows the global production of NO exceeding 120 million tonnes (MT) annually [17].

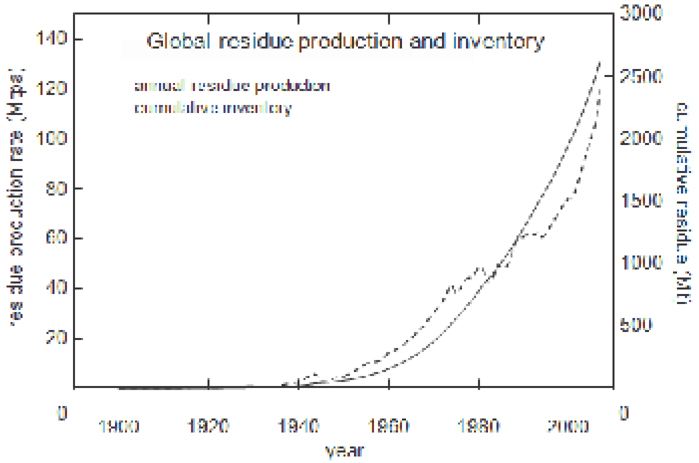

Fig. 1. *Global production and inventory production of red mud* [17]

As environmental legislation contains strict regulations regarding the disposal of untreated waste directly or unprocessed, and RM is subject to these regulations, storing it in any circumstances is prohibited [4]. Although there are many areas to use red sludge, recycling technology to meet environmental requirements and economic aspects has not yet been put into practice.

3. Experimental results

Red mud samples, uncalcined and calcined samples, were analyzed in terms of chemical composition using X-ray fluorescence spectrometry (XRF), a qualitative analysis was performed to determine the mineralogical composition and the phases of red mud by X-ray diffraction method (XRD), and determination of structure and elemental composition by electron microscope (SEM).

3.1. Materials and methods

In order to conduct the experiment it was used the red mud resulted from the Bayer alumina obtaining process, namely the dump from ALUM Tulcea. Freshly dried red mud grain was brought to 0.5 mm, after which a sample weight of 10 g was subjected to calcinationin a furnace type Lens Thermal Design, at a calcination temperature of 600°C with a heating rate of 10 °C/minute, an a hold time of 45 minutes. After calcination there was a weight loss of the sample subjected to calcination of about 23%.

3.2. XRF analysis

XRF analysis was performed with an analyzer type INOVIX Systems with a slot width of 1 cm^2. The measurements revealed the chemical composition of the item expressed as a percentage of red mud uncalcined and calcined respectively and are tabulated in Table 1 or Table 2. Following the results obtained for the sample calcined ash, it was observed a decreased percentage of iron and increased percentage of Al, Si, and Ti due to chemical reactions. The changes that occurred at that temperature increase is observed in the SEM images and by XRD analysis of these samples.

Table 1. *Elemental chemical composition of the uncalcined sample*

Element	Si	Al	Fe	Ti	Others elements	Total
Weigth (%)	7.20	8.58	78.43	5.33	0.46	100
Error (%)	0.19	0.48	0.86	0.35	0.03	--

Table 2. *Elemental chemical composition of the calcined sample*

Element	Si	Al	Fe	Ti	Loss of ignition	Total
Weigth (%)	11.01	12	69.99	6.3	0.70	100
Error (%)	0.23	0.56	0.88	0.42	0.01	---

3.3. XRD analysis

X-ray diffraction analysis (XRD) of the samples of fresh red mud and red mud calcined at calcination temperature of 600 °C were performed with DRON III analyzer, X-ray diffractometer, the endowment of the University of "Dunărea de Jos". This analyzer uses Co Ka radiation at a voltage of 30 kV, a current of 30 mA intensity 2θ and scans the wavelength of 1.78896 Å, with a range between 40° and 80°. By analyzing and characterizing the phases present in red mud many researchers [19-22] observed that the types of red mud differ and vary depending on the area, [23] how to extract alumina [24], on its age, on the warehouse [25]. Red mud is a industrial complex waste even though chemical analysis of the red mud mostly used in this study indicates the presence of calcium, silicon, iron and aluminum, and small amounts of titanium and sodium. Figure 2 shows the diffraction pattern of uncalcined red mud. The analysis of the diffraction pattern points out that the most important phases present in the uncalcined red mud are calcium carbonate as calcite ($CaCO_3$) and aragonite ($CaCO_3$), iron oxides, hematite (Fe_2O_3), otherwise observed in [26], respectively [27]. Sglavo *et. al* [19], considered that gibbsit, aluminum hydroxide ($Al(OH)_3$), aluminum oxide are decomposed at around 400 °C, crystallinity and stability are much less than the ones of aluminum oxide of corundum (α-Al_2O_3). It should be noted that, when the temperature rises up to 600 °C, aragonite peaks decrease and disappear completely at around 600 °C but calcium oxide can be detected in the samples treated at 500 and even 600 °C, suggesting that decomposition of aragonite in CaO is in the range 500-600 °C.

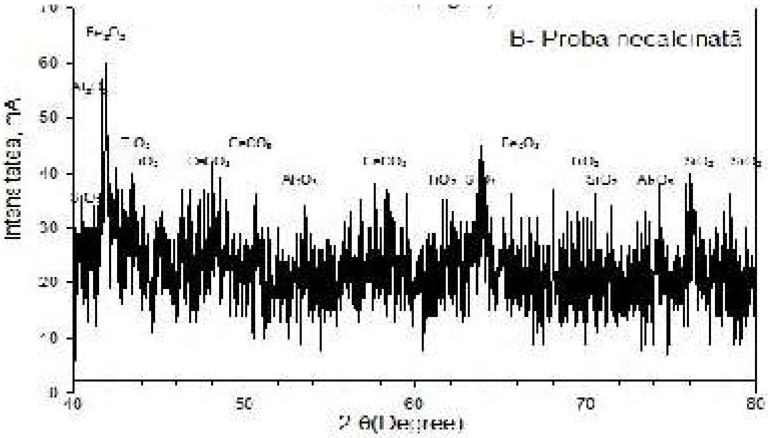

Fig. 2. XRD spectrum diffractograms patterns of the uncalcined sample

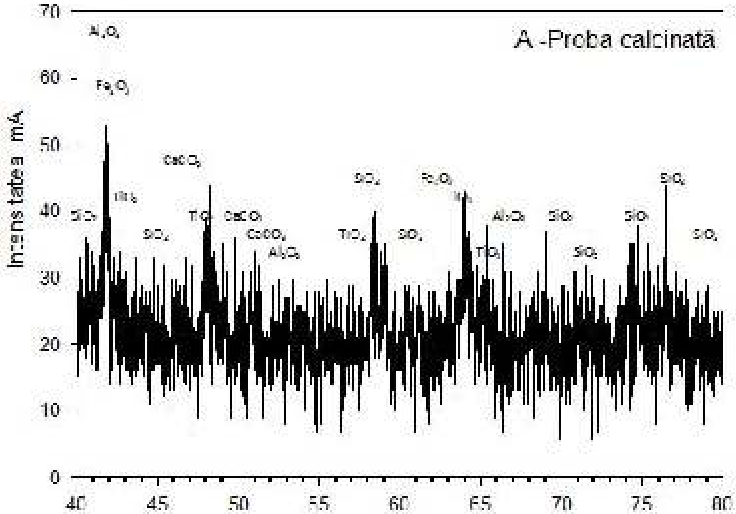

Fig. 3. XRD spectrum diffractograms patterns of the calcined sample

By comparing the observed spectra to both an increase in the intensity of peaks corresponding to oxides of aluminum, silicon, titanium, when calcined sample and a corresponding decrease in peak intensity of iron oxides, which is observed in X-ray fluorescence analysis, the mass of uncalcined sample elements is different compared to the calcined sample.

3.4. SEM analysis

SEM analysis of the structure of the scanning microscopy was conducted in the laboratories of UDJG, the type QUANTA analyzer 200, which is provided with an EDAX analyzer type.

These analyses were carried out on sample calcined at 600 °C and uncalcined sample to reveal structural changes that occur as a result of the heat treatment applied. In Figures 4 and 5 are shown SEM images of an uncalcined sample and calcined sample in Figures 6 and in Figure 7 are shown the images spectra of samples of red mud and elemental chemical composition of these samples, and in Figures 8 and 9 are given maps of the layout of the main chemical components of red mud uncalcined and calcined samples.

Through the comparison of the SEM image of the uncalcined and calcined red mud, SEM image at 600 °C, it is noted that the red mud particles at 600°C are low-crystalline or have amorphous form.

This indicates that the red mud calcined at 600°C is more reactive than the uncalcined one, and can provide a good cementitious property when used in combination to obtain a new binder, otherwise shown in other studies [28-30].

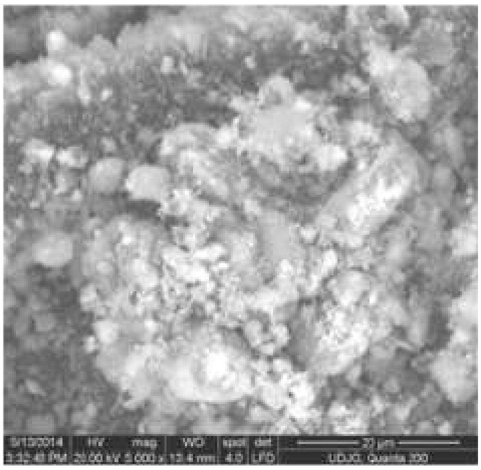

Fig.4. *SEM image of an uncalcinated sample*

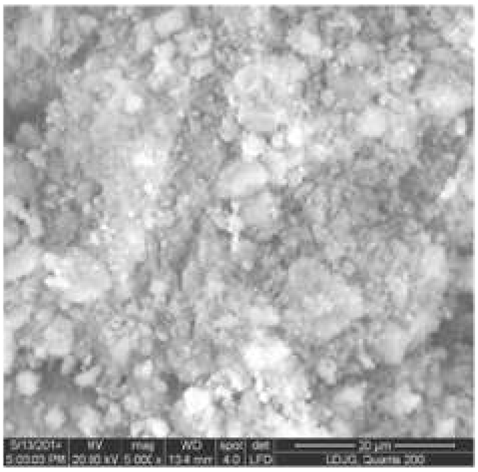

Fig. 5. *SEM image of a calcinated sample at 600 °C*

Table 3. *The elemental chemical composition of the uncalcinated sample, EDAX analysis*

Element	C	O	Na	Al	Si	Ca	Ti	Fe
Mass (%)	18.06	40.81	5.33	7.87	4.25	3.01	3.20	17.47
Atomic mass (%)	29	49.21	4.47	5.63	2.92	1.45	1.29	6.03

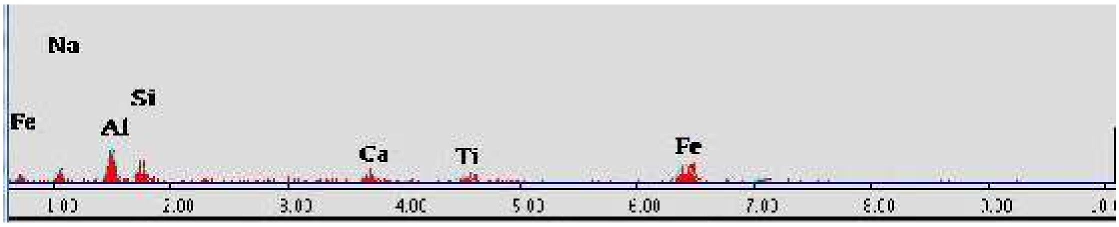

Fig. 6. *Uncalcined sample spectrum image*

Table 4. *Elemental chemical composition of the calcined sample by EDAX analysis*

Element	C	O	Na	Al	Si	Ca	Ti	Fe
Mass (%)	6.00	40.76	6.40	11.31	8.29	4.14	2.95	20.14
Atomic mass (%)	10.93	55.80	6.10	9.18	6.46	2.26	1.35	7.90

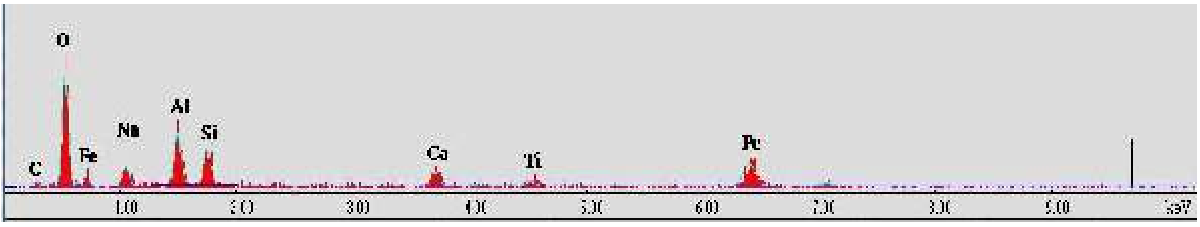

Fig. 7. *Calcined sample spectrum image*

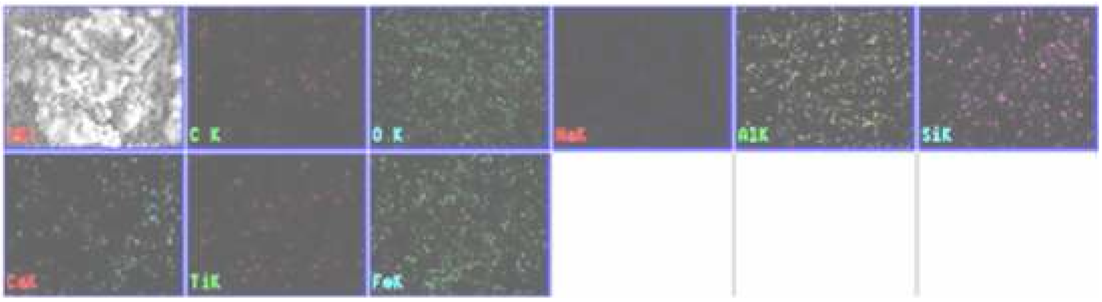

Fig. 8. *Distribution maps of the main chemical elements in the uncalcined sample*

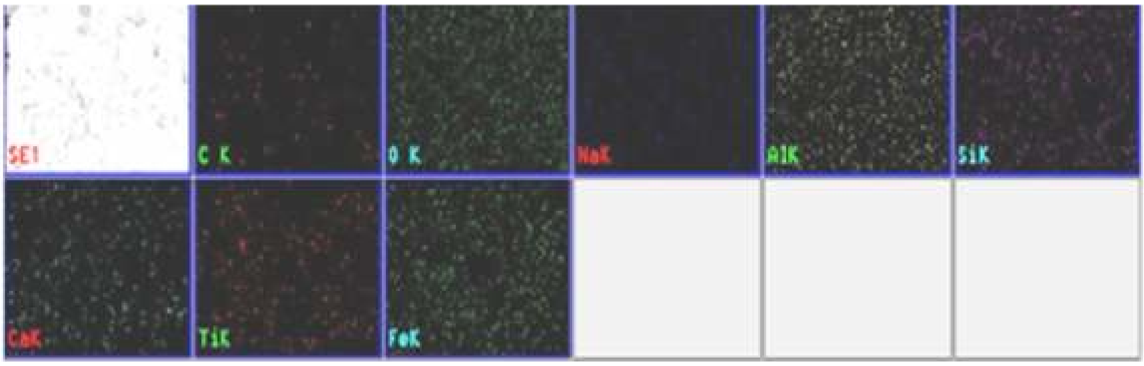

Fig. 9. *Distribution maps of the main chemical elements in the sample calcined at 600 °C*

From the analysis of scanned images by scanning electron microscopy it was observed that changes have occurred in the morphology and structure of the calcined sample, as evidenced by the overall appearance of the amorphous phase compared to the sample subjected to the calcination treatment phase is predominant crystalline phase. The explanation for these changes is that during the ignition chemically and physically bound water was removed and some metastable phase, for example silica, in the form of tridymite, has been converted into the stable phase, namely the lower cristobalite, which has been demonstrated by XRD analysis.

4. Conclusion

1. Geopolymers are materials produced by geosyntesis of an aluminosilicate material in a strongly alkaline solution and have developed several lines of operation. Literature has highlighted advantages of geopolymers synthesis, such as the fact that these materials are obtained at a low production cost, contributing to lower environmental pollution, and are long-lasting materials.

2. The results on the characterization of red mud from the point of view of the chemical composition, structure and morphology are comparable to some data from the literature on capitalization of red mud geopolymers in building materials.

3. XRF analyses, XRD and SEM performed on red mud pointed out the fact that after calcination, red mud uncalcined amorphous phases were transformed into crystalline phase that helps to form a material with geopolymeric properties, obtaining useful and superior construction materials.

Acknowledgements

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ELASTIC MODULUS OF COATINGS BY PENDULUM IMPACT TEST

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ABSTRACT

The pendulum impact scratch device with high precision system in measuring normal and tangential forces during scratching has been used to study elastic modulus of coatings. The criterion for evaluation of elastic modulus of coating and its experimental principle have been described and a series SiC and SiN thin films coated by PNCVD have been tested. The test results indicate that elastic modulus of SiC coatings has a good line relationship with Si content and there is a peak value in middle Si content. The experimental results also show that the newly developed device is useful in the evaluation of elastic modulus of coating especially under dynamic state and the method is characterised by reliability, validity and simplicity.

KEYWORDS: coatings, elastic modulus, pendulum impact test

1. Introduction

Being an active research topic in the field of materials sciences and technology surface coatings have been applied in many industries.

Their performances are related to mechanical properties such as cohesion strength and elastic modulus, etc. The stress in coatings is a main reason to make coating invalid, which may occur during the process of manufacture and machining or appears due to temperature change, phase transformations and magnetic field [1-2].

Elastic modulus (E) is an important factor for the determination of coating stress and it is usually measured by microbending and microtensile test. In bending tests the errors are due to inaccuracies in measuring geometry, deformation of the beam as well as simple model. There are many practical difficulties associated with achieving a straight portion at the beginning of the stress–strain curve in tensile test. Therefore it is urgent to develop effective and practical techniques for evaluating dynamic elastic modulus of coatings and for promoting the widespread use of coating technology.

In this paper, the single pendulum impact scratching device with high precise measuring system has been developed [3].

Using the device a novel tribological method for evaluating elastic modulus of coating has been established and the experimental results have been discussed.

2. Experimental procedure

2.1. Instrument and parameters measurement

The single pendulum impact scratch device is based on the combination of an impact tester and a scratch tester. This new developed instrument has a swinging pendulum (length *L*) with a sintered hard metal (YT15) stylus at the top of hammer (weight *M*). In order to control the incursion depth of grooves on the surface of specimen there is an adjustable specimen holder with a precision regulator for lifting or dropping samples, as in Fig. 1.

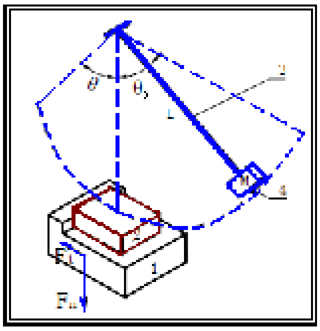

Fig. 1. *Diagram of single pendulum impact scratch device (1 - Adjustable specimen holder; 2 - Specimen; 3 - Pendulum; 4 - Stylus; Fn - Normal force; Ft - Tangential force;* θ_0 *- Initial angle;* θ *- Final angle)*

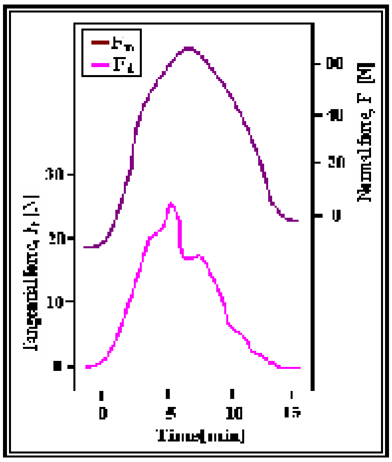

Fig. 2. *Typical curves of Ft and Fn vs time during a scratching process*

The specimen holder is constructed by a rigid frame and strain gauges are mounted in the frame for measuring normal force (*n F*) and tangential forces (*t F*) simultaneously in scratching and the forces curves can be recorded continuously by a digital storage oscilloscope [4].

Typical force curves of a single-pass impact scratch are shown in Figure 2.

Table 1 shows the parameters and precision of the single pendulum impact scratch device.

During impact scratching test a series of grooves with different sizes were produced for each specimen by changing the height of holder. After the test the geometry of grooves such as length (*l*), depth (*h*), width (*b*) were determined by measurement microscope and a profilometer in order to calculate the maximal normal projective area of stylus (A_N) and the maximal cross-sectional area of groove (A_T).

Table 1. *The parameters and precision of the single pendulum impact scratch device*

Parameters	Simbol	Unit	Variable range	Precision
Pendulum length	L	mm	362	0.5
Tangential force	F_t	N	2 ~ 100	0.8
Normal force	F_n	N	5 ~ 200	1.25
Speed of stylus	v	m/s	0.64 ~ 4.42	0.005
Specimen size	-	mm	30 x 50 x 1 ~ 4	-
Lifting (dropping) of Specimen holde	-	mm	0 ~ 5.00	0.002

2.2. Elastic modulus criterion

In typical and traditional situation, due to the un symmetry of depth of microindentation in loading and unloading processes, the elastic deformation of materials could be obtained by continuously recording the indenter displacement as a function of the applied load.

A similar treatment as those used in microindentation techniques is employed in the present study [5-6].

There is almost the same process of loading in incursion and unloading in sweepback during single pendulum impact scratching test (SPIST). As shown in Fig. 3, from the maximal normal force *F N* and the recovery behavior of groove in sweepback process at the deepest place, the mean slope of unloading curve K_e could be expressed as follows:

$$K_e = 2 / \pi^{1/2} \beta E_r$$

where: β is geometric shape factor, E_r is the synthetic elastic modulus of indenter and tested material, S_c is the contact area of indenter, *h* is the indentation depth [7].

Ke is a constant for certain material and it is obtained by fitting a series of F_N *vs.* (y - h) $S_c^{½}$ from different grooves.

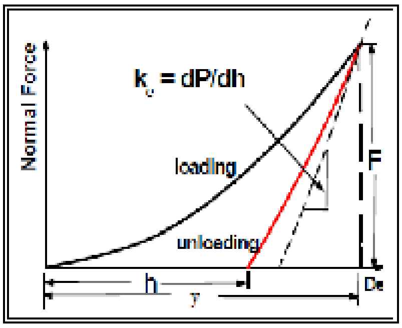

Fig. 3. *Normal force vs depth of groove from loading and unloading in pendulum testing*

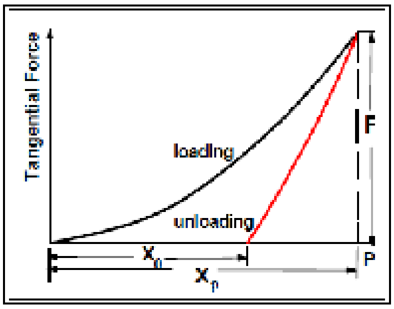

Fig. 4. *Tangential force vs position of stylus from loading and unloading in pendulum testing*

According to the same principle, as shown in Fig. 4, meantime notice groove length $L = 2x_p - x_0$, i.e. $x_p - x_0 = L - x_0$, the shear process could also be described by the equation:

$$F_T = k_g (L - x_p) S_t^{1/2}$$

where: x_p is the groove length part under loading and x_0 is part under unloading, S_t is the contact area of stylus in tangential direction, k_g is also a constant for certain material and obtained the same as k_e by a series of grooves from the test. Fig. 5 and Fig. 6 show relations both in normal and tangential force vs normal and tangential displacement and square root of the corresponding area of cobalt samples. The slope k_e of F_N vs. $(y - h) S_c^{1/2}$ and the slope k_g of F_T vs. $(L - x_p) S_t^{1/2}$, can be obtained by fitting curves [8].

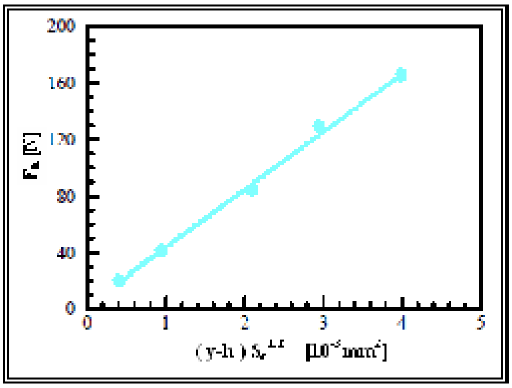

Fig. 5. *Normal force vs displacement by square root of contact area of a series of grooves on cobalt specimen*

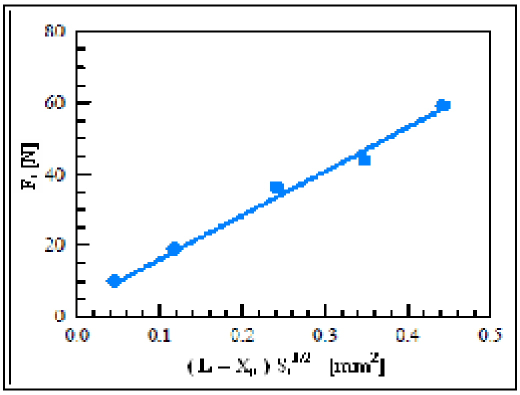

Fig. 6 *.Tangential force vs displacement by square root of contact area of a series of grooves on cobalt specimen*

The relation of *E* and *G* is:

$$E = 2 (1 + \upsilon) G$$

The *E* of any material or coating could be determined by the following expression:

$$E = 4G - 4G^2 [1/E_r - (1 - \upsilon_i^2)/E_i]$$

To verify growth mechanisms of SiN_x thin films, the bulge test specimens were cross sectioned and observed using scanning electron microscopy.

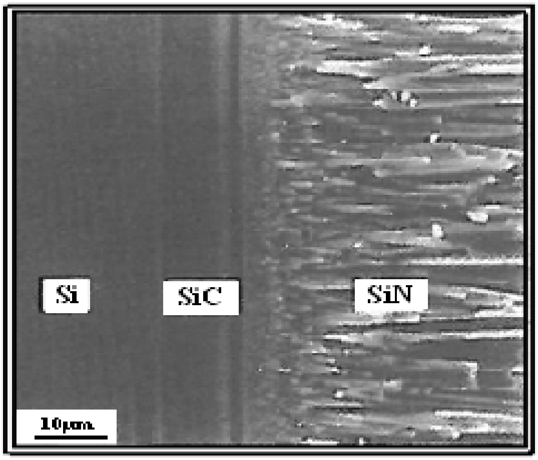

Fig. 7. *SEM micrographs showing the cross section of thin deposited on silicon wafer Si (100)*

Both coatings exhibit columnar morphology that arises from transverse fracture along the weak, low density intercolumnar regions. These are usually two distinct growth morphologies within the film thickness. The columnar structure is almost perpendicular to coating surface [9-10].

The SEM cross sectional views (Fig. 7) showed the microstructure throughout the film thickness is not uniform. This means that the biaxial measurements should be considered as mean values corresponding to modulus average of different layers.

3. Result and discussions

A series of SiN coatings with different content was obtained by chemical vapour deposit at normal pressure (PNCVD). Their elastic modulus was measured by SPIST and the test results were shown in Fig. 8. From Fig. 8, the elastic modulus of pure silicon coating was 140 GPa, which is lower than that of bulk (237 GPa) and E of SiN coating was 180 GPa. The scattered E of similar coatings was due to different composition, CVD process and method [11]. Comparing to the scattered result, coating’s E from SPIST is on the high side, which is due to the fact that in this test E is calculated by the maximum normal force and the maximum normal strain and this method decreases the effects of porosity and layer structure. However coating’s E from this test is more efficient than other test on the aspect of expressing dynamic behavior of coatings.

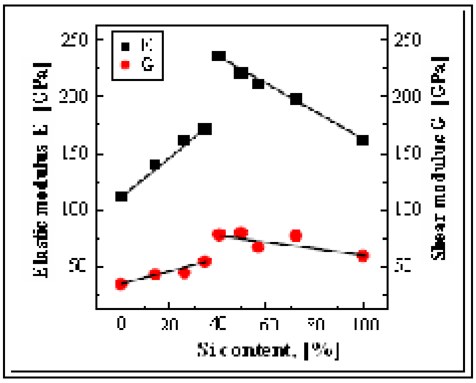

***Fig. 8.** The relation between Si content, E and G*

Fig. 8 shows the relation between E or G and silicon content. For SiC and SiN coating, the curves are divided into two segments and the relationship can be described by a line’s regularity. In SiC coating E and G of coating increase with silicon content and in SiN coating E and G decrease with Si content, therefore E and G of coating appear to reach a peak value when SiC content is similar to SiN content. The relationship between E and content is important to design a stepped coating [12]. To realize the continue transition of mechanical property, the peak value of E and G should be decreased as low as possible.The elastic modulus of three kinds of Si(C,N) coatings on silicon substrate obtained by Chemical Vapour Deosition was also measured by SPIST. SiC coating and thickness of Si(C,N) coatings were shown in Table 2.

***Table 2**. Si content and thickness of Si (C,N) coatings*

Coating	**Low Si**	**Middle Si**	**High Si**
Si content (wt %)	2.5	4	6
Thickness (µm)	10	10	10

Some of Si(C,N) coatings were heated for 4 hours at different temperature.

Fig. 9 showed the relationship between E of coatings and Si content, temperature of heat treatment.

Form Fig. 9 it can be seen that with SiN coating increasing E decreases, mainly due to the fact that the more Si content the more brittle the coating is. It can also be seen in Fig. 9 that there is a maximum point of E at heating temperature of 1090 °C for three coatings. As far as SiN coating is concerned, LSi coating has the largest E (240 GPa) after heat treatment at 1090 ℃ for 4 hours and HSi coating has the least E (137 GPa) without heat treatment, which corresponds to the result (140 GPa ~ 237 GPa). To obtain good mechanical property of coating, the appropriate content and mode of heat treatment must be selected. The advantage of this method comparing to traditional ways is that it can simulate service environment, especially under shearing action induced by dynamic loading [13].

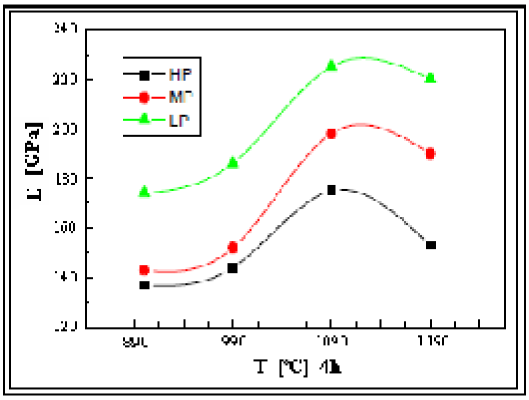

***Fig. 9**. The relationship between E and the procedure of heat treatment*

4. Conclusions

The single pendulum impact scratch device with precise measurement of normal and tangential forces has been used to study the elastic modulus of coatings. The criterion for evaluating elastic modulus of coating is defined and its efficiency is identified by a series of SiC and SiN thin films coated by PNCVD. The measurement technique not only emphasizes the evaluation of elastic modulus of coating under dynamic state but it also is characterized by reliability, validity and simplicity.

The relationship between E of SiC coatings and their content can be divided into two segments, which present different line’s regularity respectively and a peak value appears in the middle of the content. The content of Si and the temperature of heat treatment have an important influence on E of SiN coating and LSi coating possesses the largest E after heat treatment at 1090°C for 4 hours.

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PARTICULARITIES OF THE MANAGEMENT SYSTEM FOR PHONE MOBILES WASTE IN ROMANIA

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ABSTRACT

The main objective of this paper is to characterize the management system for mobile phones in Romania. The dimension of cell phone waste flow and the problems related to the collecting and recycling of this waste were considered. The study includes the characterization of behaviour of Romanian consumers, the regulations framework and the responsibilities of all actors involved in the cell phones lifecycle. The recycling and collecting practices in this sector are presented.

KEYWORDS: waste management, mobile phones, collecting, recycling, infrastructure, education

1. Introduction

The important objectives of phone mobiles management, like for other categories of EEE are: reducing the volume of waste and thus minimizing of amount of unusable materials disposed; materials recycling with economic and environmental benefits; reduction of pollution in environmental factors by the waste discharged and improper treated. The waste management system can be evaluated based on: structural framework (policies and regulations, industries, society, culture and education); current situation of existing recycling system; impact of waste fate on the environment factors and human health. In principal, an efficient management for mobile phones waste is based on improvement of collection operation and application of the best technologies for recycling. In this way, used mobile phones are prevented to reach in landfills or in common waste incinerators.

Romania as member state of the European Union has implemented the Directives on Waste Electrical and Electronic Equipment (WEEE) and began to organise for optimisation of the management system of these devices reached at their end lifecycle. The public authorities working with all actors involved in the EEE domain, as network operators, mobile devices dealers, recyclers, consumers, NGOs etc. Together they must solve the major problems related to management of all categories of WEEE to achieve recycling targets imposed by legislation in the field.

In this paper have been identified and evaluated weaknesses of the phone mobiles waste management system at present in Romania in accordance with the social, economical and political particularities from our country.

2. Major issues related to the cell phones waste in Romania

The issues related to the wastes of mobile phones that must be accounted at implementation of an efficient management system are following:

- dimension of cell phone waste flow;
- legal framework (for example, for ban on the disposal of waste into the environment, the management of hazardous substances, the constraints under recycling operations etc.);
- political framework (involvement of public authorities in establishing of environmental policies at municipalities level etc.);
- identify all those involved in the management of cell phones and determining their role and responsibilities in the management of mobile phones;
- culture of recycling and environmental education (awareness of mobile phone users in relation to the importance of collecting and recycling, as well as the negative effects of dumped waste, understanding consumers' attitudes towards programs, policies and opportunities of WEEE recycling, skills training in relation to giving back of equipment no longer used in contrast to their abandonment into the environment);

- existence of infrastructure for handling such materials (e.g., existence takeover points, facilities for the collection).

These are solved into states responsible for environment and oriented to develop a sustainable society [1-5].

The problems related to the wastes of mobile phones in Romania are considered and analyse realised was focused on these major components.

3. Dimension of cell phone waste flow

There are several factors that determined the cell phone waste flow in Romania. The volume of mobile phone waste is determined by the penetration rate of mobile phone services, the equipments placed on the market and by their useful life. The option chosen by consumers in rapport with unwanted device is also important. The destination of phone phones collected from consumers and the capability for theirs proper treatment in Romania influence the magnitude of waste flow.

The beginning of mobile telephony in Romania is dated back to 1995, when *Mobifon* and *Mobil Rom* came into the possession of licenses for telecommunication GSM system into Romanian market [6]. Since then to the present to the present, the number of subscribers at has known a huge increasing: from approximately 212,000 subscribers at the end of 1997 to 22.7 millions in middle of 2012. The maximum was recorded at the end of 2010, when about 24.4 million persons benefited from mobile services. The decreased rate of penetration in the coming years is attributed to the economic crisis. Mobile phone sales are annual increased as result of: the growth of new users (persons who not have cell phones before, or require additional phones); users who choose to leave their current provider and to choice another; enhancement of users number who buy a new phone for upgrading and replacement their old handset. According to research company GFK Romania analysis only in 2008, in our country have sold over five million mobile phones. Also, in 2010 were sold on the official channels between 4.5 and 5 million mobile phones. In 2012, according to estimates of the telecommunications market, sales of mobile phones were about 3-3.5 million units, of which 1 million were smart phones. It is estimated that at present, Romania has 1.3 mobile phones per capita. In these circumstances, a Romanian who dwells in city buys, on average, a new cell phone at least once a year [7].

The research realised by *The Gallup Organization* Romania in the period March-April 2010 (for *National Authority for Management and Regulation in Communications - ANCOM* in Romania, targeted on market for electronic communications services and on the lifetime of the mobile terminals at the first user) shown that the average useful life is 3 years. About the first utilisation, the respondents have estimated that they replaced the mobile phone after about 13 months [8].

The research of the organisation named *Forum for the Future* (which has investigated the impact of the second-hand mobile phone market in Romania, realized in 2004) report that the second-hand phones are significantly cheaper than new ones. Therefore, in 2004, almost a third of mobile phone users in Bucharest use second-hand phones, predominantly by persons with lower-income. Romania is one of the favourite destinations of the refurbished phones that are brought and brought from other countries. The mobile phone companies and retailers do not supply data on the volume of this market (Figure 1) [9]. The sales of the second hand phone have exploded in last years affected by crisis.

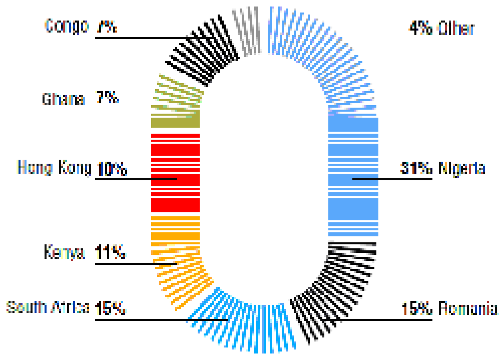

***Fig. 1.** Destination country for some phones collected via Vodafone, period 2004/2005 (Sorce: Fonebak) [9]*

Regarding the quantity of cell phones waste accumulated in Romania, don't are published information. Starting with 2006, the quantities of WEEE collected (not generated) were be counted. These data are about the quantities of categories covered by Directive EU within ANNEX IA [10].

There are not information for mobile phones, only for category of IT and telecommunications equipment [11, 12]. Also in present those few information on mobile phone waste generated in Romania are mostly approximated.

4. Consumers behaviour

The main contributors at flow of cell phone waste are the consumers. Many Romanians who have purchased a new phone, have donate their old equipment to a family member, poorer relatives or friends who can not afford to purchase such a device. In many cases the consumers tend to want to keep their old phone as spare. But, in many cases exist the tendency for users to temporarily store the old equipment often due to emotional attachment to old equipment (these form so-called „hibernation equipments stocks” or stock from „drawers”). Others choose to sold or to trade when purchase the new phone.

The consumer behaviour (together with other factors as the infrastructure, awareness system, the convenience offered to the people etc.) influences the fate of mobile phones at their end life cycle. In this point the biggest challenge in waste recycling is the collection of the unused equipments from the consumers. The consumer plays a big part in the management chain. So the recycling behaviour of the individual is crucial for the recycling process. In Romania, as well as in other countries when the organisation of recycling process started recently, the collection activity must be motivated. There are few ways to stimulate the collection. Is necessary to be diversified the incentives provided to encourage return of the handsets based on examples put in practice into states with performing system for WEEE management [13]

Concerning Romanian consumer, it highlights the lack of a responsible attitude and behaviour appropriate for his mobile phone fate when stops its using. Due to the unawareness or ignorance of the harmful effects of uncontrolled management, the nonconforming solutions applied to old cell phones can damage to environment or human health. The uncontrolled disposal or applied of inappropriate treatment (as example, combustion as for solid municipal waste) lead to removing of harmful pollution emissions. Also the mobile phone owners are not aware of the importance of the collection and the advantages of recycling that means the recovery of materials and reducing of energy consumed. Added to this is the environmental impact at extraction of raw materials and additional costs for this activity. The deficiency in education and lack of responsible attitude make as the collection of cell phones in Romania to be made sluggishly and with difficulties. These weaknesses could be rehabilitated by cultivating the responsible behaviour at all consumers, by increasing the level of education, information and involvement. The change of public attitudes towards WEEE and the increasing of awareness for the negative impact of WEEE on the environment and human health are processes that are in the initial stage. The raising awareness and the providing of easy return ways are key factors in increasing the return rate of used devices and for creating the skills for collecting and recycling.

5. Regulation framework for WEEE

In general WEEE waste management has a short history in Romania. The implementation of WEE waste management system has beginning in 2005. Then were transposed into national laws two major directives of the European Parliament and of the Council: Directive on waste electrical and electronic equipment or Directive 2002/96/EC; Directive on restriction of the use of certain hazardous substances, named RoHS Directive, or Directive 2002/95/EEC. This was mandatory for EU accession. These main regulations together with other secondary legislation and government ordinances make up the legal framework for WEEE management in Romania.

For Romania alignment with other EU members is required the organization of management system for WEEE. That is able to ensure the targets introduced at Community level for recycling rates. These were recently updated. The new WEEE collection target for EU member states becomes: 45% of electronic equipments sold, applicable from 2016; in a second step, 65% of equipments that were sold, or 85% of the electronic waste collected, from 2019. Romania, like other countries in Central and Eastern Europe enjoying from a transition period, translated by achieving the following targets: in the first stage (2016-2019), a collection rates between of 40% and 45%; the delaying of the collection rate achievement of 65% (applicable in the EU from 2019) until a date decided by the Member State, but not later than 2021.

The collection target for which Romania is accountable to the European Commission can be achieved with optimal operating costs only through a sound management of WEEE. The main sources of mobile phone waste in Romania are from formal sector (importers, producers, retailers, individuals and collectives consumers, traders) and from informal sectors (dismantlers, recyclers).

6. Tasks and responsibilities

National legislation establishes objectives and responsibilities for all stakeholders. To all actors involved in EEE management have assigned the following objectives: waste prevention by reusing, recycling and other forms of materials recovery in order to reduce the amount of waste eliminated into the environment; improving the environmental performance of all operators linked at the life cycle of equipments (producers, distributors and consumers), particularly for those that are directly involved in the treatment of electrical and electronic equipments waste. The players that have responsibilities for organisation and optimisation of mobile phones management system are: public authorities, producers, network providers, retailers, users, recyclers, NGOs etc. Regarding the responsibilities, these are clearly summarized further.

- Producers are responsible for financing the collection, treatment, recovery and disposal of waste that originate from their products. Their obligations can be performed individually or by joining a collective system or associations. They have obligation to take back the devices that no longer used to treat, recycle and store them safely.

- Suppliers of services and devices dealers are obliged to take back the old equipments from users and to give them to authorized recyclers.

- Central authority is responsible to establish the legislation framework for proper WEEE management.

- Local authorities must organize the collection points, the waste collection logistics and their functionality.

- Consumers must be responsible for the fate of their phones if do not use them anymore, facilitating its recycling and preventing the uncontrolled disposal of waste into the environment.

Central authorities are responsible for the non-compliance of the collection system and the lack of a coherent strategy for waste management at level of entire country. The frequent changes of authorities at central and local level lead to repeated changes in previous decisions so that the long-term solutions do not get to be implemented and short-term decisions are insufficiently grounded. Locally, the collection is hampered by delays of public authorities to fulfil their obligations under the Law 1037/2010 concerning the management of WEEE. They have the obligation to separately collect WEEE from individual consumers and to provide the sites for setting up the functional collection points for the authorised collector operators (by the National and County Agency for Environmental Protection).

Also in cooperation they must adopt a functional financial mechanism adapted to the two major conceptual alternatives to implement the WEEE management system [14]. One is national collection system, when a dominant system is responsible for the collection, recycling and financing of all (or most) of WEEE from national territory. A producer association or more can operate. These companies are non-governmental and non-profit societies that are specialised on some categories of products. Their activity is focused to achieve the maximum efficiency in the recycling process, to identify the markets for materials recovered and to reuse them. Other alternative is the competitive clearinghouse system which consists of creating a national framework in which multiple partners can provide recycling services.

Romanian Government has decided that „National System of Collecting” to represent overall strategy of WEEE sector and by so-called „collective organizations” to cover all WEEE categories defined by EU Directives and Romanian legislation.

From the point of view of the EEE manufacturers/providers, they can fulfil their obligations for management of their products, individually or jointly by creating such collective organizations. They develop directly or through these organizations, the services necessary for the management of WEEE, i.e. activities of collection, transport, treatment, recycling, storage etc. The costs for these services and for other activities (e.g. for the public awareness campaigns and for education of consumers) and the administrative costs are covered by visible fee or they are included in the price of products sold. In Romania were founded and have activity a number of collective organizations approved in accordance with WEEE legislation (Order 1225/2005): ECOTIC, RoRec, RECOLAMP, ENVIRON, CCR Logistics Systems RO S.R.L., ECOPOINT, ECOMOLD, etc.

Collective organizations are designed to provide efficient services to their partners who are EEE producers or telephone service providers. A collective organization complying the obligations on behalf of EEE producers: organizes special collecting points, via retailers provides exchange system one-on-one and based on diverse benefits; ensures the transport, treatment, recycling and disposal of waste; organizes the public awareness activities; make reports of data to environmental authorities, etc. The agreements with producers must be very serious. At the non-compliance of collective organizations with their obligations in respect with regulations, producers are responsible.

Romanian legislative framework allows the creating of new collective organizations and also the recording of individual companies for WEEE recycling. As result, it becomes possible as more collective organizations and companies to be specialised in the management of the same type of WEEE. In this situation, the responsibilities for achieving the targets at the national level are not divided between individual actors. Accordingly is necessary to establish individual collection obligations, the definition of individual targets for WEEE recycling rates.

Romania does not manufacture mobile phones. Nokia, a Finnish multinational corporation, has closed at the end of 2011 the components factory in Jucu, Cluj County (an investment of 60 euro millions, inaugurated in 2008). In this situation, the telephone networks companies in Romania are primarily interested in the management of mobile phones. They provide telecommunication services and devices through own dealers or their partners. They are providers at international level which have subsidiaries into Romania. Ordered by number of subscribers, they are: Orange Romania with 10,383,481 subscribers, in function with valid SIM at 30 September 2013 (www.orange.ro);Vodafone Romania, the second largest mobile operator, with a customer base that reached a total of 8.08129 million subscribers on 31 March 2013 (www.vodafone.ro); Cosmote Romania with a market share of approximately 24.5% at the end of 2012 (www.cosmote.ro); RCS & RDS which had, in mid-2013, 1.1 million customers for mobile services, thus is the smallest player on the market after Orange, Vodafone and Cosmote (www.rcs-rds.ro). The mobile telecommunications operators agreed to joint at various collection programs to encourage people to donate their phones, educational programs for forming the culture of collection and recycling. They form with other EEE producers the authorized collective associations (Orange with CCR Logistics Systems RO SRL; Vodafone with RoRec; Cosmote and Environ).

Together they have implemented various collection programs of mobile phones from consumers or for own unsold or undelivered devices by following schemes: take back, buy-back, providing of diverse incentives to collect and recycle discarded cell phones, donations, charity etc.) [15].

At national level, buy-back programs for mobile phones were introduced on Romanian market by Orange since December 2009 and by Vodafone in 2011 (www.vodafone.ro).

Vodafone Romania was the first telecommunications company that launched in 2007 *The National Program for Recycling Mobile Phones and Accessories* (for batteries, chargers, hands-free, data cables) (www.rcs-rds.ro). Cosmote Romania and Germanos, in partnership with „Environ Association” (http://www.environ.ro/), based on „National System Battery Recycling” program, have developed a large electronic waste collection campaign called *I Love Recycling* [16].

Two providers companies have initiated a new measure for environmental protection and for the information of customers. They have introduced the eco-labelling for mobile devices commercialized. The criteria adopted by EU eco-label for some EEE (not yet for mobile phones) helps the consumers to identify products and services that have a reduced environmental impact throughout their life cycle, from the extraction of raw material through to equipments production and use, also for waste disposal [17]. In partnership with World Wildlife Fund and with expertise of BIO Intelligence Service expertise, Orange has introduced nationally, in 2011, an eco-label for its phones intended to be sold (For beginning, the eco-labelling is available only for online store Orange). Based on information received from the manufacturer, every phone receives an overall score (out of 5) according to five indicators related to: amount of greenhouse gases emitted during the main stages in the life cycle; energy consumed during use and standby as a measure of energy efficiency; amount of valuable materials (gold, silver, etc.) in the product, as the measure for the conservation of natural resources; if it can be easily dismantled and recycled based on the their composition, design and the recycling technologies available; the presence of toxic and hazardous chemicals and substances that are dangerous for human health and the environment [15]. Also Vodafone attaches the eco-label at its mobile phones. It is named „Eco-Score”. This is the eco-label under which Vodafone promotes the ecological efficiency of its mobile phones (in partnership with *SKM Enviros* from UK and *Bureau Veritas* from France). By assessing of 162 criteria (106 criteria for the product itself and 56 for the activity of the manufacturer) the rating system is from 1 to 5: 1 represents the highest impact on the environment, while 5, the lowest impact (www.orange.ro, www.vodafone.ro).

Romania has received technical assistance through PHARE programs to educate people on waste management and to implement the implementation of Directive 2002/96 on WEEE. Some NGOs have regularly organized national awareness campaigns and education, fundraising galas for environmental projects and campaigns for waste collection. Also, with external assistance in 2007 was launched a national campaign to collect WEEE called *Great Disposal* (*The Big Get Rid of Waste*). In conducting its existing collective organizations, local authorities, health agencies, collection companies, local and regional agencies for environmental protection were involved. Its effects were reflected in the continued growth of the quantity of WEEE collected at each event [18]. The collective associations, some economic agents, commercial and banking companies started a "Green Corner" program. This action is materialized by offering a WEEE collection infrastructure in areas easily accessible or with intense people traffic.

As a novelty into collection activity based on compensation of WEEE from retailers, *Green Group* has installed so called „ecoATM” or „green recycler” (Figure 2).

***Fig. 2.** EcoATM for cell phones and other EEE*

This machine works in a few steps and offers instant cash to consumers that have returned its unwanted mobile phone. Is a new way to sell used cell phones (or other electronic/electric equipments).

This was promoted in Romania through the voluntary agreement project signed between *Green Group*, Ministry of Environment and Climate Change and *Big Networks Commercial Association* of Romania. The first machines were installed in March 2013 at Cora stores in Bucharest and other cities (Buzău, Ploieşti, Arad, Baia Mare, Drobeta Turnu Severin, Constanța, Bacău și Cluj) (www.greenweee.ro).

7. Existence of infrastructure for collection and recycling

If are considered the value of recycling rate and the amount of equipment collected, it can be appreciated that in Romania, organization of WEEE management in general and waste mobile phones, in particular, is at the beginning.

The collection and recycling are processes that still operate slowly. In 2008 Romania had the lowest recovery rate WEEE in the EU (Figure 3).

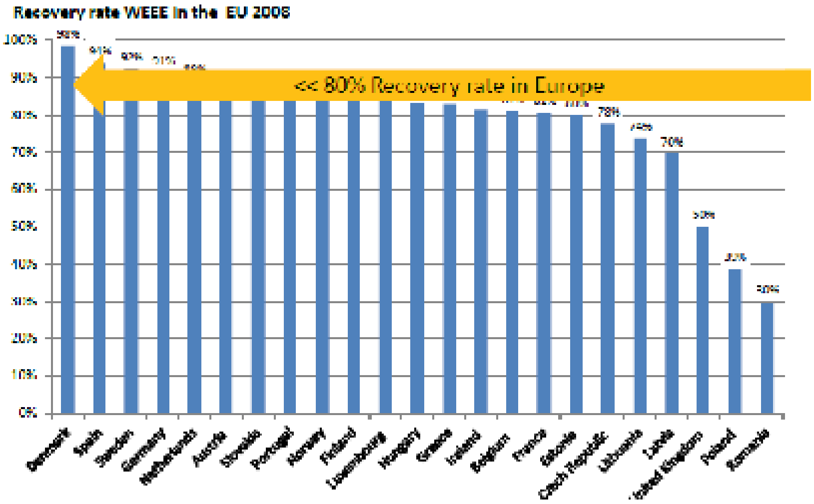

***Fig. 3.** DEEE recycling in EU states, 2008 [19]*

At passing of years the situation from Romania seems to not have more changed: WEEE collection rate in 2010 remains lowest in Europe (Figure 4).

In Romania, the collection of mobile phones as well as of other types of WEEE, is organized through the canals: collection events in a special day for WEEE from households (with lower addressability at mobile phones waste); giving back to the retailers the old mobile device when is acquiring the new one (by following scheme: free take back, discounts, buy-back); return direct at the special points for separate collection that are organized by municipalities, recycling/reuse/refurbishment companies, collective organizations and others. The surveys have shown that for a management system that is at early stage such as this one from Romania, the incentives provided to mobile phones owners can encourage the return of handsets.

Regarding materials recycling from mobile phone waste, the variety and complexity of materials (especially the presence of Au, Ag, Pt, Pd, rare metals that are considered „critical metals for future sustainable technologies” in accordance with demand growth, supply risks due to scarcity of natural reserves, recovery potential) and the presence of hazardous substances (halogens, brominates flame retardants, Cd, Sb, Pb etc.) requires the adequate facilities for treatment. Efficient and environmentally sound treatment of waste requires advanced technology [21-23]. This requires sophisticated facilities that cannot be duplicated in every country (is not economic to duplicate in any country).

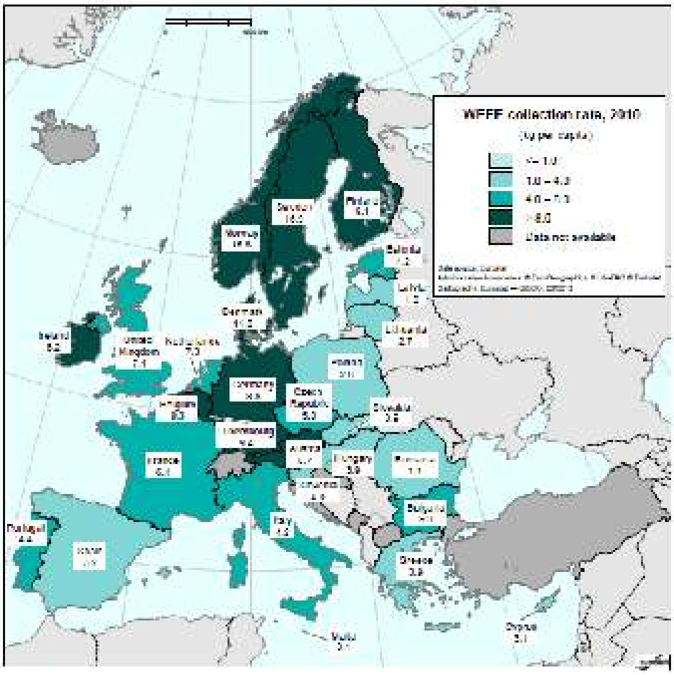

Fig. 4. WEEE collection rate in 2010 [20]

In the world were perfected the efficient technologies and few suitable plants already exist in Europe [24-29]. Romania do not has any units for recovering the valuable materials from these complex waste and therefore and it is not feasible to build such a unit. At end-of-life, the most phones collected were exported. Also, there not exists a market for materials resulted from the dismantling and/or recycling of EEE waste.

The certified companies from Romania are specialized only in: collection; transport; storage; dismantling with recovering of components; some operations for sorting and selecting of materials. Moreover, after 1989, Romanian metallurgical plants from non-ferrous industry have been closed and decommissioned. These would be able to upgrade their production flows in accordance with environmental regulations and work safety. Also these would be able to acquire the modern equipments and to adapt their technology to extract the valuable metals (Cu, Au, Ag) from mobile phones waste. In present, *GreenWEEE International* had an initiative to build at Frasinu, near to Buzău, the first plant that addresses to recycling of WEEE, ensuring all their stages of treatment. The investment is worth 10 million euros.

The recycling unit has a total area of 10,795 m^2, of which 6,100 m^2 for production and processing. This annual capacity is over 50,000 tonnes of WEEE recycled (http://www.greenweee.ro/).

8. Conclusions

The initiating and developing a sustainable waste management system (which in fact requires a long period of time) is hampered by a number of factors specific to our country.

The recycling strategy must be based on the economic sustainability, technical feasibility, and on educational support. The mobile phones recycling must be supported into a sustainable manner by organizing a formal institutional networks formed by private actors (network telecom operators, retailers, RRR companies, collective organizations, consumers) that are responsible for phone device life cycle and by public authorities (central and local) which are responsible in the development of guidelines and regulation framework within which private actors can be able to function. In accordance with the legislative requirements of the European Union and of Romania, a sustainable financial mechanism should be able to operate for ensuring the coverage of all costs of waste management, to contribute to their effective operation by establishing a competitive climate and to ensure the incentives. In Romania, in the managing of mobile phones can be identified a number of weaknesses that are common to all categories of WEEE. They must be solved.

Also must be sustained the education programs for forming the correct habit and normal attitude towards a product reached at end of life cycle.

The recycling culture can be formed in collaboration with schools, universities and other large communities or companies. The mobile phones collection must be encouraged by public authorities and private actors involved into mobile phones management. The collected system must take into account the low level of awareness of Romanian citizens for advantages of recycling and for environment protection. As many high visibility collection points, especially in high-traffic areas must be organized. At this moment the take back process is stimulated mainly by motivation of consumers. Accordingly there must diversify the incentives provided to encourage return of handsets. Successful solutions utilised in other countries can be adopted: free postage; charity donation; envelopes, bags, boxes; courier collection, cash payment; other as discounts, store credits; prize draws; environmental incentive; mobile phone airtime; mobile phone bill discount. Finally, for an efficient management system of phone mobiles waste is essential the logical and long-term cooperation and interaction of all players involved in the developing of a responsible attitude, the forming of the recycling culture, and applying in practice of correct recycling solutions with respect to environment and people.

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EXPERIMENTAL RESEARCH ON HEATING BEHAVIOR OF SOME STEELS DURING HOT METALLURGICAL PROCESSING

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ABSTRACT

The heating of steel semi-products in view of hot rolling process or heat treatments is achieved at the large scale in propulsion ovens for the increase of their deformability and to improving mechanical characteristics of finite products.

The main heating defects (oxidation and decarburation, overgrown grain size of steels) represent processes of alteration of the superficial layers or the decrease of the physical and mechanical characteristics of the finished products.

This paper presents the results of experimental researches on the oxidation susceptibility, variation of the depth of the decarburized layer and the susceptibility to overheat of two ship steel grades (A36 and E36 grade), during the heating for the hot metallurgical processing of the semi-products. It is the deepening of the researches about heating behavior of naval steels with different chemical compositions.

KEYWORDS: oxidation susceptibility, decarburized layer, susceptibility to overheat, main defects, ship steel grades, metallurgical processing

1. Introduction

The performance of obtaining products or providing services is ensured through a primordial factor called quality.

Maintaining performance requires continuous quality improvement and quality assurance includes all planned systematic actions necessary to provide adequate confidence that a product or service satisfies the quality requirements [15]. The quality of a steel product is determined primarily by the properties of the material which in turn depend on its nature, (type) characterized by chemical composition and by particular structure. The structure of a metal material can be modified by thermal treatment and / or thermomechanical, so product quality is directly influenced and in the greatest extent through the modification of its properties.

On steel products market quality of a product is defined by identifying the concept with one of the important features of the product, which is obviously superior in comparison to similar products. A rational use of a steel product for a given application is a complex and schematic matter that actually means providing steel grades that meet the maximum strength and durability characteristics under a minimum cost price. Capitalizing fully technological properties of steels contributes to process in optimal conditions the blank to obtain a finished product with optimum features. Defined as material sizes, heat treatment technological characteristics are expressed quantitatively by experimentally determined values, under conventional set, so those sizes to allow the comparison of different metallic materials or of the same metallic material with different structural states (ie values of critical points, critical transformation speed, susceptibility to overheating, susceptibility to deformation and rupture etc.).

Thus, susceptibility to overheating [3, 4] of steels characterizes kinetics of crystal growth of austenite formed by heating slowly to a temperature in the range of its stability. The size of the crystals formed in the austenite steels with different chemical compositions or with similar chemical composition but from different batches, depends in different ways on the temperature and duration of heating for the austenitising. Therefore, to characterize a steel overheating susceptibility we should determine the grain size of austenite formed, in heating conditions (temperature and holding time) set in a conventional manner, for different groups of steel.

Characterization of the behavior of a metallic material in the chemical interaction with the environment where the heating and cooling are made for a certain type of hot metallurgical processing (plastic deformation, heat treatment) is done using thermodynamic characteristics that define the chemical affinity of metallic material to the components of the environmental [3]. For this purpose, there are used the appropriate thermodynamic characteristics as the oxygen potential of the metal oxide, the activity of carbon, nitrogen activity, etc., whose values depend on the chemical composition and temperature of the metallic material. Using the values of the chemical characteristics of metallic materials can be selected, chemical compositions of the media heating / cooling, which at the temperature that the metallurgical process in being performed exerts on the superficial layers of metallic materials products, chemical actions corresponding prescriptions. Given these theoretical considerations, this paper aims to highlight the results of laboratory scale investigations on the susceptibility to oxidation and susceptibility to overheating of naval steels during heating of the products for to increase their deformability and the heat treatment applied.

2. Materials and experimental conditions

Heating steel semi-products to hot rolling furnaces powered (Specific conditions of the steel Plant in Galati) aims to reduce rolling resistance to deformation or heat treatment (normalization, improvement) requiredby the standard product.

The main heating defects (oxidation and decarburization of steels) are processes that destroy superficial layers of heated material that leading to significant increases of the fuel consumption and lower of the furnace productivity (increased consumption of steel). Overcoming decarburized layer thickness over a certain value means discarding the material. The steel surface is oxidized more intense as the temperature and duration of heating are higher. Also if slabs have lower temperatures than those required by technological they return for a new heating. In this situation there is an increase in fuel consumption per ton of steel [14].

Using a suitable heating technologies of the slabs for rolling,, contributes substantially to the reducing of energy consumption.

The rolling can be achieved with higher values of passage reductions, the wear of subassemblies being entered in the normal range.

By maintaining a constant temperature during treatment are avoided rejects and technological limitations that arise from overheating or over maintaining, thus reducing losses by oxidation and respecting the scheduled quality of the treated product.

In shipbuilding, the highest amount of material is in the hull. The hull is made of sheets, strips, rods and profiles with thickness of maximum 50 mm, hot rolled weldable steels. In general, steel tables for constructions in transportation industry (marine, rail, land, etc.) can be obtained from the manufacturing flow of heavy plate mill No. 1 or No. 2 of the plant from Galati.

As mentioned, this paper is a development of previous experimental research [14] on the behavior at heating of the steel plate products for ships. It is planned to study the heating behavior of semi-finished steel, fine grained E36 in comparison with steel grade A36 (table 1). The author wished to study especially the heating behavior of flat steel products E36 given the results of the author's previous research, which demonstrated the possibility of performing the specific heat treatment (normalizing, annealing, etc.) with heating at lower temperatures (termical treatment with heating in the intercritical range of steel), with the important advantage of reducing susceptibility to oxidation and overheating.

Generally, constructions and naval parts are subject to the rules and specifications RNR or International Ship Register. The standard 8326-86 covers hot rolled steel sheets, with thickness between 4 mm and 60 mm used in welded naval constructions, primarily for bearing structure elements of river and sea vessels of different dimensions: small, medium and heavy sizes which are manufactured in accordance with the Romanian Naval Register. Under this standard, the tables for shipbuilding are classified into: normal strength steel sheets with minimum yield strength value of 235 N/mm^2 and high strength sheet steel with minimum yield strength value of 315 N/mm^2. The table below shows the chemical composition of steel samples under study.

***Table 1**. Chemical composition of the steels studied*

Steel Grade	Chemical composition (%)											
	C	Mn	Si	S	P	Cr	Ni	Mo	Al	Cu	Nb	V/Ti
E36	0.15	1.40	0.30	0.020	0.018	-	-	-	0.043	-	-	-
A36	0.17	1.45	0.27	0.017	0.029	-	-	-	0.033	-	0.031	0.021

Rectangular samples with dimensions of 10x10x50mm were machined and then metallographically prepared until mirror gloss. After degreasing in alcohol the samples were kept in desiccator for weighing.

Fig. 1. *Machined samples*

Experiments were performed in the laboratory in electric furnaces with forced bars.

The samples were heated at temperatures: 900°C, 1000° C, 1100° C, 1200° C with holding times of: 1 hour, 2 hours, 3 hours, 5 hours, 8 hours, in the oxidation atmosphere of the furnace.

Placing in the oven was made on a special holder that allowed exposure to the oxidant environment of all sample surfaces.

After oxidation the samples were subjected to mechanical removal of the corrosion products and were reweighted. Losses of weight were determined at oxidation temperatures and durations of maintenance experienced. The oxidation rate was also determined on each sample according to the experimental thermic regime (working temperature and holding time). In order to study the structural changes, the samples were cut. Sectional area of 10x10 mm size was metallographic prepared.

The microstructure was revealed by chemical attack: 2% nital and X100 magnification.

It has been measured the depth of the decarburized layer and it was determined the granulation score of the microstructure and Widmannstatten structure, by comparing with the standard images.

Next we proceeded to the processing of the experimental data. To facilitate interpretation and to elucidate the behavior at heating of the two brands of steel, graphs were plotted which easily illustrate the objective of the experiments.

3. Experimental results

Table 2*. The loss of mass from the oxidation of steel samples depending on the heating regime*

Heating temperature	**Holding time**	**Average mass loss A 36**	**Average mass loss E 36**
[^{0}C]	[h]	[g/m^2]	
900	1	4.68	30.45
	3	22.08	34.46
	5	23.37	32.44
	8	-	29.50
	3	-	100.07
1000	1	25.45	32.99
	3	48.51	94.48
	5	69.93	80.35
1100	1	29.44	97.47
	3	69.31	94.16
	5	73.20	194.31
1200	1	-	61.70

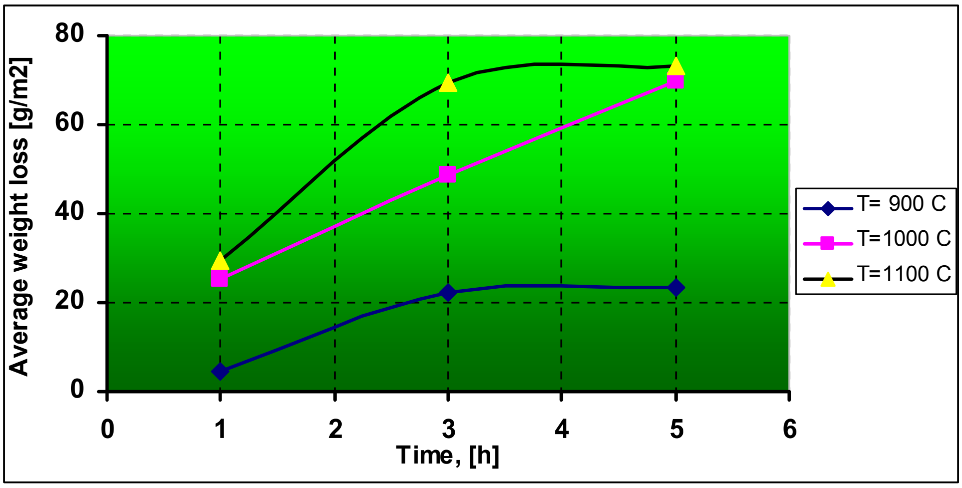

Fig. 2. Mass losses at the oxidation of grade A36

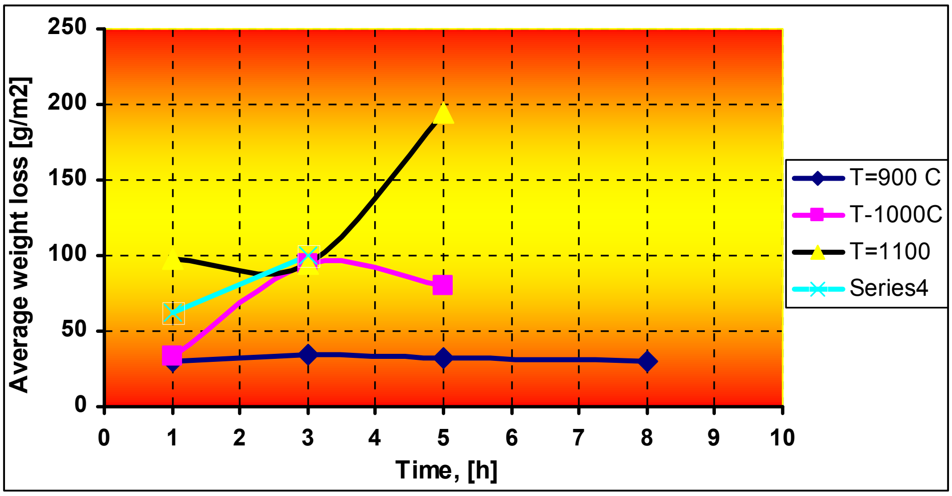

Fig. 3. Mass losses at the oxidation of grade E36

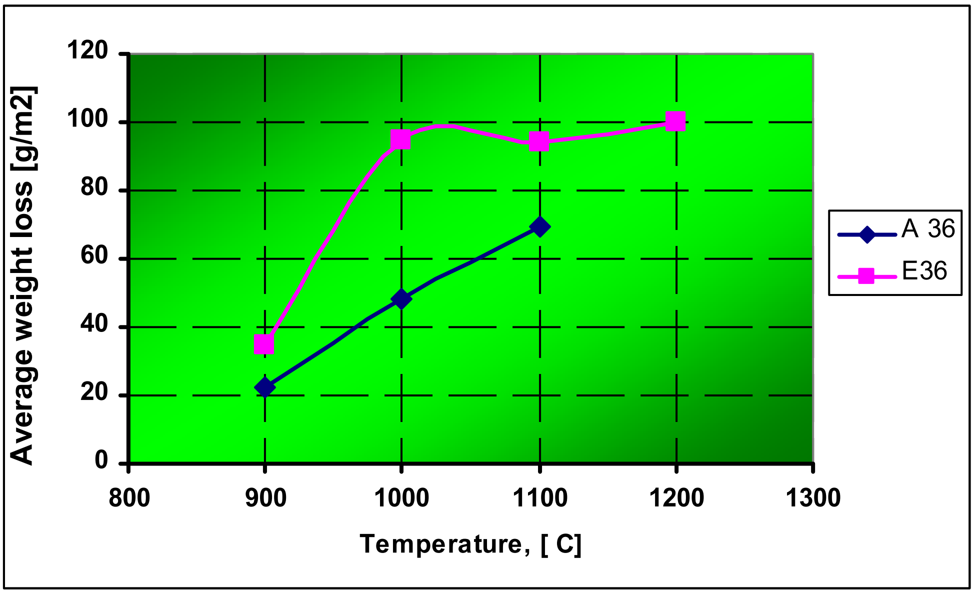

Fig. 4. Variation of mass losses with the temperature, on 3 hour duration, at grades A36 and E36

***Table 3**. The speed of oxidation of the steel samples according to the heating regime*

Heating temperature	**Holding time**	**Average speed of oxidation A 36**	**Average speed of oxidation E 36**
[^{0}C]	[h]	[g/m^{2}h]	
900	1	4.68	15.23
	3	7.36	11.55
	5	4.67	6.49
	8	-	3.69
1000	1	25.45	32.99
	3	16.17	31.49
	5	13.99	16.07
1100	1	29.44	97.47
	3	23.10	47.08
	5	-	38.86
1200	1		61.70
	3		33.36

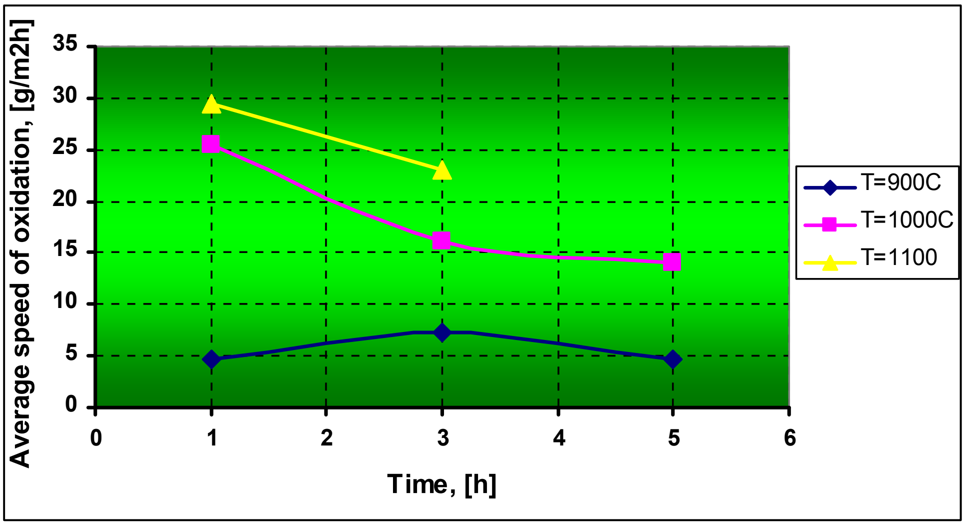

***Fig. 5.** Average speed of oxidation of the A36 steel samples according to the heating regime*

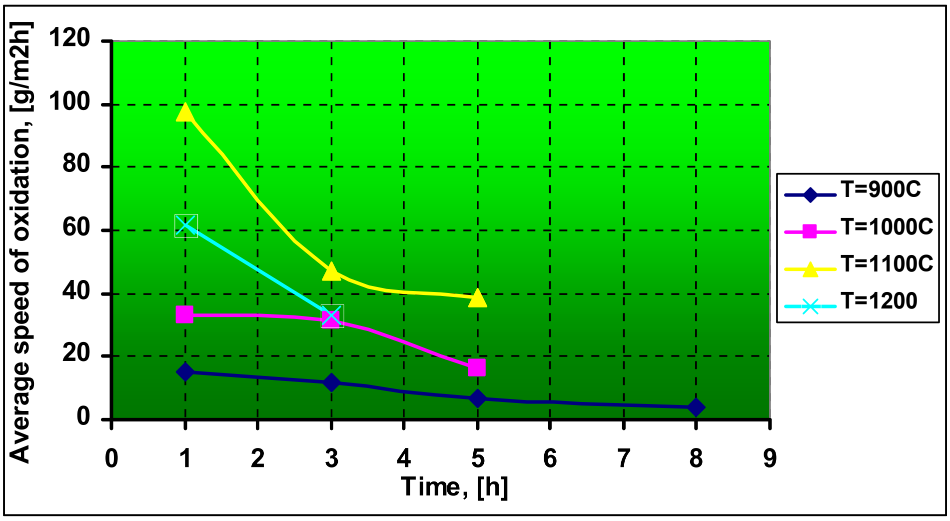

***Fig. 6.** Average speed of oxidation of the E36 steel samples* according to the heating regime

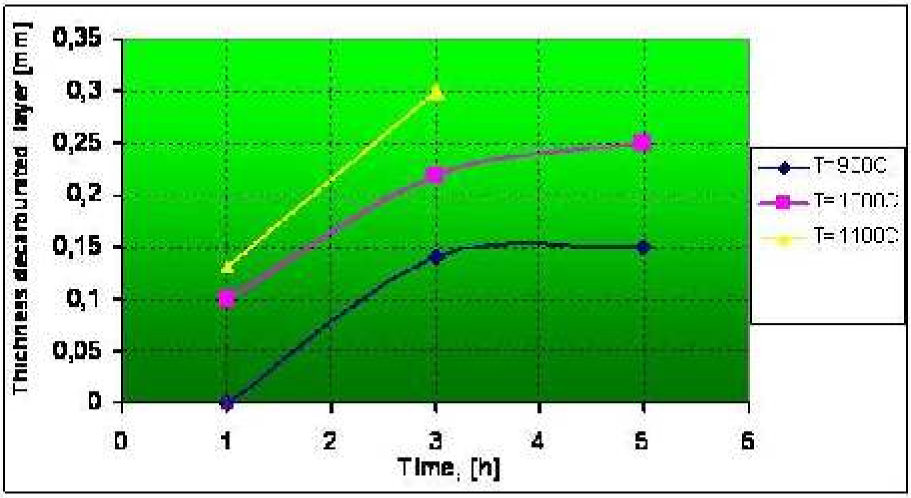

Fig. 7. Variation of the depth of the decarburized layer with the maintenance duration and heating temperature for the grade A36

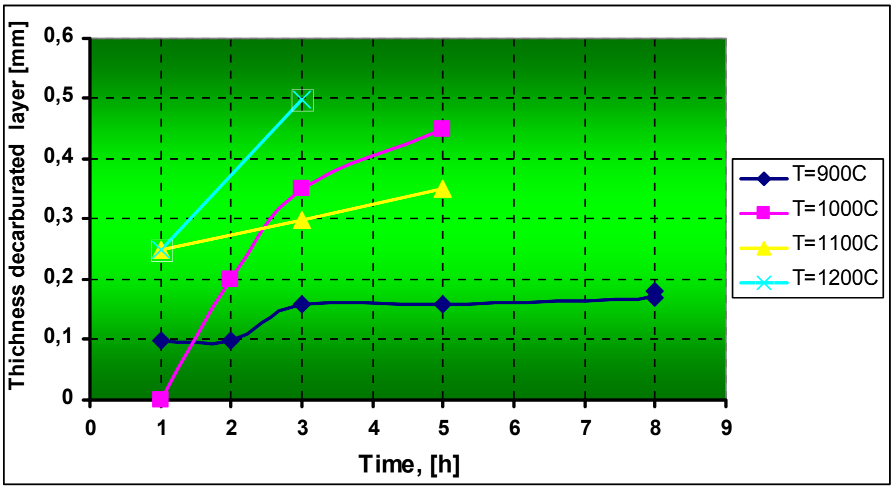

Fig. 8. Variation of the depth of the decarburized layer with the maintenance duration and heating temperature for the grade E36

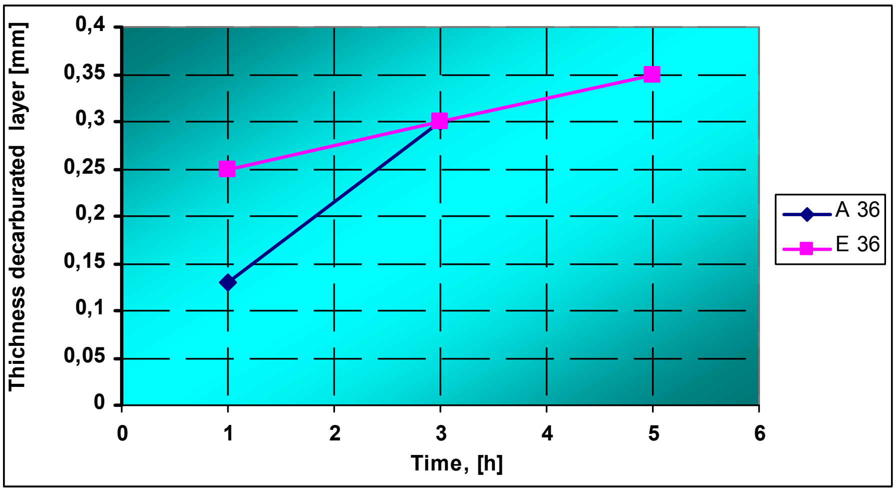

Fig. 9. Variation of the depth of the decarburized layer with the maintenance duration at 1100°C for the grades A36 and E36

Below there is presented the graphic variation of the depth of decarburization measured on the studied steel samples according to the experimental heating regime.

The microscopical aspects on the structural changes of the heated steel samples taken from shipbuilding plates

Steels analyzed and presented in Table 1 are additionally deoxidized with aluminum and present a medium to fine granulation.

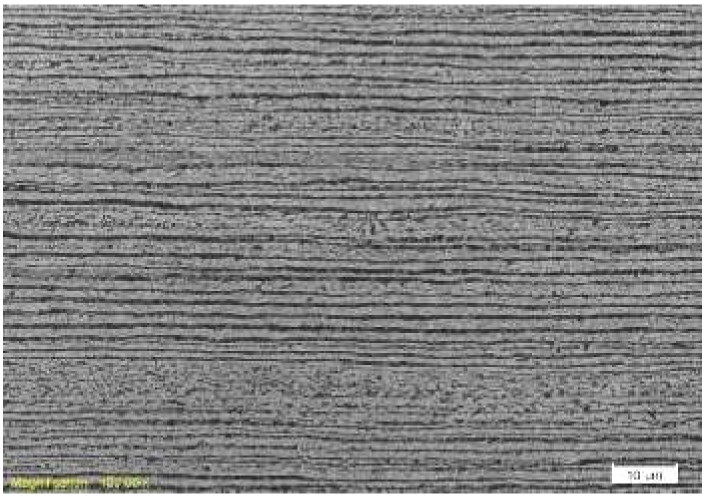

***Fig. 10**. Rolled State (X100, natal 3%), sample from shipbuilding steel A36, thickness 16 mm, ferrite and pearlite grains scoring 8-9, forming alternative rows score 4*

To observe the growing trend of austenitic grain together with increasing temperature and duration of maintenance, in the laboratory it was simulated the hot metallurgical processing through performing the heating of the samples at different temperatures and durations. The results for the A 36 steel highlight the growth of the austenitic grain for the next thermic regimes experimented: temperature of 880°C and 930°C and maintaing time of 2, 3, and 5min/mm.

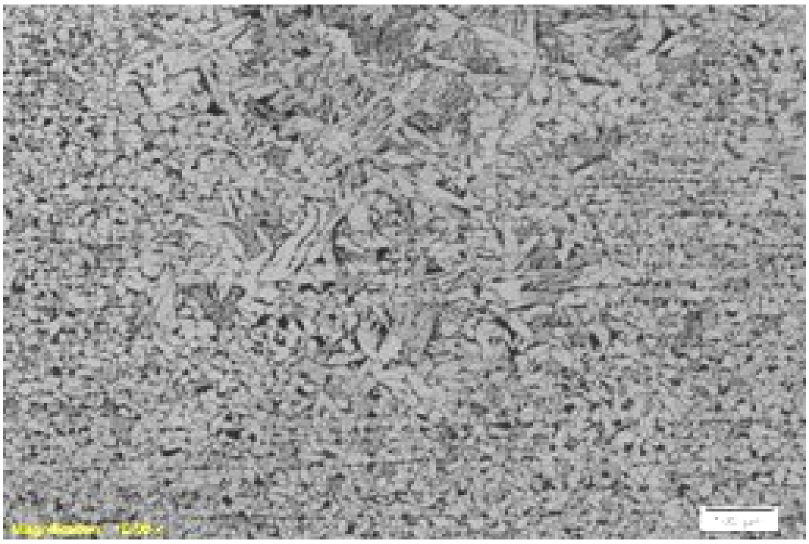

***Fig. 11.** Wd structure score 3-4, A36 samples subjected to heating regime: temperature 880°C / 3.0 min / mm holding time*

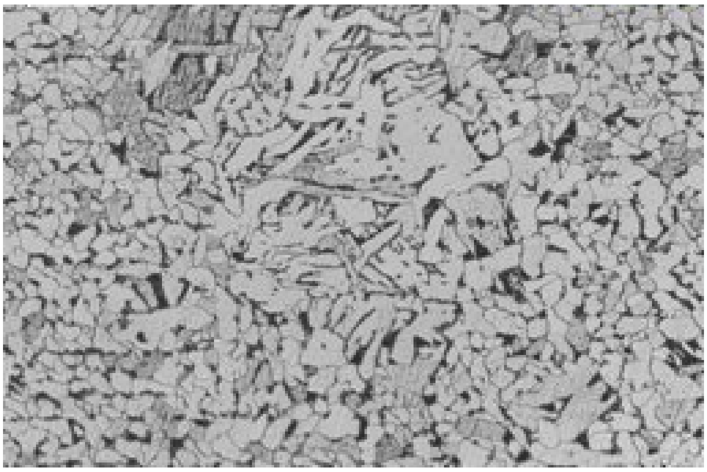

Fig. 12. *Wd structure score 3-4 A36 samples subjected to heating regime: temperature 930°C / 3.0 min / mm holding time*

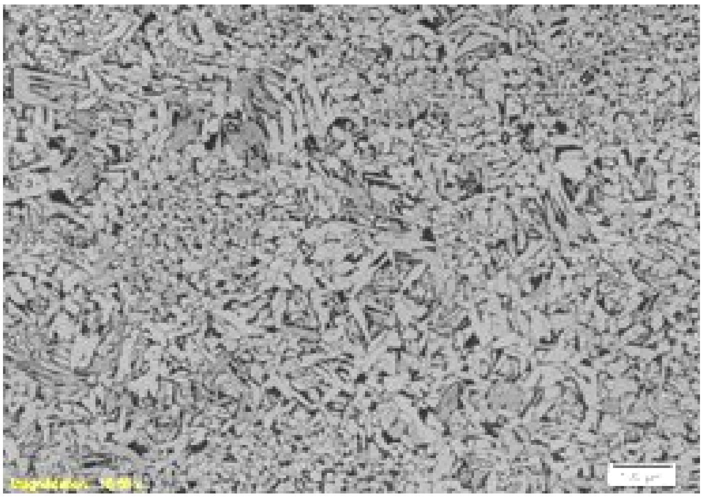

Fig. 13. *Wd structure score 4 A36 samples subjected to heating regime: temperature 880°C / 5.0 min / mm holding time*

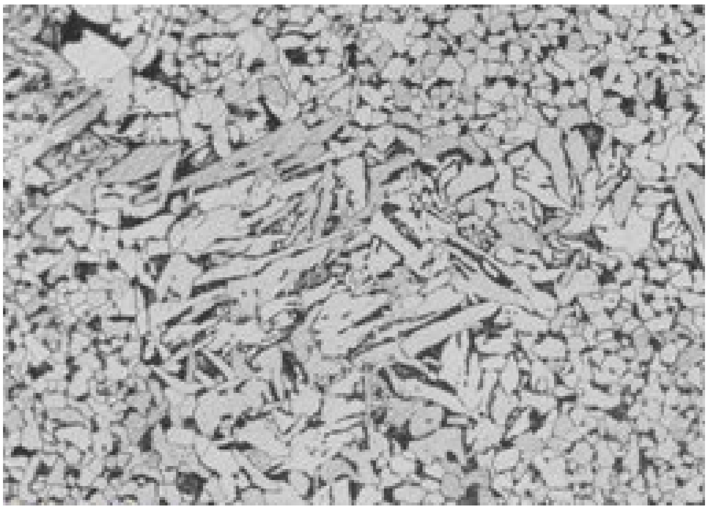

Fig. 14. *Wd structure score 4 A36 samples subjected to heating regime: temperature 930°C / 5.0 min / mm holding time*

4. Conclusions

The analysis of the oxidized samples revealed the presence of a porous oxide layer that detaches easily from the surface by rubbing, and a bright appearance coating, adhering to the surface, which is removed only by hot etching. The weight loss by oxidation / unit area, due to the formation of porous oxide, non-stick, it is negligible at 900˚C and increases with the temperature in the range of 900-1100˚C, for both steel grades studied. At a temperature of 1200˚C, the weight loss recorded for quality E36 is lower than at the temperature of 1100˚C, fact explained by the formation of adhesive oxide in larger quantities.

Of the two steel grades considered, at least in the temperature range 900-1100˚C, the oxidation process was more intense at E36 brand. The speed of oxidation increases with increasing temperature, higher in the first stage of oxidation, for 1 hour, and then decreases with the lasting period, being maximum at temperature of 1100˚C. Oxidation rate is also higher for steel E36. The depth of the decarburized layer increases with higher temperature (as a result of increased diffusion processes) and is less influenced by the duration of maintaining the temperature at 900°C. The influence of the maintenance period on the decarburization process is accentuated when the temperature rises.

Quality steel E36 exhibited higher decarburization tendency compared with to that of A36 steel, a conclusion that allows the adoption of appropriate technological solutions to hot metallurgical processing of products belonging to this quality of steel.

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RECYCLING OF CELLULOSIC WASTE IN THE ENERGY SECTOR

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ABSTRACT

Biomass is one of the Earth's most abundant and precious resources. It offers not only food but also energy, materials used for construction, chemicals and much more. Biomass has always been used for generating energy since fire was discovered. The term of biomass covers a wide range of products, derived products and waste obtained from agriculture, forestry, including those derived from farming, domestic and industrial waste. This paper aims at investigating the main characteristics of the briquettes made out of wood, wood chips and sawdust.

KEYWORDS: biomass, briquettes, renewable energy

1. Introduction

Biomass is one of the Earth's most abundant and precious resources. It offers not only food but also energy, materials used for construction, chemicals and much more. Biomass has always been used for generating energy since fire was discovered. The term of biomass covers a wide range of products, derived products and waste obtained from agriculture, forestry, including those derived from farming, domestic and industrial waste [1]. The use of biomass for obtaining energy can bring significant social and economic benefits for both rural and urban areas. The current lack to access convenient energy sources is limiting the quality of life worldwide, especially in the rural areas of less developed countries. Biomass cultivation is an intense rural activity, which can lead to the increase in the job opportunities in the rural areas and can stop the migration from villages to cities. At the same time it offers the possibility to develop other rural industries [2]. Below are shown the future estimated costs of a kWh produced by various technologies including biomass (Table 1) [3].

Table 1. *The future estimated costs produced by various technologies* [1]

Technology	Costs in 2020 [Euro cent/kWh]	Cost Trend in 2050
Combined Production of Electricity and Heat in Large Units	< 3.2	limited reduction
Combined Production of Electricity and Heat in Small Units	4.0-5.6	sustained reduction
Photovoltaic	15.9-25.4	sustained reduction
Onshore Wind Turbines	2.4-4.0	reduction
Offshore Wind Farms	3.2-4.8	reduction
Biomass Energy	4.0-6.4	reduction
Fossil Fuel Energy	4.8-7.2	unknown
Nuclear	4.8-6.4	reduction
Combined Cycle with Gas Turbine (CCGT)	3.2-3.7	limited reduction
Combined Cycle with Integrated Coal Gasification (IGCC)	4.8-5.6	reduction

2. Experimental research

The main biomass source is wood. Besides wood, there is a wide variety of other resources like:

- crops for energy purposes;
- fast growing trees: poplar, willow, eucalyptus;

Waste:

- wood obtained from chopping the trees and from constructions;
- derived products:
- waste from wood processing (sawdust, shavings).

The technological technique of processing wood is shown in Figure 1 [4].

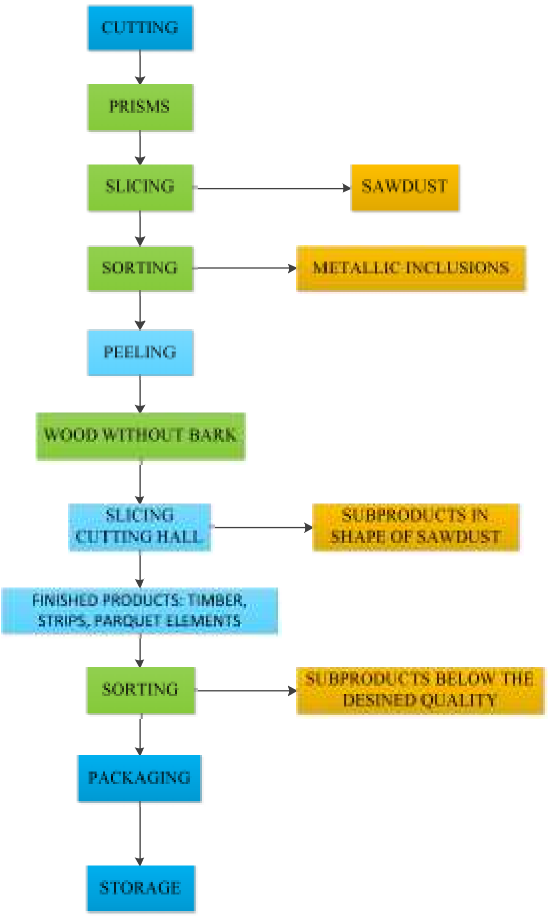

Fig. 1. *The technological process of wood processing*

Through briquetting the volume of sawdust is lowered so this eases the transportation and the storage. The experiments done on the briquettes have proven that they have a high caloric power of approx. 4200 kcal/kg. Also the heating costs are much lower in the case of using briquettes.

An important advantage of briquettes is that they can be easily lighted and the quantity of ash, as a result of their combustion is very little. If there are taken into account the costs and efforts for chopping and transporting the wood, the use of briquettes can be considered an economic and ecologic solution [5].

To conclude, the briquetting process consists of a production line with a waste sorter, heating system, sawdust dryer, briquetting machinery and auxiliary elements used in transportation. The stages of this process are as follows:

1. The first stage consists in the separation of sawdust from all other waste sawdust which may affect the proper functioning of the machinery.

2. It is followed by the operation of heating and drying the wastes, because the wet sawdust cannot be turned into briquettes. For this reason very useful assets are a heating system and a sawdust dryer, which give a maximum humidity of 17% (these are the optimal process conditions).

3. The final stage involves starting the briquetting machine, which turns the sawdust into briquettes; the machine presses the sawdust until the air from the wood chips is evacuated [6].

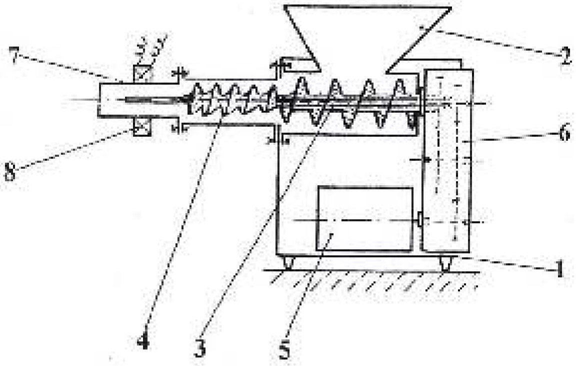

Fig. 2. *Screw briquetting plant scheme*

They do not contain additives as resins are naturally found in the briquettes and they have the scope to keep them compact, thus no additives are required. By using the wastes after the wood processing we obtain a valuable product, respecting and protecting nature [7].

Waste and environmental damage reduction after burning: after burning the briquettes, it remains very little ash, not more than 10% from the initial burned quantity; this ash can be used as soil.

Good price/efficiency ratio – heating costs based on sawdust briquettes is up to 60% less than the costs where petrol is used [8].

Higher efficiency than wood – due to the low water content and due to the material’s density.

For wood, after combustion the ash quantity is up to 50% from the initial wood amount, compared to the sawdust briquette which is 10%.

High caloric value – sawdust briquettes have the caloric value between 4000-5500 Kcal/Kg, while for wood is between 1800-2000 Kcal/Kg.

Long combustion interval – higher than wood or charcoal.

Biomass can be considered as one of the most important renewable energy sources. In general terms, it can be said that biomass includes a wide range of materials such as: agricultural and technical plants, agricultural and forestry waste, etc. This paper aims at investigating the main characteristics of briquettes made out of wood, wood chips and sawdust [9, 10].

Different manufacturing companies show that sawdust briquettes are blocks of sawdust or organic solid blocks made out of wood chips. These are obtained at a high pressure and without extra additives and can be used for burning solid fuels, barbecue fire, water boilers, central heating, etc. The characteristics of the wooden briquettes are as follows (based on the European standards ONORM M7135 in Austria and DIN 51731 in Germany): operative humidity 4.6%, ashes mass 0.2%, amount of sulfur 0.01% and caloric power for the absolute dry mass of the briquettes 20370 kJ/kg [11, 12].

Main advantages of the briquettes in comparison with the massive wood:

- low ash content;
- lack of odour;
- high caloric value;
- long combustion period;
- high combustion temperature;
- combustion with sparks;
- no emission of toxic gases.

These sawdust briquettes can successfully replace brown coal, wood and natural gas.

For the tests there were used technological splinters and sawdust. The raw material was taken from the tenoning machine found in the university’s laboratory. There were used two types of debris, wood chips and sawdust from spruce (Picea abies L) and beech (Fagus silvatica L). To prevent the blockage of the tenoning machine, for each type of raw material was extracted alittle sawdust (0.5×0.5 mm). In this way the technological splinters were defined as a fraction greater than 5×5 mm and the sawdust as a fraction between 0.5×0.5 and 5×5 mm.

The above values represent the sieve mesh sizes. The experiments were performed on a machine with two briquetting pistons for compression, as depicted in Figure 3.

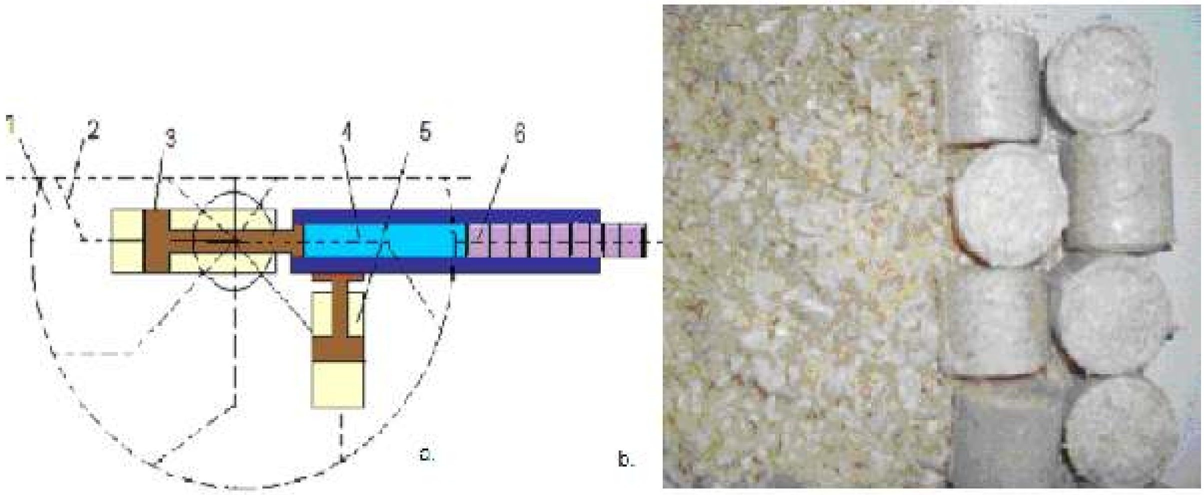

Fig. 3. *Briquetting machine (a) and briquettes (b): 1 – silo storage; 2 – pallet supply; 3 – main compression piston; 4 – extrusion canal; 5 – supply and compression of secondary piston; 6 – compressed briquettes*

The briquetting machine created the wooden briquettes by pressing with two hydraulic pistons, one for the power supply and the primary compression, and the second (the main one), for a strong compression.

Depending on the amount of the wooden chips introduced in the compression canal (Canal 4), there can be obtained briquettes of different lengths (range 20-90 mm), but with the same diameter (40 mm).

2.1. Briquettes density

Analysing the briquettes density (defined as the ratio between mass and volume), it can be observed that different densities are obtained from different types of raw material.

The density of briquettes made out of spruce (837 and 878 kg/m^3) is less than the one obtained from beech wood (896 and 921 kg/m^3), this is due to the fact that the spruce’s density (450 kg/m^3) is less than the beech’s density (680 kg/m^3). There is no proportionality between these two densities, because the ratios are 1.86 and 1.95 (1.31 for spruce and 1.35 for beech).

This means that the spruce is a more compressible species, due to the porous structure.

On the other hand, it appears that the technological shavings are less compressible than the sawdust for both species and the reason is that dimensions of the raising coefficients are different.

2.2. Resistance to compression

The resistance to compression shows the consistency and compacting of the briquettes. There is no similar resistance in this field, only just some similarities with the massive wood, wooden fibres and concrete. On this basis was developed a new procedure to determine the resistance to compression, perpendicular to the briquette’s length. The upper platen usually represents the main part of the machinery. The results are shown in Table 2.

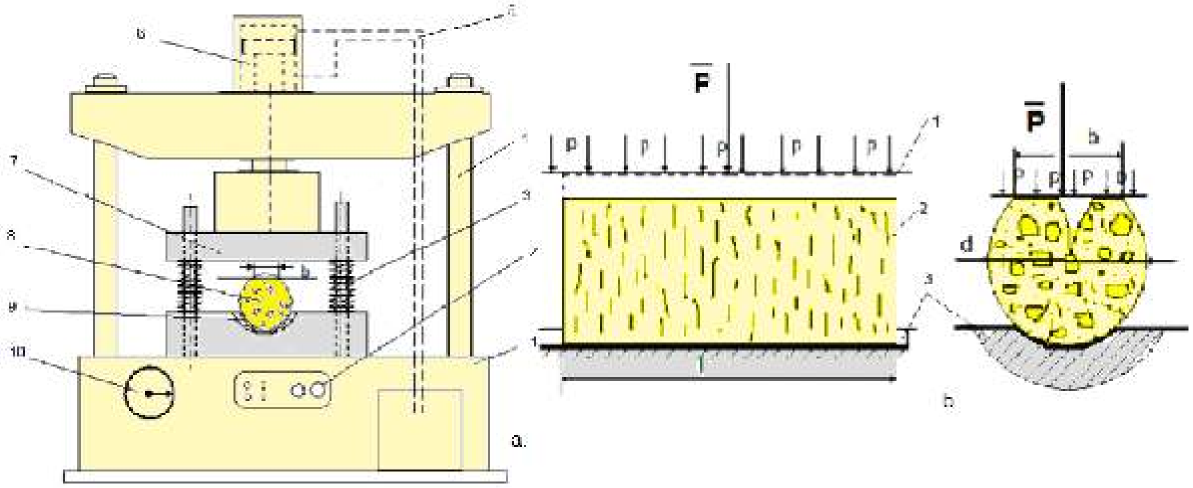

Fig. 3. *Determination of resistance to compression of briquettes – testing machine: 1 - frame; 2 - picture; 3 - springs; 4 - columns; 5 - pipes with hydraulic agent; 6 - cylinder-piston; 7- upper platen; 8 - briquette; 9 – lower platen; 1 0 – dial; – working principle: 1- area of force’s application; 2 - briquette; 3 – lower platen*

Table 2. *Compressive strength of briquettes*

No.	**Diameter**	**Force [N]**	**Dimensions of pressing plan [mm]**		**Compressive strength [N/mm^2]**
			Length	**Width**	
1	Ø = 40 mm	3700	75	35	1.409
2		3300	74	32	1.393
3		1400	45	28	1.111
4		1600	38	30	1.403
5		1600	37	37	1.168
6		1500	30	26	1.923
7		1800	37	24	2.027
8		2100	26	37	2.182
9		2000	48	31	1.344
10		2200	62	30	1.182
Medium value of compressive strength [N/mm^2]					1.514

These characteristics determine the quality of the briquettes which were obtained using various machines (usually mechanical or hydraulic) and provide data regarding the fields where these can be used (stoves, central heating or power plants). The following research will be focused on the calorific value of briquettes and the wood biomass from which these were obtained. The importance of the studies carried out on this topic is given by the fact that briquettes are organic products made from biomass, gathered from the individual households, but mostly from wood processing companies.

3. Conclusions

In terms of biomass consumption in Romania are used different bio-fuels, as follows:

- wood-based fuels, used for industrial and steam boilers or for water heating used in various industrial heating processes;
- wood-based fuels, used in warm water boilers, with outputs of thermal power varying between 0.7 MW and Unit 7 MW;
- stoves and wood - stoves and/or various agricultural waste, used for individual heating and food warming, etc.

The advantages of using briquettes for heating our houses are numerous. Here are a few reasons why these should be used:

Cost by 80% less than the fossil fuel cost;

It is a renewable energy source;

Heating systems based on briquettes do not contribute to the decrease in the ozone level; they are considered to be in line with the Kyoto agreement regarding the gas emissions in the atmosphere;

Wood briquettes are easily transported (compact bags);

No trees are cut for the briquette’s production; they are made out of the wood waste;

The heating systems based on briquettes are mostly automatic systems, which require very limited involvement from the operator;

Briquette’s costs are stable and they are not subject to the foreign manufactures’ increase;

Briquettes are burning at a very high temperature, eliminating very few remains (100 kg of briquettes produce only 0.5 kg of ash);

The American agency of environmental protection considers heat from wood briquettes to be one of the cleanest burnings and one of the most renewable energy source on the planet;

The main practical direction in research for improving the properties of wood briquettes is the activation of lignin from the wood particles, especially in the outer areas.

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SIDERURGY SLAGS RECOVERY IN BUILDING INDUSTRY

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ABSTRACT

During the metallurgical processes of iron and steel elaboration, besides the basic products, it results a serious of secondary products (wastes) in high quantities but with a high recycle – recovery potential, and their reintroduction in the economic circuits. In this paper, we are going to refer strictly to the working and the recovery of the blast furnace slags, respectively to LD converter slags, without insisting on the formation mechanism and slag reactions.

KEYWORDS: slag, recovery, magnetic separation, ferrous particles

1. Introduction

The blast furnace slags got variety of uses, both in state directly worked in the metallurgical plants in a non-processing cool state. Having in view the technological demands of the fabrication process of the cements, especially from point a view of the finesse crushing as well as of the chemical composition, in this respect it is imposed in advanced iron elimination of the converter slag.

2. The blast furnace slag

The totality of the non-reductible oxides as well as different metals combinations enter in the structure of the blast furnace slags.

The sterile of the iron ores as well as the coke ash contain mainly SiO_2 and Al_2O_3. In order to raise the stability of SiO_2 and also the other non-reductible compounds in the slags, in the furnace process, CaO is introduced either through limestone directly in the furnace charge by means of the agglomerate. For the same goal and also for the improvement of the slag properties the MnO is used.

The introduction of the CaO and MnO in the furnace charging is made in a well balanced ratio, correlated with the SiO_2 and Al_2O_3 contents, brought by the metallic charge and cokes.

The reason for the flux introduction is based on the formation of complex chemical combinations with low melting points, smaller than of every oxide in the composition taken separately. In the furnace slags these, as main components, cover about 90% from the totality of constituents.

The ratio between the calcium and magnesium oxides and that of acids oxides, meaning SiO_2 and Al_2O_3, represents the degree of chemical activity of the slags known under the name of basicity number.

Basicity number can be analyzed under many aspects, function of the number of base oxides, respectively acid oxides which were taken into consideration. In order words, the whole basicity number can be calculated by using the following relation:

$$I_b = \frac{(CaO + MgO + FeO + MnO)\%}{(SiO_2 + Al_2O_3)\%} \tag{1}$$

For the current usage conditions utilization, the appreciation of the slag basicity is made only by simple ratio:

$$I_b = \frac{(CaO)\%}{(SiO_2)\%} \tag{2}$$

The acid slags are recognized by the filiform aspect during the following process; they have a glassy aspect, brown when they are enough hot or dark brown towards black when they are cold, the content of the FeO for these ones surpassing 2-3% in composition. The basic slag generally recognized with values of 1.2-1.4 of the basicity number given by the ratio CaO/SiO_2 are much higher, the crystalline lattice is breakable during the following processes, they are more fluid, gather an important quantity of heat because of special refractoriness. In Table 1 several chemical compositions of some furnace slags are given.

Table 1. *The chemical compositions of some furnace slags*

Sample	**Composition,** [%]						
	SiO_2	**Al_2O_3**	**CaO**	**MgO**	**MnO**	**FeO**	**CaS**
1	28.1	22.1	41.14	3.0	0.46	0.20	5
2	32.11	15.06	45.17	1.0	0.45	0.21	6
3	32.42	12.16	46.37	1.2	0.7	0.75	5
4	38.40	10.10	41.9	2.5	1.88	0.22	5

The blast furnace slags processing

The most used working procedure of the blast furnace slags is granulation, the product having uses especially in a cement industry. The crystalline slag can be used for the pavement fabrication or in roads building, after having been breakable.

The slags which have a high content of CaO can be used in agriculture, for acid soil treatment. The expansion slag can be used as a thermo-isolator in building industry. The slag as a glass wadding can be used also as a thermo-isolator.

3. The LD converter slag

At the steel elaboration in LD converters, taking as example Arcelor Mittal Steel Galati, important slag quantities result. The characteristics of this slag are much more different from those of blast furnace slags. These differences consist both in the chemical composition and in working possibilities.

Because these slags contain also iron in free state there is no possibility of a sudden cooling through granulation and expansion. In the chemical composition, the LD converter slag we have FeO 16-22%; SiO_2 8-12%; CaO 41-53%; MgO 1-3%; Al_2O_3 3-5% and others.

The processing of LD converter slag

Because of its composition, the LD converter slag has another working technological process as follows: the liquid slag is transported by means of slag ladle towards the slag dump where processing takes place; in this place the slag ladle are poured out, in the working front where, for two weeks, the slag is sprayed with water in order to be cooled. After the cooling process it is taken with excavator and it is poured out in the maturation front. In these fronts, the slag will stay six months while, periodically, it is sprayed with water. In this way a part of calcium oxides and other levigables components are eliminated.

At the end of the maturation process, the slag enters in the working cycle which contains more technological operations such as:

- excavation and transport at the processing plant;
- sorting and eliminating rough iron;
- breakage;
- magnetic separation of ferrous components;
- sorting on particle size range;
- dispatch to customers.

The aggregates resulting from this process, called „LIDONIT" have a high hardness and it is useful for roads building, roads repairs, ditches and billows protection, hydro-technical works.

4. The obtaining of the cements from metallurgical slags

Taking into account the physical and chemical properties of the metallurgical slags, mentioned above, we began from the idea of eliminating the iron (under free form and under oxides form) and the calcium oxides from the steel works slags; the remaining quantity can be used as raw materials basis for some refractory products.

Two kinds of Lidonit were used for making experiments. After a fine divided crushing of the two samples, there were made chemical analyses in the laboratory. In Table 2 we can see the composition of the two samples.

Table 2. *The composition of the samples*

Sample	**Fe**	**Mn**	**SiO_2**	**CaO**	**MgO**	**Al_2O_3**	**PC**
	[%]						
Sample 1	22.64	5.49	11.49	41.20	1.95	3.70	abs.
Sample 2	22.50	5.56	11.35	41.28	1.76	3.80	abs.

After the chemical analysis it followed the sampling of 100g from each sample, ± 0.001g.

Both samples were magnetically separated, in order to eliminate the iron, obtaining the following results: -sample 1: from 100g were magnetically separated 31.4g and remaining 68.6g.

- sample 2: from 100g were magnetically separated 31.4g and remaining 69.9g.

After this separation, it followed a new set a chemical analysis for the processed samples, the results are shown in Table 3.

Table 3. *The composition of the samples*

Sample	Elements, [%]						
	Fe	Mn	SiO_2	CaO	MgO	Al_2O3	PC
Sample 1 A (31.4 g)	76.35	2.54	5.75	4.56	1.04	1.85	abs.
Sample 2 A (68.6 g)	5.91	3.52	15.56	48.47	2.24	6.53	abs
Sample 1 B (30.1 g)	72.87	2.28	6.12	4.98	2.07	2.15	abs
Sample 2 B (69.9 g)	7.27	4.01	17.24	49.11	2.69	7.01	abs

Then, we had in view eliminating the calcium oxides from sample 2A, respectively, 2B, by combining them with water; according to the reaction $CaO + H_2O = Ca(OH)_2$, at one of the samples, there is a small quantity of water, after about 48 hours, this one was subdued to a series of hydrolyze reactions, after which a dense and tough mass was made similar to cement.

In order to find new opportunities for high recovery of the metallurgical slags, with the aim of obtaining some common cement, at acceptable price – quality ratio, we are going to refer to some information from the cement industry and construction materials.

Hidratation of the mineralogical component of a cement

The cement is obtained by calcinations a mixture of chalkstone and clay in adequate proportions in order to obtain the final requested composition.

The components, finely crushed and well mixed are burnt in tubular rotary furnaces, at 1400 – 1450^{0}C. The material which, after a beginning of melting process, takes the shape of brown (clincher) grains, is then crushed very fine (15% residues on the separating screen with 4900 hole on cm^2), an important operation for obtaining a good quality.

The cement is a mixture of calcium basic silicate, calcium aluminates and ferrous calcium.

The strengthening of the cement during the hydration process takes place because of the formation of hydroxides and aluminates calcium, while the silicates are transformed into calcium colloidal hydro-silicates, by means of which the mass adherence is made.

The hydration – hydrolyze of the calcium silicates

The cement being a silicate binding, the hydration - hydrolyze of the calcium silicates has an essential role in the strengthening process. From the two calcium silicates components of the Portland cement the tri-calcium silicate and bi-calcium silicate, the first presents, in comparison with water a much higher reactivity (capacity of hydrolyze) at the interaction with water of the calcium silicates, at the beginning on the binding grains surfaces are formed a calcium hydro-silicate rich in the calcium oxide with the ratio Co / SiO_2 (C / S) similar to that of the anhydride substrate (hydrate I) which is later transform the with high speed in a slow basic hydro-silicate – hydrate II (C/S ≈ 0.8 – 1.5), this one transforming in a stable hydro-compound - hydrate III (C/S ≈ 1.5 – 2). The products of the interaction between the calcium silicates and the water present forms with different degrees of ordinations, with very small submicroscopic dimensions (gels).

The ratio CaO/SiO_2 of the hydro-silicates from straightened calcium silicate paste depends, especially, on the hydration. Under normal conditions of temperature and pressure, it is stated, generally, that the final value of the ratio C/S is between 1.6 and 1.9. Although the composition of the phases existing in paste of $3\ CaO\cdot SiO_2$ (C_3S) and β-$2CaO\cdot SiO_2$ (C_2S) is the same, the ratio which are establish between them are different, is emphasized especially the bigger proportion of calcium hydroxide from the paste of tri-calcium silicate (C_3S).

The tri-calcium silicate interact quickly with water, thus in a couple of minutes around binding grains is appears a network of fibrous calcium hydro silicates.

These forms grow and fill rapidly spaces between the grains of tri-calcium silicate. The specific surfaces of the calcium hydro silicates from the calcium silicate pastes which straighten, the surfaces correlated with its structural compositional characteristics is between 1x10^5 and 4.5x10^5 m^2/kg, fact that leads to a medium size of the particles (considered spherical) of 80 – 100Å. The specific surfaces decrease at the same time with growth of molar ratio CaO/SiO_2. Aluminates and calcium ferrite-aluminates influence in a high degree both the straightening process and the properties of the cement stone. The tri-calcium aluminates are characterized by interaction speeds with water higher then calcium silicates. The chemical composition of the cement is given in Table 4.

***Table 4.** The chemical composition of the cement*

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	SO_3	CO_2+H_2O
18-26%	4-12%	2-5%	58-66%	1-5%	0-2%	0.5-2.5%	0.5-5%

4. Experimental results

Following these aspects we can notes some similarities regarding the composition of the metallurgical slags and of the Portland cements. By using both kinds of slags (furnace and LD converter), in some proportions through very fine crushing in ball mills and by adding some additive (sodium silicate, gyps, lime) it is possible to obtain a kind a cement with good properties but with a low cost. In this way we raise the value of the slags and of the slags aggregate which now are sold with 4 – 6 USD / tons.

In the practical experiments from the same samples lot we pasted to a crushing and a magnetic separation of the iron.

Up to now these were made experiments on four different dosing and on there basis they were made the same number of samples.

The samples were made in conformity with SR EN 196-1 and SR EN 196-3 / 2002, with the dimensions shown in Figure 1.

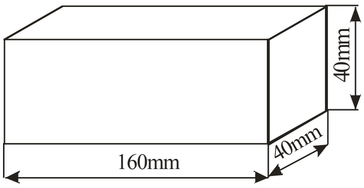

***Fig.1.** Sample dimensions*

For the experiment they were made the following samples:

1. Lidonit (570g) + $CaSO_4 \cdot H_2O$ (30g) + water (285g);
2. Lidonit (510g) + $CaSO_4 \cdot H_2O$ (30g) + CaO (60g);
3. Lidonit (250g) + granulated slag (250g) + CaO (50g) + gyps (50g);
4. Lidonit (230g) + granulated slag (230g) + cement (50g) + CaO (60g) + gyps(30g).

In Figure 2 it is represented a plant of magnetic separation; which can achieve a iron separation about 99%.

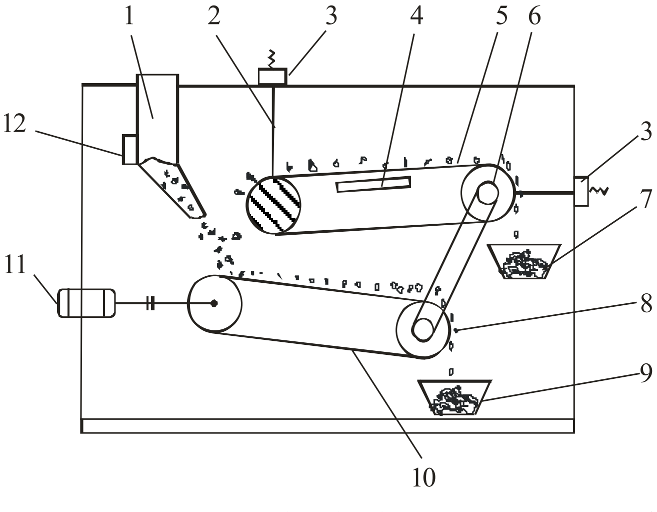

***Fig. 2.** Plant for magnetic separation: 1-powders bunker; 2-rotor; 3-system for tension of the strip; 4-demagnetizor; 5-superior strip; 6-wheel for strap; 7-vat for ferrous particles; 8-mineral particles; 9-vat for minerals; 10-inferior strip; 11-motor; 12-vibrating machine*

5. Conclusions

Having in view the technological demands of the fabrication process of the cements, especially from point a view of the finesse crushing as well as of the chemical composition, in this respect it is imposed in advanced iron elimination of the converter slag. Regarding the separation of the iron from the slag we can use successfully a magnetic separation plant of the steel powders resulting from the finishing operation.

This metallic powder contains a quantity of mineral components torn off from rectification stone during the chip less process (Al_2O_3 and SiO_2). Removing the mineral components included in the metallic powder is made with special plant based on magnetic attraction phenomena.

Another economic advantage regarding the above mentioned things is represented by the recovery of the ferrous particles magnetically separated. Having in view the fact that the separated metallic fraction contains over 70% Fe and iron oxides, these can be sending to the Agglomeration section or it can be combined with the cokes powder from UCC and, in the presence of a binding, to be made ferro-coke briquette.

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EMPHASIZING THE TOXICITY OF HEAVY METAL IONS ON PLANTS: MONITORING WITH AN AMINO ACIDS ASSAY

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ABSTRACT

In order to emphasize modifications on living organisms resulted from interaction with heavy metals, we applied a simple, sensitive, quick, inexpensive and reproducible method. It evaluates modifications through determining released amino acids. This method comprises three stages: treating plants with the investigated heavy metals, extracting resulted amino acids and dosing them with a ninhydrin reagent. The colored solution resulted from ninhydrin dosing is spectrophotometrically measured at 516nm. The Lambert-Beer law is valid within the concentration field of 0-20 μg mL^{-1}.

KEYWORDS: biostructure; determining amino acids; hypoxia; germination tests; heavy metals; ninhydrin reagent

1. Introduction

One of the main worldwide issues today is represented by the need of protecting the environment and human health. This requires prevention and monitoring the pollutant contamination of our environment and alimentary products [1].

Life, as presence and manifestation in the universe, is a paradox. On one hand it is a truism, manifesting through an amazing variety of forms and properties; on the other hand, the phenomena complexity overwhelms us in such a way that all proposed patterns are, *grosso modo*, invariably limitative and reductionist [2]. Also, life is characterized by a series of conservation functions, such as defense, motion and adapting, and species perpetuation functions, such as multiplication or reproduction. It is known that most animal creatures can’t live more than several minutes without air to breathe, more than several days without water to quench thirst and maintain hydration, or more than several weeks without food to quench hunger. In absence of these supplies, life is not possible [3, 4].

Numerous physicochemical theories have been advanced to explain the nature of living matter, like the membrane, absorption and the association-induction theory. Modern biology has developed in light of molecular conception, but has not succeeded in offering a satisfactory explanation regarding the nature of living matter yet. It does not differentiate between ‘dead’ and ‘alive’. Moreover, these theories are not detailed enough for all obtained experimental data [5].

Metals with toxic potential usually present multiple harmful effects, affecting most tissues and organs and interfering with the enzymatic processes that ensure a proper organism functioning. Human exposure to metals is produced during their passing through the physical and biologic environmental compartments; the physical and chemical form of metals can change, the concentration ratio can be altered, so that metals can selectively accumulate in the trophic chain [6, 7]. Man is always exposed to a complex mixture of elements that are found in aliments, the main metal exposure source. Toxicity and metabolizing are strongly dependent on diet factors, like the chemical composition of aliments and the protein source nature. In order to estimate the potential of metallic interactions in living organisms, it is necessary to examine the relations between the ionic properties and the ions capacity of binding to organic ligands. The type of amino acids from the area of affinity with metallic ions of metalloenzymes defines, at least partially, the category of metallic ion that will be bound and will correspond to their function [8, 9].

Stress provoked by heavy metals is a major problem which affects agricultural productivity. Natural flora presents differences of tolerance for heavy metals. Some plants develop well in a soil enriched with toxic heavy metals, while others can’t develop at all [10, 13].

In consequence, we used a simple method to monitor the state of living organisms, state which is dependent on their biostructure integrity. This paper refers to a spectrophotometric amino acids determination assay. Amino acids are extracted in 1M sucrose solution form plant’s biostructure, in order to emphasize a normal state or one altered by heavy metals [14].

2. Materials and methods

Reagents used for research were of analytical purity, while water solutions and suspensions were prepared with bidistilled water of high purity (milliQ, R = 18.2 Ω).

Treatment solutions: $HgCl_2$, $NiCl_2$, $Cd(NO_3)_2$, $Pb(NO_3)_2$, $BaCl_2$, $CuCl_2$ and $AgNO_3$ with concentration $2x10^{-3}$M. Blank was distilled water.

Ninhydrin reagent. 0, 4 g of ninhydrin and 0, 4 g of $Cd(NO_3)_2 \bullet 4H_2O$ were dissolved in 25 ml buffer solution with pH = 5, 5. Completion up to 100 mL was done with glycerin. Solution is prepared extemporaneous.

Buffer solution. 54, 4 g of crystalized sodium acetate was dissolved in approx. 50 mL of heated distilled water. After cooling, 10 mL of glacial acetic acid was added, as well as distilled water up to 100 mL. If necessary, pH value is corrected at 5, 5 with glacial acetic acid, respectively with sodium hydroxide.

Alcoholic solution, 80 % (v/v).

Amino acids standard solutions. A stock solution with concentration of 1 mg/mL was prepared by dissolving 0, 1 g from every amino acid in 100 mL of distilled water. Standard solutions were obtained through their corresponding dilutions. Calibration curves were traced with alanine.

Other amino acids solutions. In order to verify the proposed method, solutions containing 20μg mL^{-1} mixture of different amino acids were taken into account.

Biological material. Corn seeds (*Triticum aestivum*), Gasprom sort, acquired from the Agricultural Research Station Suceava.

Instruments. Absorbance spectra were recorded with a Libbra S35 PC UV/VIS spectrophotometer endowed with quartz cuvettes with optical path length of 1 cm.

Germination determining. Lots of 20 seeds each were treated with different solutions of biostructural inhibitors, then left to germinate on filter paper in Petri dishes. Treatment duration is 1 hour, after which seeds are disposed in Petri dishes as uniformly as possible, on double filter paper, together with a treatment solution.

Seeds are watered daily with 5 mL of bidistilled water. After 7 days, germinated, abnormal and dead seeds are counted, as well as resulted plantlets. Plants are cut from the seed level, then measured and weighed (height, H, in cm and mass, m, in g).

Extracting released amino acids. Corn plantlets (3-5 g) were harvested from the seed level and had their base soaked in 10 mL of distilled water (blank) or in the treatment solution for 1 hour. Also, during the experiments, the leaf samples were cut in 1 cm-long pieces and soaked in treatment solution for 1 hour. Next, treated samples were dabbed with filter paper and carefully introduced in appropriate tubes. Extraction solutions were added (10 mL or 20 mL) in the tubes that had been obliquely held so that the biological material remained soaked in liquid. Tubes were slowly rotated from time to time during the entire extraction. The method can be used to prove the effect of hypoxia on plants biostructure for the first time.

Determinations. 1 mL of amino acid extract from seeds or plants was pipetted in regular tubes. 1 mL of ninhydrin reagent was added.

The mixture was energetically stirred. Next, tubes were maintained in a 100 °C water bath for 60 minutes, then cooled at room temperature. 5 mL of alcoholic solution were added in each tube.

After stirring, the colored solution absorbance was read at 516 nm in quartz cuvettes against the blank. In the same conditions, the blank solution remained colorless.

Calibration curve was traced in the 0 – 20 μg mL^{-1} domain with alanine.

Statistic calculus. The standard deviation (S) and the standard deviation of the mean (sx) were calculated.

3. Results and discussions

Testing structural modifications undergone by corn seeds exposed to heavy metals treatment can be done easily, economically, quickly and spectacularly by using corn seeds exposed to germination. Germination determining will follow these steps: lots of 20 seeds each will be treated with different solutions of biostrutural inhibitors, then left to germinate on filter paper in Petri dishes. Treatment duration is 1 hour, after which seeds are uniformly disposed in Petri dishes, on double filter paper, together with the treatment solution.

Seeds are to be watered daily with 5 mL of bidistilled water.

After 7 days, germinated, abnormal and dead seeds are counted, as well as the resulted plantlets. Then, plantlets are cut from the seed level, measured and weighed (height, H, in cm and mass, m, in g).

Germination tests with various heavy metals of concentration 2x10^{-3} M.

Solutions of $Pb(NO_3)_2$ and $BaCl_2$ of concentration 2x10^{-3} M inhibit corn growing, whereas compounds with Hg^{2+}, Ni^{2+}, Cd^{2+} and Cu^{2+} of the same concentration have proved to be toxic for corn seeds (Fig. 1). In principle, watery solutions of Pb^{2+} and Ba^{2+} have approximately the same effect on corn seeds as the blank treatment (distilled water). Using the others metals leads to a decrease in plantlets height. Toxicity can be produced by the effect of Hg^{2+}, Ni^{2+}, Cd^{2+} and Cu^{2+} on seed developing, which can be more toxic than solutions of $Pb(NO_3)_2$ and $BaCl_2$.

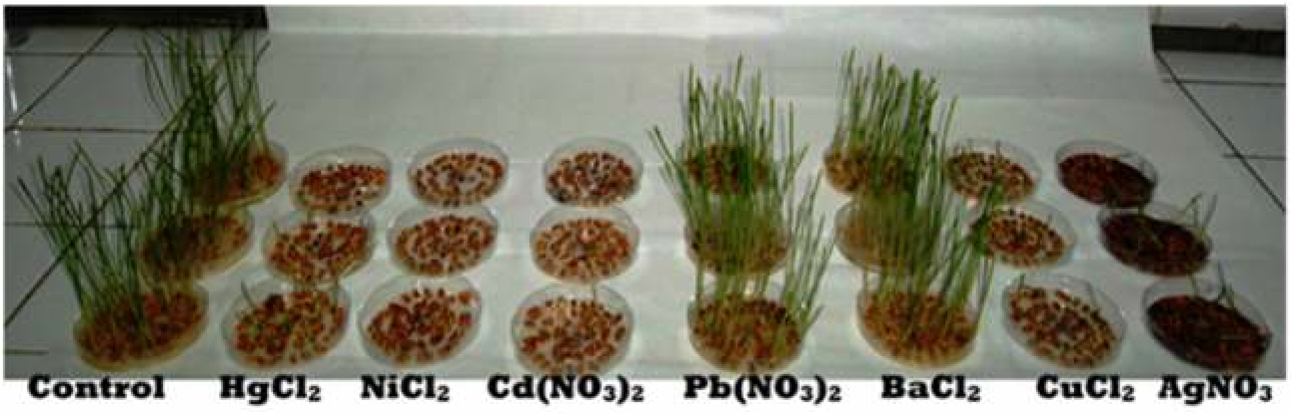

Fig. 1. *Effect of heavy metals on corn seeds during the 7 day - germination process*

Table 1. *Effect of heavy metals on corn seeds germination (50 seeds)*

Treatment *)	Plantlets	No. germinated seeds	No. dead seeds	Length plantlets (cm)	Weight plantlets (g)
Control	35.66±0.33	0.66±0.3	13.66±0.33	2.40±0.09	393.10±11.26
$HgCl_2$	11.66±0.66	3.33±0.33	35±7.57	0.33±0.21	30±1.3
$NiCl_2$	0	1.66±0.33	48.33±0.33	0	0
$Cd(NO_3)_2$	1±0.33	11.66±2.84	37.33±3.52	0.01±0.001	1.94±0.15
$Pb(NO_3)_2$	28.66±3.38	1.33±0.01	20±2.08	1.87±0.56	272.43±6.22
$BaCl_2x2H_2O$	35.43±0.88	0.66±0.01	12.36±0.88	2.315±0.2	360.13±10.09
$CuCl_2$	4.66±0.33	3.33±1.33	42±1.52	0.09±0.01	11.83±1.1
$AgNO_3$	9.33±3.17	6±1.73	34.66±3.75	0.28±0.1	37.60±5.98
*) mean of three independent values					

In this experiment, it is clearly noticeable that heavy metals have an inhibitory effect upon corn plantlets height (Table 1). For example, the most toxic heavy metals have proved to be Ni (H = 0 cm) and Cd (H = 0.013 cm). However, Ba had approximately the same stimulating effect as distilled water (length = 2.315 cm, and respectively 2.40 cm).

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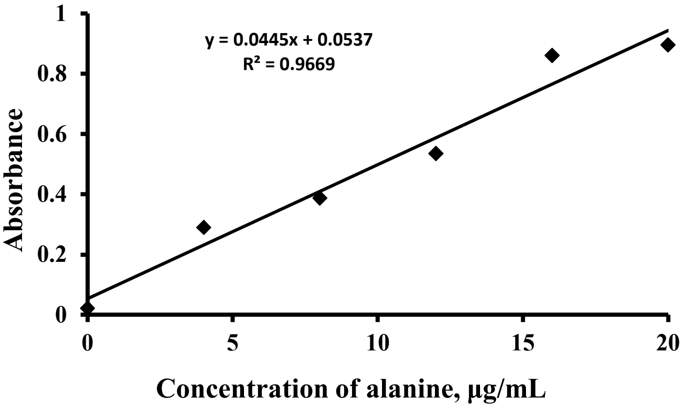

Fig. 2. *Calibration curve when determining amino acids from the extraction solution*

Calibration Curve. Absorbance of colored solutions was proportional with the alanine concentration within the entire concentration field of 0–20 μg·mL^{-1}, its increase being linear (Fig. 2). When others amino acids were used, different calibration curves were obtained.

The maximum absorbance was measured at glycine, and the minimum at hydroxyproline (Table 2). Therefore, because analyzed samples have different amino acid compositions, the calibration curve must be traced with the most suitable amino acid for each sample.

The molar absorption coefficient of the amino acid and of the amino acids mixture from the extraction solution should have similar values.
Thus, the exact amino acid which is used for achieving the calibration curve needs to be mentioned.

Table 2. *Absorbance and molar absorptivity of certain amino acids in conditions of ninhydrin reaction*[a]

Amino acid	Absorbance	Molar absorptivity	Absorbance (%, 21 hours later)
Alanine	0.790 ± 0.035	$1.758 \cdot 10^3$ ± 77.9	–7.3
Lysine	0.447 ± 0.018	$1.631 \cdot 10^3$ ± 67.3	–5.3
Tryptophan	0.332 ± 0.016	$1.696 \cdot 10^3$ ± 80.1	–5.0
Phenylalanine	0.415 ± 0.014	$1.717 \cdot 10^3$ ± 55.8	–10.0
Arginine	0.372 ± 0.018	$1.619 \cdot 10^3$ ± 79.4	–3.0
Isoleucine	0.480 ± 0.017	$1.571 \cdot 10^3$ ± 56.8	–2.0
Norleucine	0.542 ± 0.020	$1.775 \cdot 10^3$ ± 65.6	–6.7
Leucine	0.551 ± 0.023	$1.806 \cdot 10^3$ ± 75.7	–4.3
Glycine	1.150 ± 0.045	$2.156 \cdot 10^3$ ± 85.8	–12.0
α-Aminobutyric acid	0.628 ± 0.030	$1.616 \cdot 10^3$ ± 78.8	+2.8
γ-Aminobutyric acid	0.449 ± 0.025	$1.156 \cdot 10^3$ ± 65.5	–7.4
Serine	0.862 ± 0.035	$2.263 \cdot 10^3$ ± 89.8	–5.0
Cystine	0.430 ± 0.015	$2.580 \cdot 10^3$ ± 90.7	+3.7
Histidine	0.573 ± 0.023	$2.224 \cdot 10^3$ ± 88.7	–2.1
Methionine	0.257 ± 0.018	$0.957 \cdot 10^3$ ± 67.5	+6.0
Cysteic acid	0.435 ± 0.016	$2.032 \cdot 10^3$ ± 73.2	–2.0
Proline	0.235 ± 0.017	$0.758 \cdot 10^3$ ± 55.8	+2.8
4-Hydroxyproline	0.055 ± 0.014	$0.181 \cdot 10^3$ ± 44.5	+3.7
Asparagine	0.505 ± 0.022	$1.662 \cdot 10^3$ ± 71.4	–10.7
Valine	0.501 ± 0.023	$1.660 \cdot 10^3$ ± 72.3	–2.0
Mean	0.500 ± 0.022	$1.640 \cdot 10^3$ ± 72.1	–3.3

[a] Mean of four replicate analyses; 20 μg mL^{-1} amino acid.

Through this method, a solution of an amino acid mixture with concentration of 20 μg mL^{-1} was analyzed, similar to that from corn plantlets (Table 3). The molar absorption coefficient for the corn amino acids mixture was 1.747 x 10^3 (mean molecular mass being 117.4 and the molar absorption coefficients being taken from Table 2). Hence, the most suitable amino acid for calibration in case of this amino acid mixture would be alanine (absorbance = 0.790; molar absorption coefficient = $1.758 \cdot 10^3$ L mol^{-1}cm^{-1}), because the molar absorption coefficient of this amino acid and of the mixture from the extraction solution have proximate values (Table 4).
Interferences.

Effect of coexistent species was studied using an alanine solution of concentration 20 μg mL^{-1}. The method proved to be weakly affected by other ninhydrin-positive substances. Still, ammonia, ammonium ion, amines etc., called ninhydrin-positive substances, also react with ninhydrin. Since plants biostructure is investigated with this method, these ninhydrin-positive substances do not dramatically affect results considering their low concentrations.

Reproducibility and sensitivity. The method is reproducible, and the Lambert-Beer law is respected within the concentration interval of 0-20 μg mL^{-1}.

Effect of various reaction conditions. Effect of reagents and reaction time and temperature upon coloring intensity were studied after the amino acid extraction in the 1M sucrose solution. In view of a complete color reaction, using 1 mL of ninhydrin reagent solution was sufficient.

The resulting colored compound has an absorbance maximum at 516 nm (500-530 nm). A minimum of 60 minutes was necessary for the color to maximally develop at 100 °C.

Table 3. *Absorbance of an amino acids mixture similar to that of corn plantlets*

Amino acid	Concentration ($\mu g\ mL^{-1}$)	Relative absorbance
Cysteine	0.63	0.027
Asparagine	7.80	0.201
Histidine	1.35	0.039
Aspartic acid	0.63	0.066
Glycine	1.70	0.043
Serine	0.21	0.060
Glutamic acid	0.25	0.022
Threonine	0.47	0.013
Alanine	3.03	0.118
Tyrosine	0.73	0.015
Methionine	0.75	0.033
Phenilalanine	2.70	0.056
Leucine	0.75	0.120
Mean	40.00	0.813

Table 4. *Values obtained from amino acid extraction from plantlets treated with Pb^{2+} and Ba^{2+} (λ=516 nm)*

	Control			**$Pb(NO_3)_2$**			**$BaCl_2 \cdot 2H_2O$**		
Absorbance	**0.773**	**0.901**	**0.879**	**0.901**	**0.858**	**0.887**	**0.397**	**0.363**	**0.795**
Absorbance	**0.887**	**0.669**	**0.852**	**0.942**	**0.516**	**1.038**	**1.429**	**0.66**	**0.465**
Absorbance	**0.780**	**0.724**	**0.888**	**1.009**	**0.961**	**0.930**	**1.277**	**1.221**	**0.643**
Mean	**0.813**	**0.764**	**0.873**	**0.950**	**0.778**	**0.951**	**1.034**	**0.748**	**0.634**
Errors	**0.07**	**0.06**	**0.01**	**0.03**	**0.13**	**0.04**	**0.32**	**0.25**	**0.09**

The colored solution's absorbance increased 7.5 times at a reaction time rise from 5 to 60 minutes (Fig. 3). Absorbance then halved when the reaction time was prolonged to 120 minutes, indicating decomposition of the formed colorant.

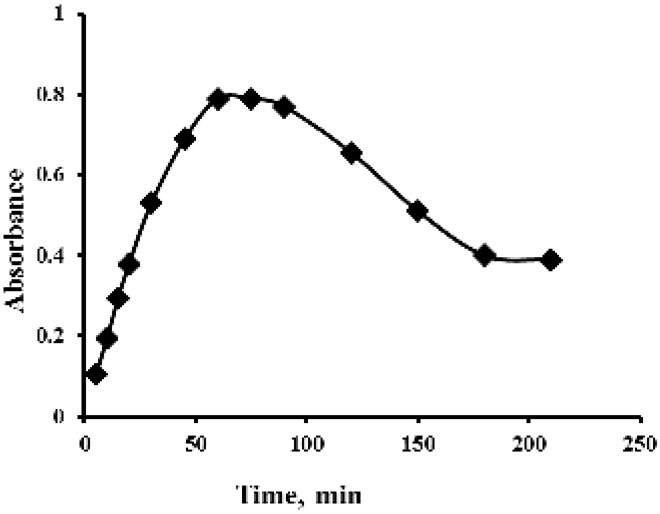

Fig. 3. *Effect of time upon ninhydrin-amino acid coloration intensity (100°C, 20 $\mu g\ mL^{-1}$ alanine)*

4. Conclusions

The chosen method is applicable when monitoring the degradation of plants biostructure through determining amino acids extracted from 1M sucrose solution. The method can also be useful for environmental analyzes (pollutants), as well as within biochemistry laboratories in general. It requires simple and easily acquirable equipment, inexpensive chemicals and glassware, and personnel with average qualifications.

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BEHAVIOR OF COLD ROLLING EMULSIONS IN THE OBTAINING PROCESS OF STEEL STRIPS

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ABSTRACT

The research was focused on determining an optimum rolling emulsion to be used on a cold rolling mill from Galfinband Galati Romania. In this plant are obtained steel strips with the thickness of 0.7-0.8 mm. The main parameters depending on which the performance of a lubricant varies were determined. These were: viscosity, pH, thickness of lubrificant film, size of emulsion particles and their distribution on the surface of the steel band, oil content in the lubricating emulsion, usage degree of emulsion, applying method. The characteristics of mineral oil, fresh and recirculated emulsions have been analysed and discussed. Also by macroscopy were analyzed the form of contaminants on the surface of the steel bands which originate from lubricating emulsion. Their appearance is analyzed in the report with their generating processes and the quality of the emulsion.

KEYWORKS: cold rolling, emulsions, characterization, surface defects

1. Introduction

To obtain an increased reduction grade in cold rolling of steel is necessary to continue lubrication in the deformation zone. At the same time, due to the thermal effect of deformation the rolls are heated. Therefore they must be continuously cooled. The operating conditions are secured in most cases by combining a lubricant with a cooling agent, resulting what is called an emulsion. The emulsion is a system consisting of two liquid phases, one dispersed in the other. This is lubricating oil in water emulsion, in which different ingredients are introduced to ensure some characteristics and for improving others. In the case of the cold rolling process, the proper lubrication can facilitate: reduction of the thickness of hot rolled strips at acceptable rolling speed; control of heat losses; corrosion protection of the steel band that will be processed and also of rolling equipment; obtaining of quality surfaces of rolling thin strips.

The lubrication reduces the friction and wear at the interface of work rolls and steel strip surface, by formation a lubricant film. So the friction coefficient at cold rolling process in lubrification condition reaches at values $\mu \sim 0.05 – 0.10$ [1 - 3]. The degree of separation of the roll and strip surfaces depends on the thickness of the lubrificant film formed at interface strip/roll. There are different regimes of lubrication at the interface and the process is conditioned by separate stages of the deformation cycle. Into hydrodynamic lubrication regime (when the strip surface and the rolls surface are completely separated by the lubricant film and so friction and wear drop to a very low level) the film thickness is directly proportional to viscosity of lubricant and the speed of rolling [4, 5].

The friction and lubrication are influenced by a number of parameters such as the properties of the material, finishing grade of the surfaces, temperature, sliding speed, contact pressure, and characteristics of the lubricant [6].

From the point of view of the lubricant and parameters that affected the friction and lubrication, respectively the parameters depending on which varies the performance of a lubricant and the friction coefficient are: viscosity, film thickness of lubricant, the pressure stability, temperature stability, and the additives used.

The chemical nature and concentration of additives are unique, being determined by the specific requirements of each mill [7]. Practically should not be exist not even two rolling lines that exactly use the same lubricating emulsion formulation. The lubricants selection for the deformation of the metal strips should be done by considering some particular factors: applying methods of lubricant; types of additives; corrosion control; cleaning performance and removal methods; compatibility with other lubricants and other oils that were previously applied; post-metal processing operations (such the coating processes for steel sheet and strip); safety in relation to the environment; recycling capacity [6, 8].

There are four major considerations in formulating of lubricants:

- to develop the best combination of chemical substances able to reduce friction and to realize the cooling;
- to use of an optimum amount of lubricant for the working area of milling rolls;
- to ensure the removing of residual residues after heat treatments applied to rolled strips;
- to ensure the best total production cost for the cold rolled steel strip manufacturer;

In accordance the characteristics of an ideal lubricant for cold rolling may result in satisfying the following list of requirements [9]:

- to provide the lubrication so rolling regime allowing the production appropriately sized bands in accordance with the beneficiaries requirements;
- to can be easily and cared for applied;
- do not aggravate the cleaning operations by spreading of surpluses on the rolling equipment;
- do not significantly impair the transfer of heat from the rolls, respectively from steel strip, to cooling medium;
- do not break down or deteriorate during the forming process;
- to be easily removed from the surface of the strip after rolling process;
- to be economical in terms of duration of use (the time until wear).

In this paper were studied some properties of lubrificant emulsion to optimise the rolling performances and the lubrification process.

The results were discussed and compared with the technological emulsion used in present in the cold rolling process of steel bands (with thickness of 0.7-0.8mm) at Galfinband plant.

2. Research and discussion

At the cold rolling mill from Galfinband plant for the preparation of lubricating oil is used an emulsifiable concentrate based on mineral oil blended with bactericide and fungicide agents which ensure a long service life. This oil is used for the preparation of a technological emulsion with good performances for lubrication and cooling in a concentration ranged between 2-5% in water. The concentrated product is a clear brown liquid and the emulsions have a milky white appearance with yellowish tint at high concentrations of oil. From the technological point of view, the amount of emulsion needed in the deformation zone is applied by spraying. This requires a certain viscosity of the emulsion.

The new emulsions with variable content of oil (2.5%, 3%, 3.5%, and 4.5%) in industrial water were prepared and used in experiments. The spraying method was used to apply precise amounts of lubricant to local areas of steel band samples. In all experiments was used on type of water and its quality was verified. This was softened and with a slightly acidic pH (6.5). Also have been tested the service emulsion samples with certain utilisation degrees and contamination. These were extracted from spraying equipments of the rolling line Galfinband plant. The macroscopic aspect of some emulsions tested according to composition and usage degree can be observed in Figure 1. The oil degradation by thermal oxidation leads to the decomposition products formation and the changes of its physical properties such as colour and odour (see Figure 1c and Figure 1d).


a. b. c. d.

Fig. 1. *Aspects of different emulsions tested: a-emulsion 2.5%; b-emulsion 5%; c-emulsion after using period of 10 days; d-emulsion waste*

The viscosity, pH, thickness of lubrificant film, size of emulsion particles and their distribution on the surface of the steel band have been analysed. The thickness of lubricant film at different emulsion concentration was determined using gravimetric standard sized samples and analytical balance. The film of oil was removed with organic solvents. The results are shown in Figure 2. As expected the deposited film thickness depends on the concentration of the emulsion on band and wear it. As the emulsion concentration is higher the larger is the film thickness resulting emulsion.

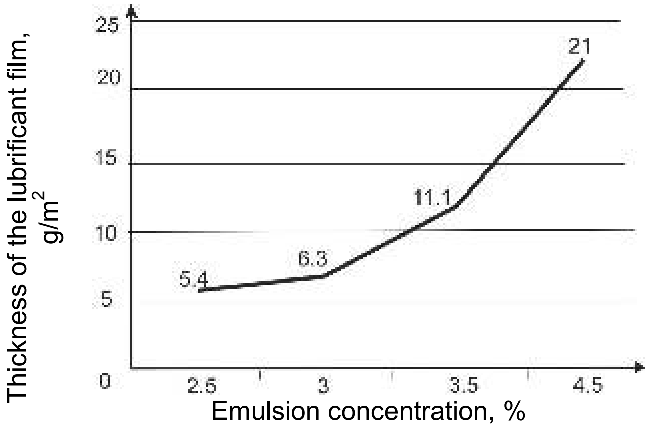


***Fig. 2.** Variation of oil film thickness with emulsion concentration in emulsion samples*

For any lubrication emulsion, the viscosity is considered as the most important parameter. The viscosity of the technological emulsion must resist at action of high pressures occurring during deformation. The coefficient of friction is dependent on viscosity of lubrificant film. An Engler viscometer has been utilising to characterise the viscosity. On this apparatus, the reading is the time t_T (in seconds) required for 200ml of the oil to flow through the device at a predefined temperature T. The conventional viscosity measured in degree Engler (^0E_T). It has been determined by ratio:

$$\text{Viscosity} = \frac{t_T}{C} \qquad (1)$$

where C is the calibration constant of the particular viscometer or time (in seconds) required for 200ml of the distilled water to flow through the same device. At temperature of 20^{0}C its value is 58 seconds.

Kinematic viscosity (cSt) can calculated with relation:

$$1^0\text{E} = 0.132\text{cSt} \qquad (2)$$

The viscosity of oil, fresh emulsions 2.5% and 4%, and the emulsion sample collected after an using period of 10 days were determined (Table 1). For each sample three determinations were made and then an average value of time for leakage was established

***Table 1**. Viscosity for different sample of emulsion sorts, respectively for oil*

Sample	Leakage time* (s)	Conventional viscosity (^{0}E$_T$)	Kinematic viscosity (cSt)
Fresh emulsion 2.5%	58.33	1.006	0.133
Fresh emulsion 4%	59.66	1.029	0.136
Emulsion sample after an using period of 10 days from Galfinband	60	1.034	0.137
Oil	890	15.345	2.03

*average value of three measurements

It can observe that viscosity does not vary greatly with the oil concentration in studied emulsion. Viscosity is more influenced by ageing process of emulsion and its contamination.

The increasing of the viscosity is significant in relation with the usage degree of emulsion. A using period of 10 days can be recommended. After this working period, the viscosity will be deteriorated significantly due to increasing of emulsion contamination.

The pH of emulsion influences the lubrificant stability and the process of residues formation on the steel surface. Also pH can affects the particle size of emulsion droplets.

A laboratory electronic device was used for measuring the pH. The results are given in Table 2.

Table 2. *pH of materials used in experiments*

Sample	Fresh emulsion 2.5-3%	Fresh emulsion 4%	Emulsion after an using period of 10 days	Oil	Water	Emulsion waste
pH	6.5	6.8	7.5	8.5	6.0	8.0

As shown by the results presented in Table 2, the chemical reactions undergone by rolling oil change the pH of samples. The emulsion used in the deformation process must ensure the formation of a continuous film on steel strip surface, resistant to high pressure applied and to temperature developed in the rolling process.

The film formed on steel samples was examined. Images of oil emulsion deposited on steel support are presented in Figure 3.

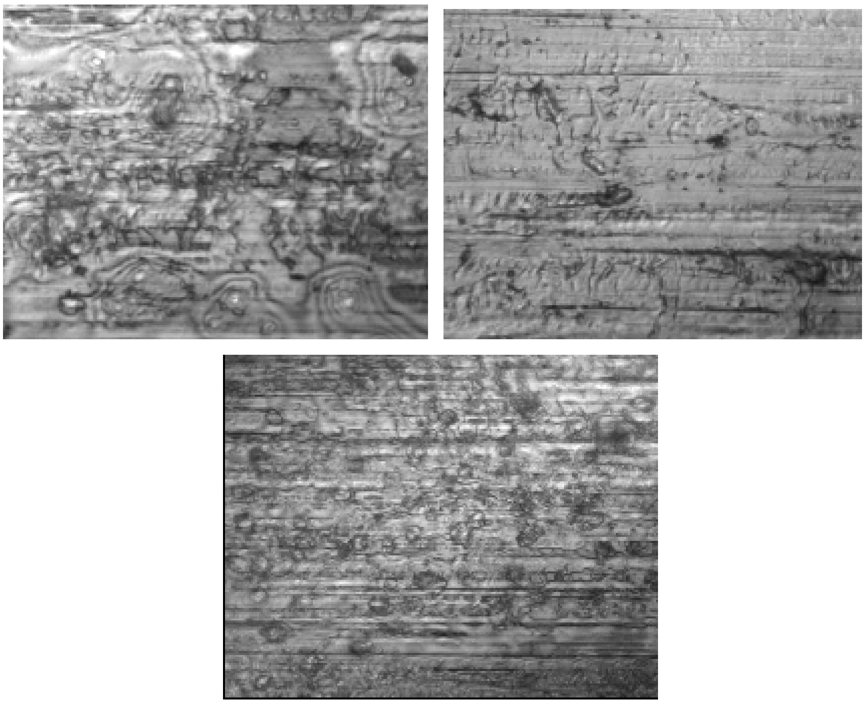
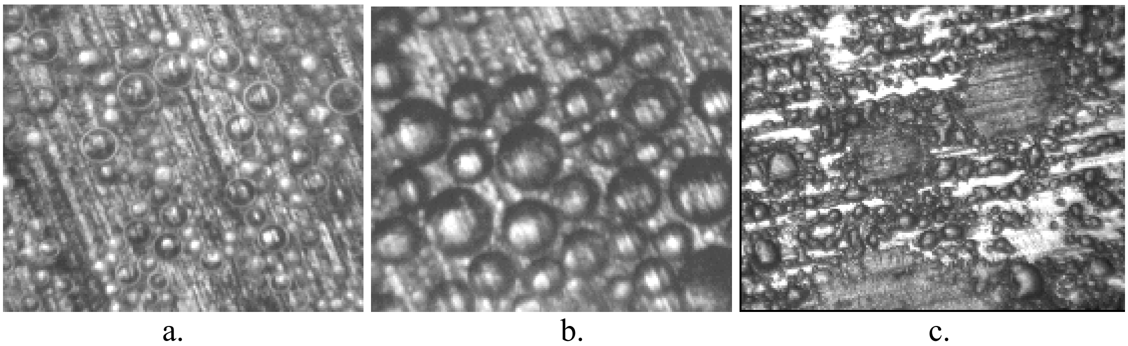


Fig. 3. *Aspects of emulsion film applied on steel band surface (x400)*

Oil in water emulsion consists of a discontinuous oil phase and a continuous water phase. At applying of emulsion film by spraying the emulsion droplets on steel surface were forming.

Their sizes and distribution were determined by optical microscopy. Figure 4 show that the emulsion droplets have a distinct sizes and different distributions depending on the characteristics of the emulsion.



a. b. c.

Fig. 4. *Emulsion droplets on surface of the steel specimens (x400): a-emulsion after an using period of 10 days; b-emulsion 3%; c-emulsion 5%*

The size of emulsion particles and their distribution are different because these are influenced by the emulsion quality.

The emulsion 3% presents oil droplets uniform dispersed and larger. Such emulsion is known as „loose” emulsion [10]. Contrarily, at increasing of oil content in lubrificant emulsion the particles sizes were modified.

In generally, is can considered that the emulsion 5% presents droplets that can be fitted into two dimensional classes. Some are larger and mostly smaller.

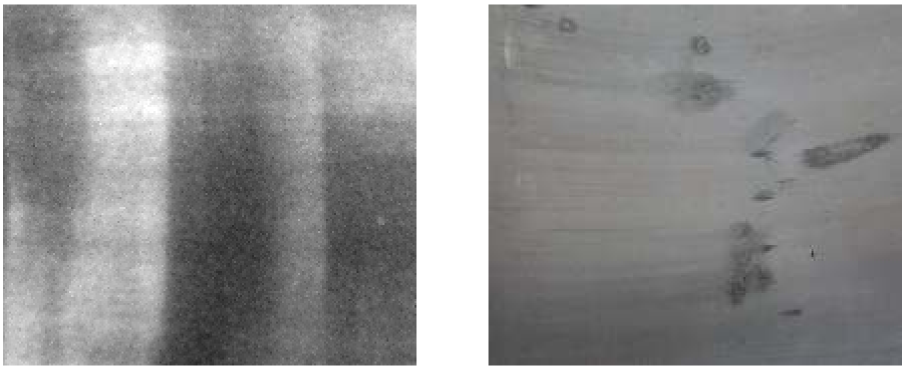
Also these droplets tend to form conglomerates. This emulsion can be classified as a „tight” emulsion [10]. The working time of 10 days bring modifications in the emulsion. Less droplets of usage emulsion (extracted from spraying equipments of the rolling line Galfinband plant) with medium sizes can be observed on surface of the steel specimens.

Part of oil emulsion was destroyed by oxidizing during rolling process. So have been formed carbonaceous residues and contaminants that adhere to the steel surface after rolling. Quality requirements of cold rolled strips impose to lubricant emulsion to generate a minimum amount of such carbonaceous products.

The organic residues on the surface of cold rolled thin strip coming from the following [7]:

- contaminants in the form of soaps or "tramp" oil contaminants such as hydraulic and bearing oils leaked from the rolling mill;
- decomposition products during oil storage and re-circulation;
- contaminants from oil decomposition during the rolling process itself.

The oil impurities, called oil contaminants, cause problems during all stages of the process for obtaining coated plates. Firstly they lead to a decrease in lubricating performance during the rolling process. The contaminating oils ("tramp" oils) should be kept to negligible levels, <0.25%. On the steel strips from Galfinband, black visible traces forming broad bands or stains in rolling direction remain after cold rolling process (Figure 5). The presented specimens have been extracted from steel strips rolled with an emulsion that had a working time of 10 days. The amount of organic residues extracted from the surface of samples analysed has been evaluated by the typical tests "tape test", where contaminants particles on the steel surface are removed using a piece of tape. A residues amount of 8 mg/m^2 was resulted after analysing of 10 samples.



a. b.

Fig. 5. *Macroscopic appearance of the strips surface at the exit of the rolling mill (x400): a- carbonaceous residues arranged in bands; b- carbonaceous residues stains*

An increase in residue levels was attributed to surface reactions between the oil and iron in form of the iron fines resulted from high levels of wear during the rolling process. Also the oil ingredients and tramp materials with high volatilisation temperatures contributed significantly to residue levels. During thermal treatment, the residual contaminants further react with: the volatile products resulted from chemical reactions of remanent rolling oil developed at temperature of thermal treatment); gaseous atmosphere from the treatment furnace; steel strip surface. The contaminants contribute to formation of areas with high carbon level on surface of steel strips following the annealing process (Figure 6).

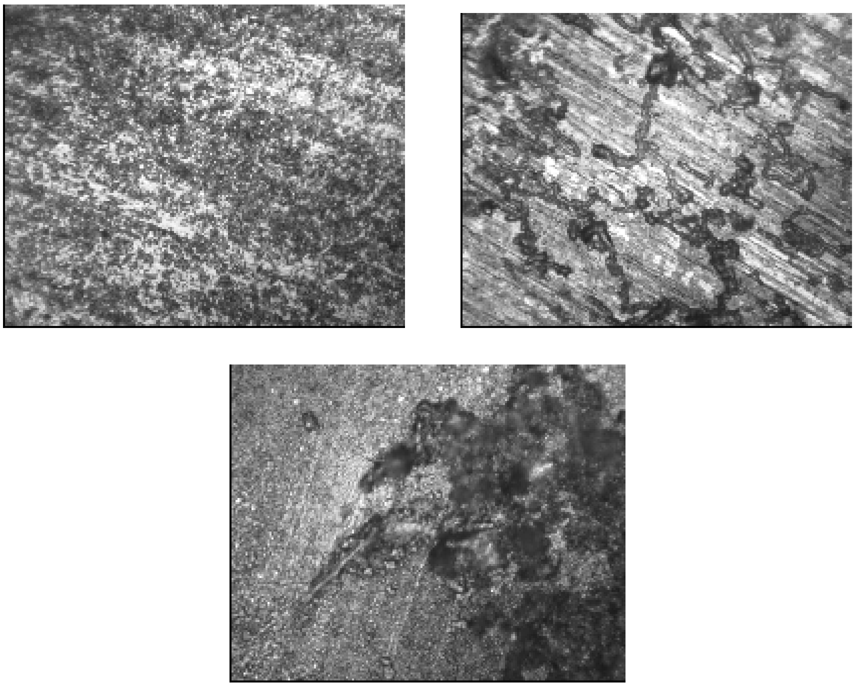


Fig. 6. *Emulsion burned on the surface of band thermal treated (x400)*

In Figure 7 are showed a clean surface (a) and a contaminated surface (b) after applying the same cleaning process as a result of the presence of emulsion burned.

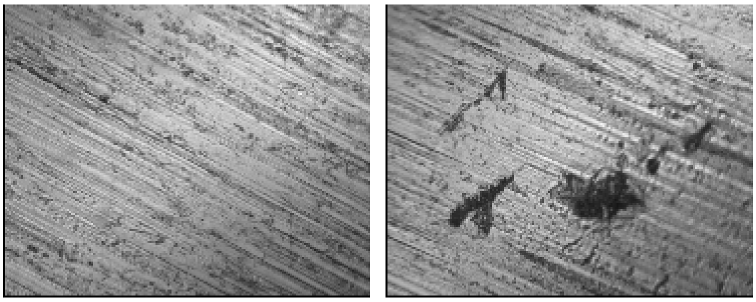


Fig. 7. *Images of steel strips surfaces after applying the cleaning process: clean (a) and contaminated (b) (x400)*

3. Conclusions

An effective lubricant system must ensure in couple steel band-rolls of milling equipment a balance between cooling and lubrication. From the point of view of the lubricant and friction, there are many parameters that affect the lubrication.

The viscosity, pH, thickness of lubrificant film, size and distribution of emulsion particles on the surface, oil content in the lubricating emulsion, usage degree of emulsion, applying method are important parameters that demonstrate the performance of a lubricant.

These have been studied in this paper. Also, the presence of contaminants and residues on the steel strips surface was analysed and put in relation with the lubrication system utilised in the cold rolling process.

The oil film thickness applied by spaying is directly proportional to the viscosity of the emulsion. In correlation with the literature is recommended the emulsions with maximum 3.5% oil.

The increasing of the viscosity is significant in relation with the usage degree of emulsion. As result a working period of 10 days can be recommended.

For the samples analysed the size of emulsion particles and their distribution are different. These are influenced by the emulsion quality and the working period. The carbonaceous residues that remain on the surface of the strip after rolling must strictly limited because have a negative influence in all subsequent stages of processing.

Research has shown that increasing the degree of contamination of the emulsion by recirculation and wear can generate an amount of carbon residue up to 8 mg/m^2.

During the heat treatment, residual products is reacted further with the gaseous products, furnace atmosphere and with the surface of the steel strip and cause the formation of areas with high carbon concentration on the surface of the strip subjected to the annealing process.

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EFFECTS EXERTED BY SLAG CARRIED OVER FROM CONVERTER IN THE LADLE ON THE ALUMINUM ASSIMILATION

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ABSTRACT

In the present paper are shown aspects of the influence exerted by the some less controlled parameters of BOF steelmaking, mainly of slag characteristics at tapping. Following the necessities to control the steel deoxidization by aluminum assimilation evaluated by soluble aluminum and its behavior, the presented data are evaluated based upon direct measurements of dissolved oxygen in steel before tapping, steel temperature before tapping, argon bubbling in tapping ladle under slag at various contents of (FeO), including its final content. The presented data are obtained in full scale plant conditions on standard weight of heats and applying an established steel making technology. It is concluded that steel temperature in final stage of steel making and (FeO) content of slag carried over from BOF to the ladle exert a strong influence on the aluminum assimilation in steel and further on the other quality characteristics of steel. A strong variability of the parameters taken into account is present and this is due to the insufficient control of the amount of slag carried over to the ladle at tapping.

KEYWORDS: steel, slag, tapping temperature, FeO in slag, aluminum assimilation

1. Introduction

In a previous paper [1] it was shown, based mainly on theoretical considerations and simulation, the influence on the chemical composition of the slag in the ladle due to some chemical compounds in the converter slag, at some fixed ratios. The present paper deals with the evaluation in industrial conditions of the effect exerted by the slag carried over from converter in the ladle on the final composition of the steel before ladle refining or continuous casting. It is known that, despite the use of slag stoppers, important variations of the amount of slag carried out from converter are transferred in the ladle in a random manner. In consequence, the whole process of the liquid steel treatment is perturbed, this causing important decreases of quality products and of the economic efficiency of steel production. Due to the necessity to achieve low carbon contents in the liquid steel before taping, heats are processed in a specific manner by oxygen blowing in the converter and usually, after that, the iron oxides content in slag is higher then desired, despite a final argon/nitrogen bubbling through bottom nozzle. This situation is important for the steel quality in the general case of many classes of steel grades [2, 3], but it is extremely critical mainly in the case of the low carbon aluminum killed steels (LCAK). In many papers it was shown by simulation that an important lose of aluminum content occurs in the presence of important amounts of slag carried out from converter in the ladle during argon bubbling. Then, the thermodynamic equilibrium conditions between aluminum and oxygen in the steel ([Al]-[O]) has been considered. Due to multiple advantages, the most convenient oxygen blowing technology of steelmaking in LD converter consists in technological operations and blowing parameters leading to the obtaining of a low carbon content $[C]_o$ at the end point (index o), corresponding to an equilibrium value (index e), $[C]_{o,e} \approx 0.05\%$ mass. In the case of thin rolled products for deep drawing and having high quality of surface, an average chemical composition of the steels in the ladle is in the following range: $C \leq 0.05\%$, $Si \leq 0.03\%$, $Mn \leq 0.2\text{-}0.4\%$, $Al_{sol}=0.015\text{-}0.40\%$. Index “sol” refers to soluble aluminum content in the steel. Many other chemical elements in the liquid steel could be specified, among them sulphur and phosphorus, many times also in restricted limits of contents, usually as limited maximal values. The selection of heats in the present paper excludes those out from the common practice, from the point of view of variability of influencing parameters taken into account. This means that those heats, where the analyzed parameters are too far out of the general trend, are not taken into account in this work.

2. The main features of the steel making technology

The schedule of steps and operations in the oxygen converter steelmaking technology is a common one and consists in the use of the process computer of each converter on the level two, taking into consideration the following final parameters of the heats:

1. - mass of heats (usually 175-180 t liquid steel);

2. - carbon content at end point ($[C]_o \leq 0.05\%$);

3. - phosphorus content at the end point ($[P]_o \leq 0.015\%$);

4. - final temperature of the liquid steel at tapping T_{tap}, according to necessities of continuous casting and/or required by necessities of a secondary treatment by different ladle metallurgy process;

5. - specific imposed value of the final slag basicity in the ladle, according to a computational relation; for the considered case it was used the value of the basicity index of slag B_{slag}=(%mass CaO)/(%SiO_2) $\approx$ 4.5. If it is applied a final argon bubbling period in converter, before taping the slag composition could be at best within the following range CaO=52-58%, SiO_2=12-14%, MnO=max.5%, MgO=max.5%, P_2O_5=1.5-2.2%, Fe_t=18-22%. A small variability of components around these Figures cannot be considered as nonconformities. From them, the process computer program establishes the necessary amounts of liquid pig iron, initially treated for advanced desulphurization and of scrap, the necessary amount of lime and the recommended oxygen blowing diagram. This last one contains also an argon post-bubbling period of a standardized duration and rate, according to the requirements imposed by the steel grade quality. At tapping, among usual addition operations of the required materials, a special addition of petroleum coke is introduced in the first moments after the beginning of steel tapping in order to reduce the activity of oxygen in the liquid steel. The aim is to decrease the content of the dissolved oxygen at levels below 400 ppm, i.e. at levels closed to those corresponding to the theoretical equilibrium [C]-[O] at the considered temperature. In order to remove the excess of the dissolved oxygen, amounts of about 60-70 Kg of petroleum coke per heat are usual additions and only in extreme cases they could increase the carbon content in the liquid steel, perhaps with no more than about 0.01%. In order to evaluate correctly the amount of petroleum coke to be added and the necessary amounts of ferromanganese and aluminum as deoxidizers, a measurement of oxygen activity using an adequate device must be performed before tapping. Usually, the amount of Al considered as necessary to deoxidize such crude liquid steel is considered to be 1 kg/t. The total amount of aluminum representing 175 Kg is introduced in several stages; in the form of blocks-100 Kg after addition of ferromanganese, when half of steel was tapped, 25 Kg granule or gross flakes in mixture with lime (800-1000 Kg/heat) and 80-100 kg of fluorine; the rest of aluminum, representing 50 kg Al is spread on the surface of the slag in the ladle, after finishing the tapping, as granules or gross flakes with the definite purpose to urge a strongly advanced deoxidization of the slag. The results of steel deoxidization operations depend on how much effective are the technological operations before mentioned, mainly on the effectiveness of aluminum assimilation in the steel and its effectiveness in the slag deoxidization, both being the key control of the steel quality for the initially mentioned purposes. The effectiveness of all final treatments in the ladle and further the quality of steels are strongly dependent on the characteristics of the carried–on slag from converter to the ladle and on its amount. These factors at the origin of a strong variability in the final steel quality and the following paragraphs are dedicated to these aspects.

3. Experimental data

Higher values of assimilation of aluminum in steel (over 25-30%) at tapping are obtained when steel before tapping contains low values of dissolved oxygen. The activities of oxygen in steel converted in mass contents must be below 600 ppm and the temperature must not exceed too much the necessities to cover losses in normal practice; a limit of about 1650 °C seems to be acceptable in the case under focus.

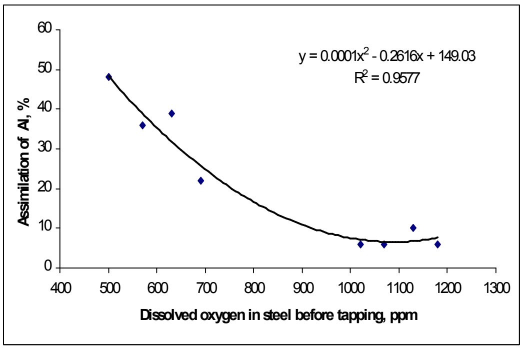

Fig. 1. *Dependence of aluminum assimilation in the ladle as function of the dissolved oxygen in steel before tapping, based on Celox measurement*

In industrial conditions of steel making in LD converters only a limited number of edificatory factors regarding the quality are available for direct measurements. The dissolved oxygen content and the temperature of the steel before tapping are among the most important. Assimilation of aluminum as function of these parameters is shown respectively in Fig. 1 and in Fig. 2. The graphical representations are linear because the highest values of correlation coefficients of dependence have been obtained for this type of dependence.

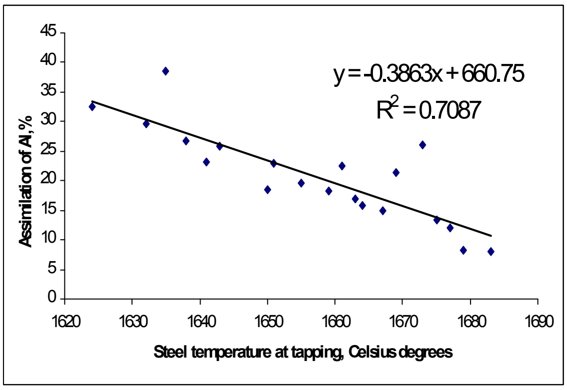

Fig. 2. *Assimilation of aluminum in steel at tapping in the ladle, as function of steel temperature in converter before tapping*

In extreme cases, when the dissolved oxygen contents exceed 1000 ppm and steel temperature at tapping is over 1670 °C assimilation of aluminum in steel is less than 10-15%, in this research. The effects of such values of these parameters are deleterious for the quality of steel products and in order to avoid them costly supplementary addition of aluminum, feed by wire, must be done. Both factors of influence present high enough values of the coefficient of determination R^2. This means that in the case of the selection of heats, making the object of the present research, the oxygen activity in steel before tapping and the steel temperature are among the most important technological factors of influence of the aluminum assimilation in the liquid steel. An important variability of aluminum assimilation, taken as objective function, is due to many other concurrent parameters, less controlled for various reasons. Among them there could be included variations of the amounts of slag carried–over at tapping, the rate of steel tapping, respectively time duration of tapping, the fastness of aluminum additions in the most adequate period of tapping. The moments of sampling of steel or Celox measurements could induce other variations of assimilation values. The amounts of carried-over slag and their content of ion oxides are two other important parameters involved in controlling the steel quality in the tapping ladle and further, in the following steps of liquid steel processing. The slag amount of carried-on slag from converter to the ladle can be supposed only as amount, despite many efforts and devices used in the purpose to limit it. It was shown [1] by numericalsimulation that amounts over 500 Kg converter slag/heat are deleterious for aluminium assimilation due to the effects of its oxidation, according to the reaction (1) taking place at interface steel-slag. This reaction occurs in both regimes of contact, permanent and transient. The first is specific to periods after argon bubbling, as state in the tapping ladle or in secondary steel metallurgy facilities, up to the moment of continuous casting that means 20-40 minutes as time duration. The second is referring to the intended technological processing, consisting in argon bubbling and several minutes after that, also in distributors at continuous casting of steel.

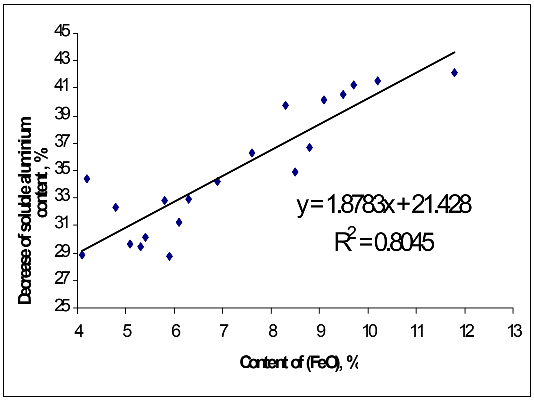

Fig. 3. *Decrease of the soluble aluminum content in steel during argon bubbling in the ladle, as function of (FeO) in slag*

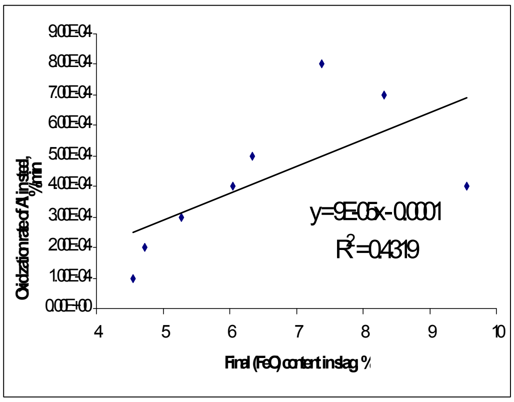

Fig. 4. *Oxidization rate of aluminum in steel after argon bubbling period as function of final content of (FeO) in slag*

The content of iron oxides in slag (FeO) influences in great measure the behavior of aluminum in the ladle. Fig. 3 and Fig. 4 show this influence by two important parameters which could be established by direct measurements. It is obvious that, at higher contents of (FeO) in the top slag in the ladle, at the same intensity of argon bubbling by porous plug in the bottom of the ladle, the values of both dependent parameters grow. There are differences of the dependence coefficient R^2. This shows that the permanent and the transient regime of contact between the top slag and the steel in the treatment ladle, influences in different measure the oxidation of aluminum in the steel. In the permanent regime, in absence of bubbling, an important part of the top slag becomes totally inactive because of the increasing of its viscosity and even because of partial solidification at surface. Mass transfer of (FeO) by diffusion from upper layers of slag to the steel-slag interface is lower in the permanent regime when argon bubbling is missing. However, as it is shown in Fig. 3, if the (FeO) content after bubbling argon is lower, the decrease rate of soluble aluminum in steel is significantly lower than in the case of higher contents of (FeO). It seems that at less than 5% (FeO) due to the combination of favorable actions of the mutually reinforcing kinetic and thermodynamic factors, shown before, the rate of oxidization of soluble aluminum decreases drastically.

The last two data in Fig. 3, at contents (FeO) <5 mass% sustain this behavior which is in fully agreement with other published data. These observations are sustained also by the data presented in Fig. 5 where the same general and particular tendencies are maintained for aluminum oxidization behavior after argon bubbling period. In Fig. 6 the evolution of assimilation of aluminum in steel as function of its content in steel is presented, in conditions of a narrow range of aluminum additions in steel, around 1 Kg/t. Factors affecting drastically the assimilation in steel. i.e. the temperature at tapping, the activity of oxygen in steel, before tapping, the content of (FeO), the tapping duration and moments of addition, contribute to the trend and data shown in Fig. 6 and are responsible for lowering of steel quality in conditions when only low contents of soluble aluminum are present.

Conclusions

Despite the application of unitary technology of steel making (BOF) in in the industrial conditions of the experimental data of the present paper, factors depending on heat charge influence the final parameters at tapping such as temperature, activity of oxygen in steel and (FeO) content.

Influences of these factors are transferred to the ladle at tapping and decrease the values of assimilation of aluminum in variable measures. Further, because of the lack of control of oxygen activity in steel, the quality of steel products become variable and this is the weak point of the technology applied in the present case. Limitation of influence of these factors is the only way to ensure the necessary levels of liquid steel quality and further of steel products.

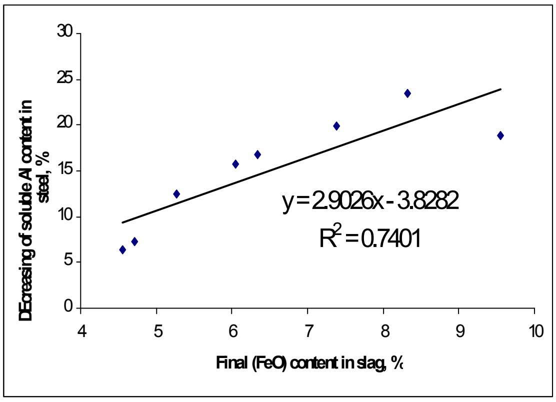

***Fig. 5.** Decreasing of the content of soluble period as function of the final content of FeO in slag*

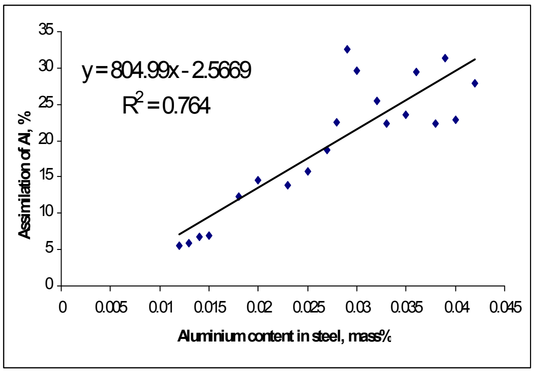

***Fig. 6.** Assimilation of aluminum as function of its content in steel in conditions of a narrow range of amounts of aluminum additions*

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RESEARCHES ON THE PRODUCTION OF COPPER-BASED COMPOSITES BY POWDER METALLURGY METHODS

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ABSTRACT

The article presents how to obtain copper matrix composite with alloy particles of NiCrBFeAl as complementary phase. The samples were obtained by powder metallurgy methods using different percentages of the additional phase: 20, 30, 40, 50% NiCrBFeAl of 60 μm average size. After cold pressing to 863 MPa pressure, the samples were sintered at 910 °C for 90 minutes. The characterization of the samples was focused on the microstructural aspects, variation of microhardness and abrasive wear behavior.

KEYWORDS: powder metallurgy, microhardness, abrasive wear

1. Introduction

The production of composite materials has applications in almost all areas of technology. Due to the special perspectives they have opened and the obvious advantages they feature, the composites will experience a permanent diversification and will attract for a long time the attention of specialists as strictly necessary materials for future technologies being considered revolutionary materials with real prospects to improve their properties. This is due to the fact that they have a number of unique mechanical properties such as low density, high mechanical strength, toughness, wear and corrosion resistance.

In the last two decades, metal matrix composites with (micrometer or nanometer) particles as complementary phase are of particular interest. In these materials the hardening particles and the strength are combined with ductility and toughness of the metal matrix.

Metal matrices have been used because of the need to obtain composites able to be used to relatively high temperatures as compared to those of organic nature. Metals have other properties too that recommend them as matrix: good mechanical properties, high thermal and electrical conductivity, high resistance to ignition, dimensional stability, good processing capability, low porosity.

Copper chosen as matrix has very good electrical and thermal conductivity and the advantage that it can be processed easily. That it why it is used in the production of composite superconducting and conducting materials as well as for the bearings and filters.

The research undertaken in this paper aimed at produceing, by powder metallurgy methods, copper matrix composites using Ni–Cr–B–Fe-Al alloy particles as complementary phase. The samples thus obtained were characterized in terms of microstructure, microhardness and wear behavior.

2. Experimental conditions

To obtain the samples, two types of powder were used: one composed of pure copper for the matrix and the other of NiCrBFeAl alloy to provide the complementary phase, which has the following chemical composition: 8.9%Cr; 4.5%Fe; 5.1%B; 2.4%Al; 0.6%Cu; the rest is Ni. The particle size of the nickel-based powder was about 60 μm.

The copper powder has an irregular shape caused by atomization of water and the nickel –based powder has a spherical shape due to gas atomization. The images of these powders are shown in Fig. 1.

There have been several samples of different concentrations of complementary phase as shown in Table 1.

The compressed samples have cylindrical shape of approximately 8x6 mm.

The compression method used was cold pressed by means of the universal mechanical testing machine. The pressure used for powder compaction was 863 MPa, determined after making several attempts.

***Table 1.** Composition of powder tablets*

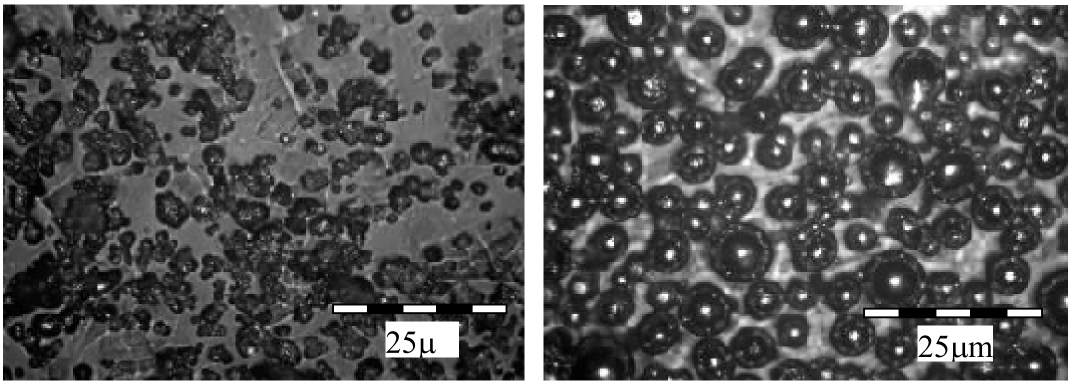
Sample code	Composition
P1	80%Cu + 20% Ni-Cr-B-Fe-Al
P2	70% Cu + 30% Ni-Cr-B-Fe-Al
P3	60%Cu + 40% Ni-Cr-B-Fe-Al
P4	50% Cu + 50% Ni-Cr-B-Fe-Al

Sintering of powder tablets was carried out in an electric furnace. The sintering temperature was 910 °C to 90 minutes exposure. After sintering, all samples were cooled slowly in the oven.

Samples were placed in a ceramic cylinder and graphite was added. The graphite has an important role in the prevention of entry of the cooling air within the cylinder, thereby providing a protection atmosphere.

The main purpose of sintering is to reduce porosity. The sintering is most often accompanied by changes in the material, some desired and some not: changes in the mechanical strength, hardness; the size and shape of the particles may also be affected, there is variation in the shape and size of the pores; it can alter the chemical composition and the crystal structure can be altered due to chemical reaction processes in the solid phase.

Microscopic analysis of powders and the samples obtained was performed using a microscope Neophot 2 with computer data acquisition.



a. b.

***Fig. 1.** Aspect of copper powder – a, and nickel–based powder – b*

Measurement of micro-hardness was carried out using microhardness meter PMT 3.

Wear behavior of the samples obtained was studied using the method for determining the mass wear to abrasion test on rotating disk. It uses a friction pin/disc couple, class IV-1.

The method involves successively pressing under the same conditions the two samples of 8x6 mm, one of the examined material, the product of the composite sintering powder and the other of a material chosen for comparison-of the sintered copper on a rotating disc covered with sanding paper grit 120. A mechanism for radial displacement of the specimen by 0.5 mm/rev provides spiral path on the rotating disk surface. A device for applying a load of 6229 N ensures pressing of the specimen perpendicularly to the sandpaper at 0.123 N/mm^2 pressure. At a speed disc of 25 rev/min, a lenght of 5.791 m has been run.

3. Results and discussions

For a metallographic study, powders were embedded in an adhesive cyanoacrylate metallographically prepared by grinding and chemical attack with a suitable reagent.

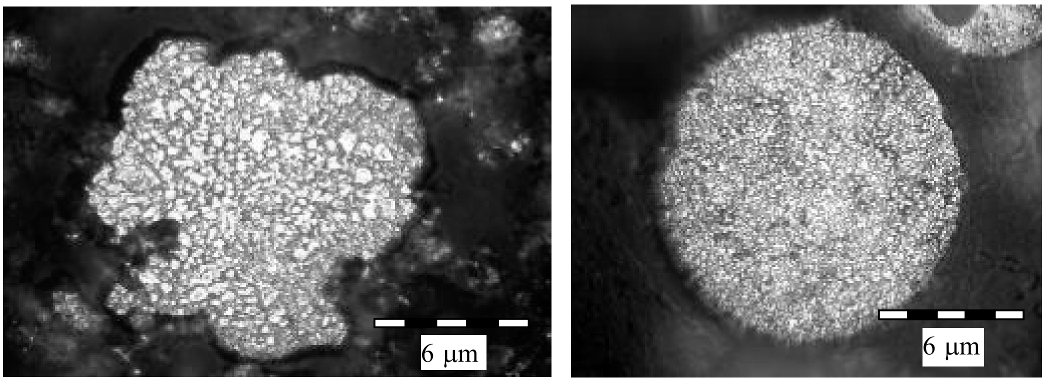
Microscopic analysis (Fig. 2) performed on copper powder particles embedded, polished and attacked with ferric chloride highlights their irregular shape and good compactness.

Microhardness determined on the polished section of the copper particles under 10 g load was HV0.01 = 516.2 MPa.

In the case of nickel base powder, the microscopic analysis on samples embedded, polished and attacked with Nital 2% highlights spherical particles and their relative compactness. Inner hollow particles are observed. Particle microstructure consists of numerous intermetallic compounds (NiB, Ni_2B, CrB, Cr_3B_4 and FeB) distributed in a very fine martensitic matrix.

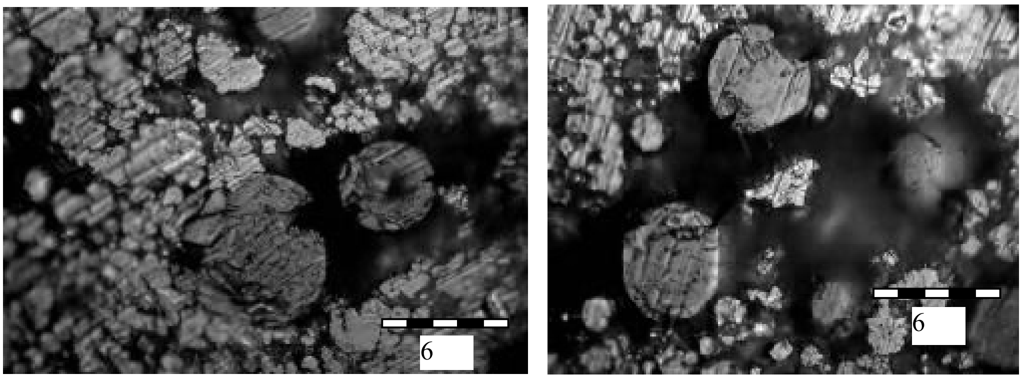
Microhardness determined on the polished section of the particles under 100 g load was HV0. 1 = 9522.2 MPa. Microscopic analysis of pressed tablets reveals the presence of pores and their shape, Figure 3.

Looking at Fig. 3 it can be seen that with increasing content of Ni-based spherical powder, there is a growth in the included phase. However there is a decrease in the sample compactness with increased percentage of included phase. This is due to the different deformation of the two types of powder.

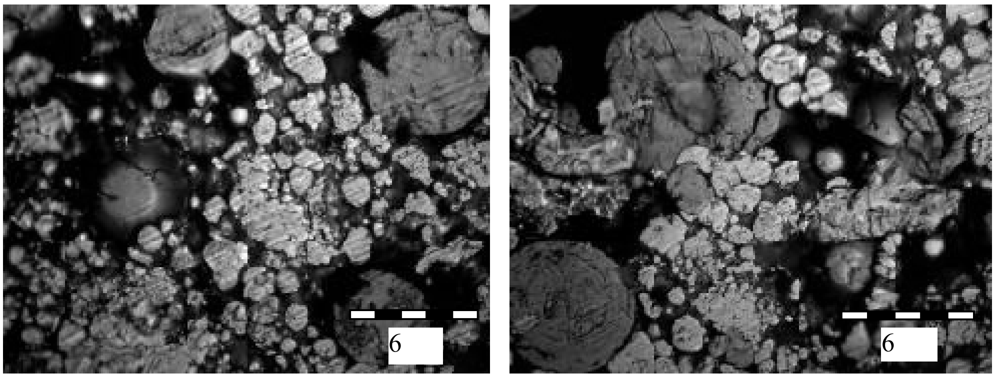


a. b.

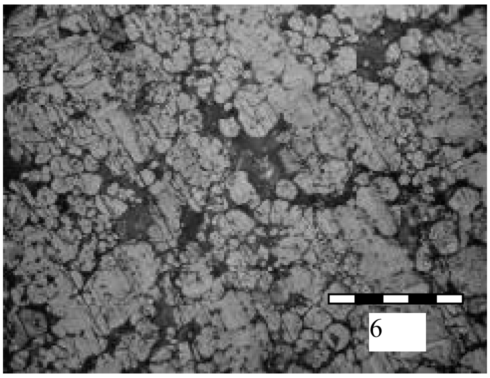
Fig. 2. *Microstructure of Cu powder – a and nickel based powder – b*



P1 - 80%Cu + 20% Ni-Cr-B-Fe-Al P2 - 70% Cu + 30% Ni-Cr-B-Fe-Al



P3 - 60%Cu + 40% Ni-Cr-B-Fe-Al P4 - 50% Cu + 50% Ni-Cr-B-Fe-Al

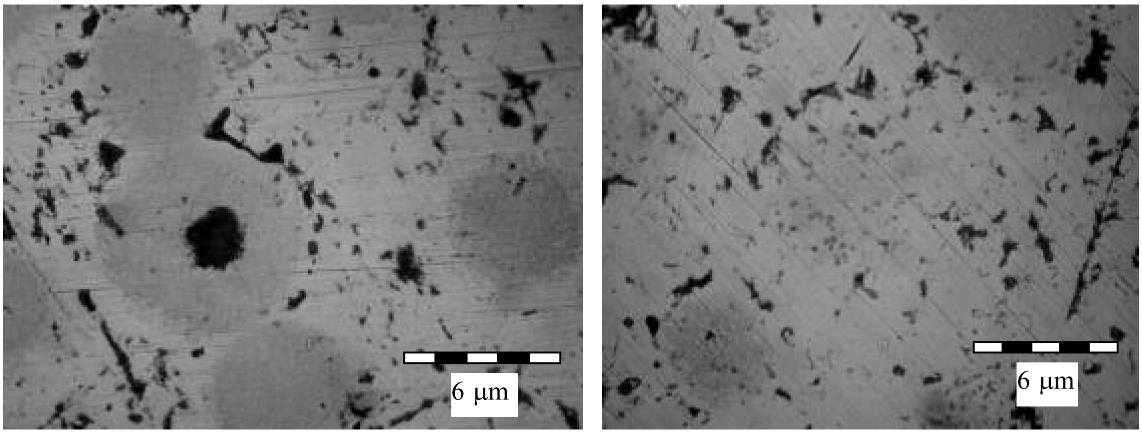


100% Cu

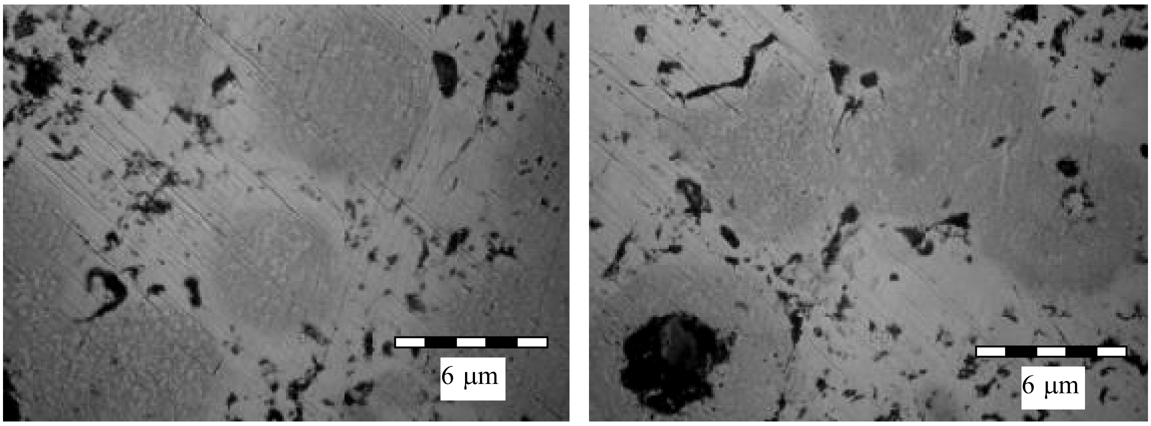
Fig. 3. *Microstructure of powder tablets in Cu matrix reinforced pressed with Ni based alloy particles*

Fig. 4 shows the microscopic appearance of the sintered unattacked samples. It is noted a reduction in porosity and a higher compaction.

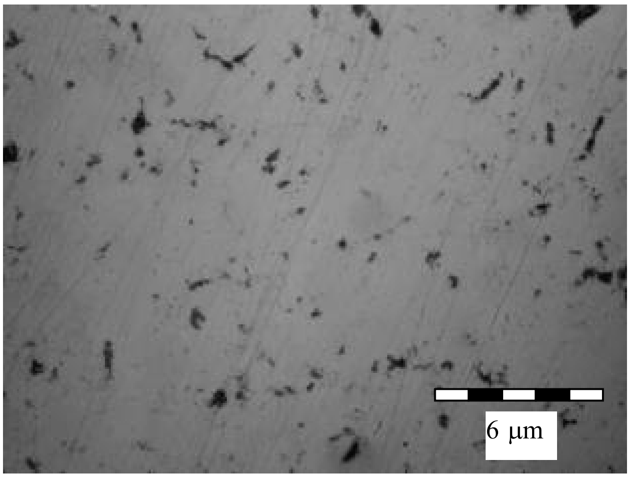
Fig. 5 shows the microscopic appearance of the tablets obtained with Cu matrix reinforced with *Ni-Cr-B-Fe-Al*, alloy particles, sintered and attacked with ferric chloride reagent. It can be seen that their structure consists of Cu showing twinned with particles of nickel based alloy comprising intermetallic compounds (NiB, Ni_2B, CrB, Cr_3B_4 and FeB) distributed in a very fine martensitic mass.



P1 80%Cu + 20% Ni-Cr-B-Fe-Al P2 70% Cu + 30% Ni-Cr-B-Fe-Al

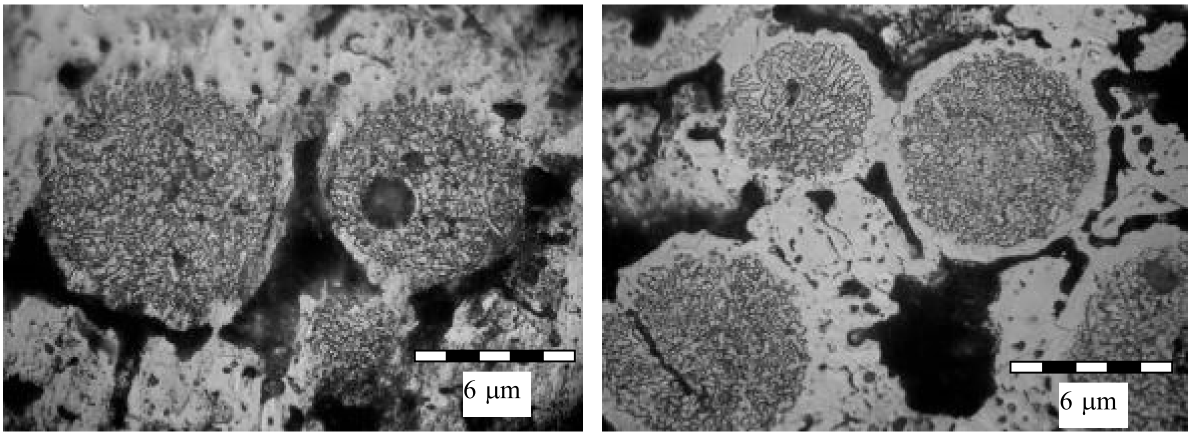


P3 60%Cu + 40% Ni-Cr-B-Fe-Al P4 50% Cu + 50% Ni-Cr-B-Fe-Al

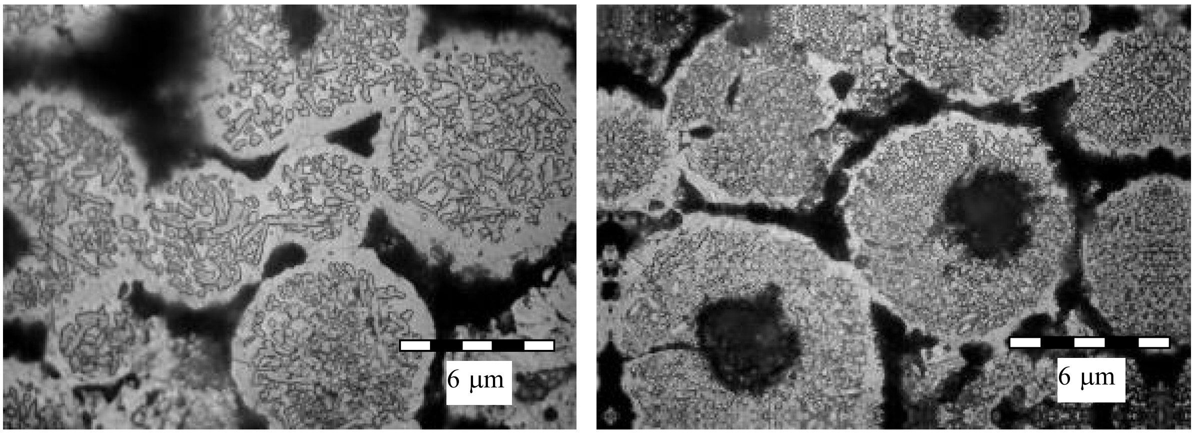


100% Cu

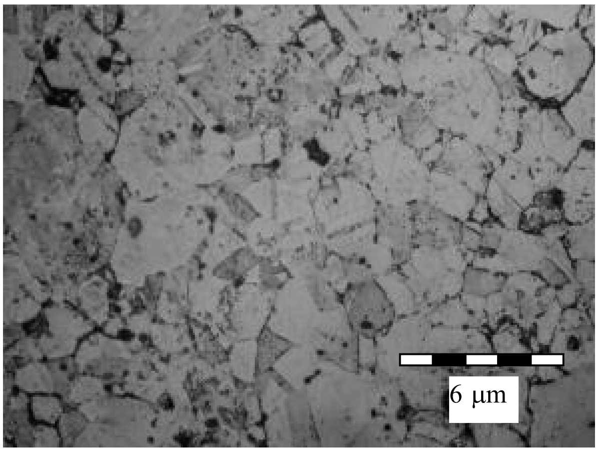
Fig. 4. *Microstructure of powder tablets in Cu matrix reinforced with sintered, unattacked Ni based alloy particles*



P1 80%Cu + 20% Ni-Cr-B-Fe-Al P2 70% Cu + 30% Ni-Cr-B-Fe-Al



P3 60%Cu + 40% Ni-Cr-B-Fe-Al P4 50% Cu + 50% Ni-Cr-B-Fe-Al



100% Cu

***Fig. 5.** Microstructure of powder tablets in Cu matrix reinforced with sintered Ni based alloy particles, sunjected to ferric chloride attack*

Microhardness $HV_{0.1}$ determined on the tablets of sintered powders took the following values: for Ni HV 0.1 = 9350 MPa, and for the Cu matrix HV 0.1 = 793.6 MPa. There is an increasing hardness of the Cu matrix vs the value reported for powder.

The Cu sintered samples and the composite Cu - NiCrBFeAl ones were tested to wear on rotary disk and sanding paper. The results obtained are shown in Table 2, which are the average of three determinations.

Analyzing the Table above we can see that the best reaction to wear is that of samples P1 and P2. The increase in the proportion of powder Ni-Cr-B-Fe-Al by 30% leads to a decrease in wear resistance due to a decrease in the degree of sample compactness when increasing the percentage of included phase and, on the other hand because of their pluking during the test. These particles give rise to additional wear of the surface examined, Fig. 6.

Figures 7 - 11 illustrate 3D images by a Image J software of the surfaces obtained from the abrasive wear test.

Analyzing the following images we see good wear behavior from samples P1 and P2, better than that of Cu sintered sample. In the darker areas it can be observed the absence of reinforcement particles that, running between the sample surface and abrasive, have led to additional wear.

Table 2. *Abrasive wear behavior of sintered powder products*

Samples	**Initial mass [g]**	**Final mass [g]**	**Mass wear [g]**	**Wear/length run [g/m]**
Cu	1.3057	1.2641	0.0416	0.007183
P1 - 80%Cu + 20% NiCrBFeAl	1.9954	1.9734	0.022	0.003798
P2 - 70% Cu + 30% NiCrBFeAl	2.0273	1.9965	0.0308	0.005318
P3 - 60%Cu + 40% NiCrBFeAl	1.3148	1.2556	0.0592	0.010222
P4 - 50% Cu + 50% NiCrBFeAl	1.3276	1.2736	0.0543	0.009324

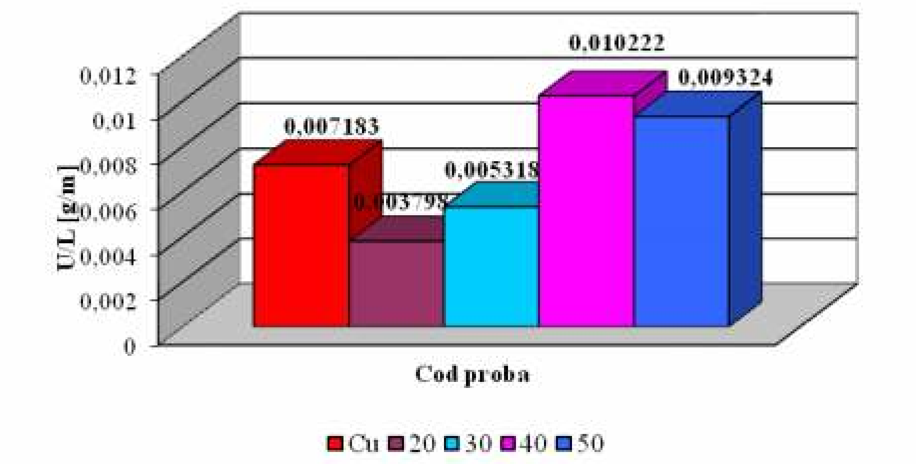


Fig. 6. *Abrasive wear behavior of sintered powder products*

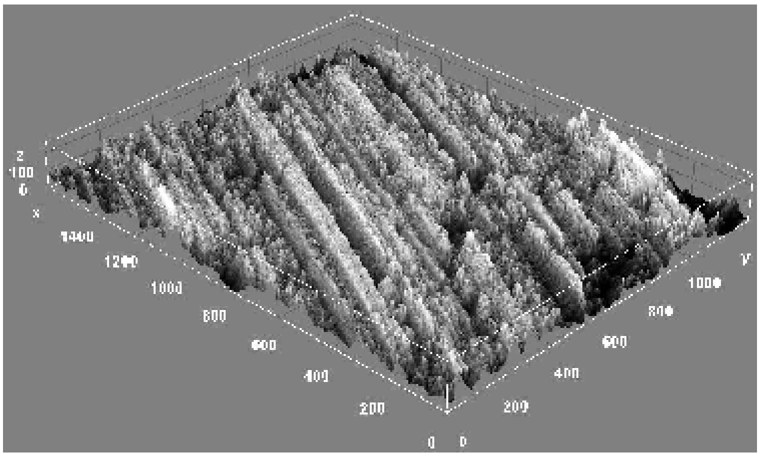


Fig. 7. *3D image of the Cu sample surface subject to abrasive wear*

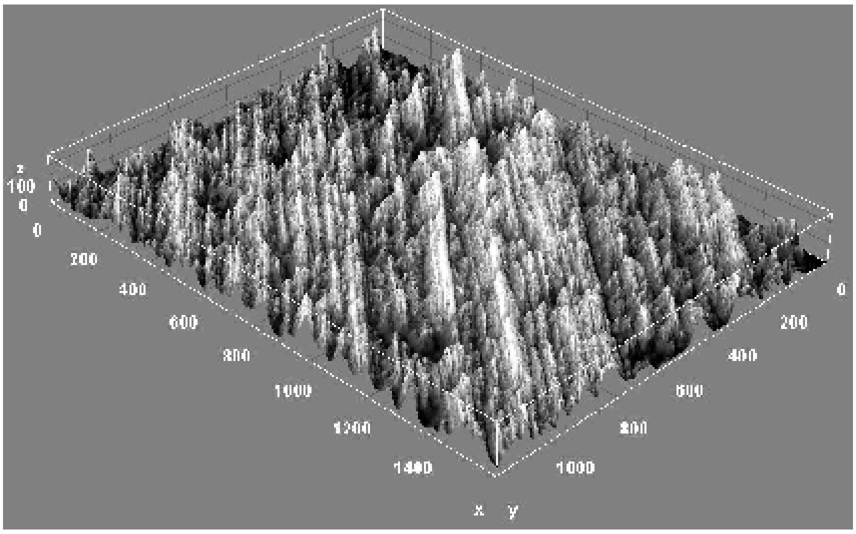


Fig. 8. *3D image of the P1 sample surface subject to abrasive wear*

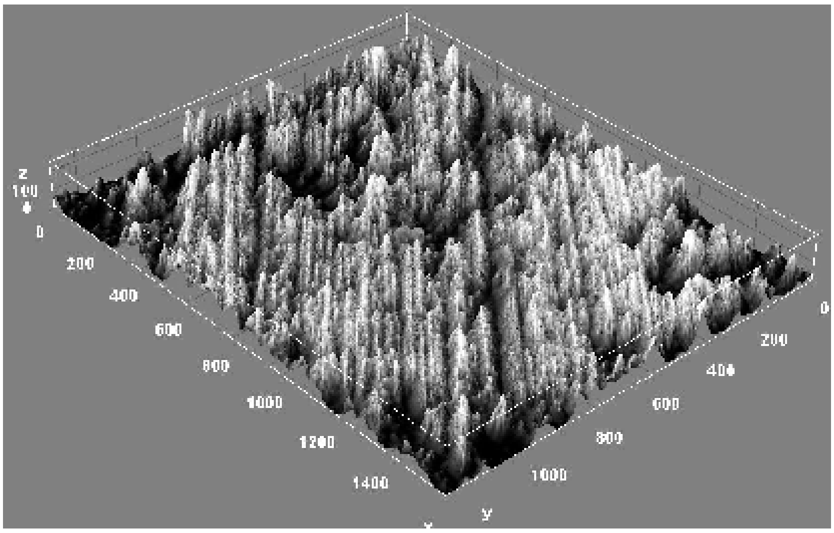


Fig. 9. *3D image of the P2 sample surface subject to abrasive wear*

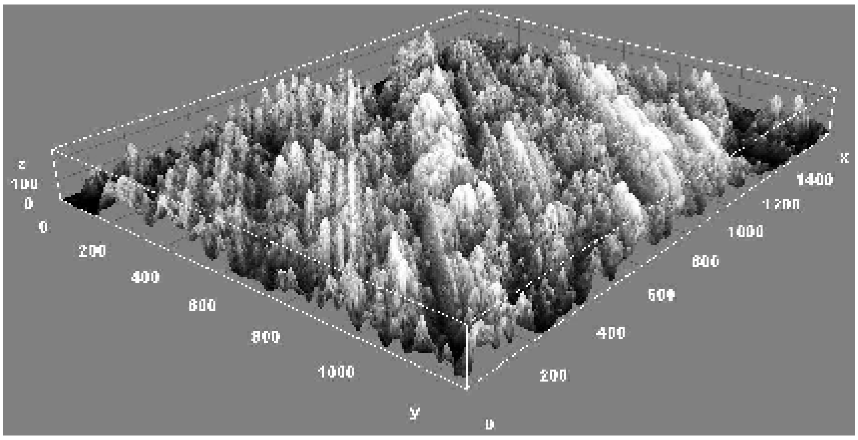


Fig. 10. *3D image of the P3 sample surface subject to abrasive wear*

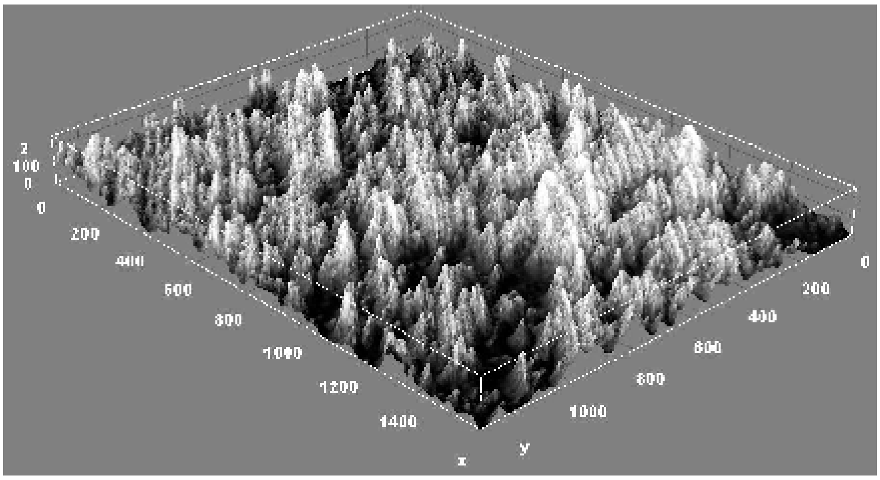


Fig. 11. *3D image of the P4 sample surface subject to abrasive wear*

4. Conclusions

❖ obtaining composites reinforced with particles of NiCrBFeAl alloy, revealed the following;

❖ the powder used in experimental research as reinforcing element has spherical shape specific to gas atomization;

❖ the powder used as matrix has an irregular shape caused by atomization in water;

❖ the compaction pressure was 863 MPa;

❖ it has been found that with increased content of NiCrBFeAl powder, of spherical shape, it is increasing the percentage of the inclusion; however there is a decrease in the degree of the sample compactness obtained through different deformation capacity of the powders;

❖ tablets powder sintering at 910 °C, for 90 minutes has reduced their porosity;

❖ microstructure of composites reinforced with Ni-based alloy particles shows a relatively uniform distribution of the included phases;

❖ it is made from Cu matrix consisting of twinned particles and nickel based alloy comprising intermetallic compounds (NiB, Ni_2B, CrB, Cr_3B_4 and FeB) distributed in a very fine martensitic mass;

❖ HV 0.1 microhardness determined on sintered powders tablets for Ni particles was HV 0.1 = 9350 MPa, and for matrix HV 0.1 = 793.6 MPa, with higher values of the powders in their initial condition;

❖ as regards the resistance to abrasive wear it was found that the best reaction to wear is shown by samples P1 and P2 with 20-30% NiCrBFeAl alloy; the increase in the NiCrBFeAl powder proportion over 30% leads to a decrease in wear resistance due to their plucking during the test. These particles give rise to additional wear of the surface considered;

❖ the 3D analysis of the surface resulting from the wear test conducted with Image J software, shows additional wear as a result of the separation of the hard particles from the NiCrBFeAl alloy.

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STRUCTURE OF THE EUTECTOID Zn-Al ALLOY OBTAINED BY DIRECTED SOLIDIFICATION

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ABSTRACT

This work analyses the structure of the eutectoid Zn-Al based alloy directionally solidified, with cooling rates ranging between 8.5-0.4 °C/sec. During cooling, the temperature gradient in the liquidus zone, respectively of the eutectoid transformation, changed within the ranges of 0.6-4.6, respectively 1.2-6.4 °C/mm. The results of the dilatometric analyses and of microhardness on different crystalline areas are presented.

KEYWORDS: Zn-Al alloys, directed solidification, microstructure, dilatometric analysis, microhardness

1. Introduction

Over the last years the category of industrial alloys based on the Zn-Al system has widely expanded, yielding standardised compositions with 8, 12, 22, 27 and 40% aluminium. Their properties have been studied in depth [1-6]. Zn-Al alloys have excellent castability, good wear and friction strength. The disadvantage of these materials is the instability of the solidification structure, what determines dimensional modifications of the castings over time. The analysis of phase transformation considered the Zn-Al thermal equilibrium diagram established by Presnyakov, Fig. 1 [3].

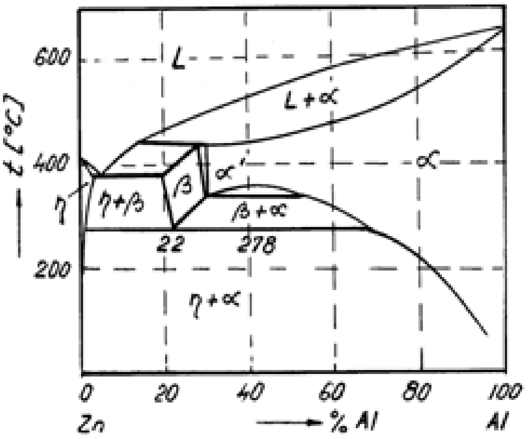


Fig. 1. *Zn-Al thermal equilibrium diagram*

According to the thermal equilibrium diagram, three important transformations occur in Zn-Al alloys rich in zinc:

- eutectoid transformation, at 278 °C (some authors indicate 272 °C, 275 °C):

$$\beta_{22\%\,Al} \rightarrow \alpha_{68.4\,\%\,Al} + \eta_{0.5\%Al} \tag{1}$$

- peritectic transformation, at 443 °C:

$$L_{14\,\%\,Al} + \alpha_{30\,\%\,Al} \rightarrow \beta_{28\%\,Al} \tag{2}$$

- eutectic transformation, at 382 °C:

$$L_{5.1\,\%\,Al} \rightarrow \alpha_{1.02\%\,Al} + \beta_{17.2\%\,Al} \tag{3}$$

In a previous paper, we have analysed the structural and dimensional modifications in a binary Zn-Al$_{22}$ alloy, solidified at various cooling rates [7].

In casting important are the magnitude and ratio of the areas with columnar and equiaxial crystals [8]. The paper presents the results of research conducted on a bar shaped part of 30 mm diameter, obtained by directed solidification.

2. Experimental determinations

The device shown in Fig. 2 was conceived for the experimental determinations aimed at inducing directed solidification.

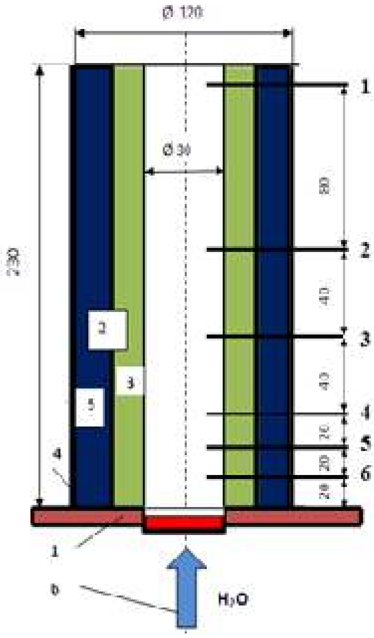


Fig. 2. Schematic of the device used for directed solidification

The device consists of a base plate (1) holding the casting mould (2) for a 30 mm diameter bar of maximum 230 mm height. In order to ensure directed extraction of heat as well as the mounting of thermocouples, the mould wall consists of two concentric cylinders, the inner one being made from heat insulating brick (3), while the exterior metal casting (4) and the interior cylinder encase a usual moulding sand.

The mould is heated by placing it over an electric heating device. Subsequently the mould is swiftly transferred from the heating to the cooling position by means of an adequate device. The base plate is cooled by a water jet (5) of adjustable flow and pressure.

Fig. 3. Set-up for the recording of the cooling curves

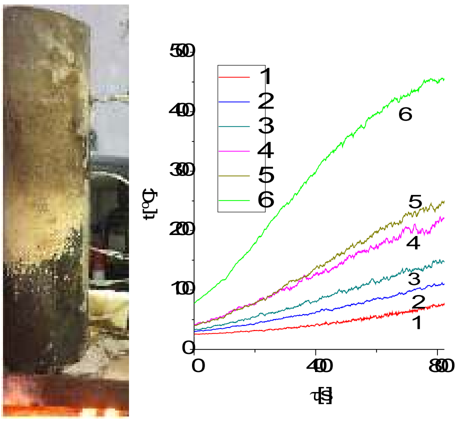
The temperature was recorded by K type thermocouples of 0.5 mm wire thickness. The tips of the thermocouples were introduced 10 mm deep into the mould cavity, as shown in Fig. 2.

The thermocouples were placed at distances of 20 (16), 40 (39), 60 (58), 100 (100), 140 (138) and 220 (218) mm from the base plate.

The real distances measured on the cylindrical cast part are indicated between brackets. Temperature recording was conducted via a ADAM - 4018 interface. Fig. 3 presents the set-up for the recording of the cooling curves.

The slightly hypereutectoid binary Zn-Al alloy with 25% Al was melted in an electrically heated crucible.

In order to ensure directed solidification, the mould assembly was preheated by means of an electric heating device, Fig. 4. a), to temperatures indicated in Fig. 4 b), while the casting temperature was of 730 °C.



a) b)

Fig. 4. Preheating of the mould

Fig. 5 shows the cooling curves recorded by means of the 6 thermocouples.

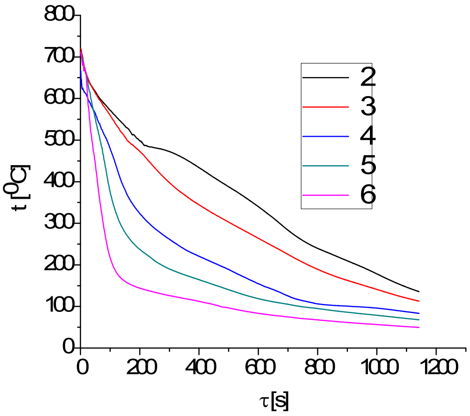


Fig. 5. Recorded cooling curves

The cooling curve for point 1 does not appear in the diagram, as the thermocouple of that area was located exactly at the level of the liquid alloy in the mould and the curve, while having certain irregularities, coincides as to its shape and quantity with the one recorded in point 2.

Only for thermocouples (TC) 2 and 3, where the cooling rates were smaller, the cooling curves feature inflection points corresponding to the structural transformations indicated by the thermal equilibrium diagram.

Based on the derivatives of the cooling curves for the extreme measuring points, namely points 6 and 2, it follows that in the melt preceding the solidification front the cooling rates range in the interval from 8.5 to - 0.4 ^{o}C/s, Fig. 6.

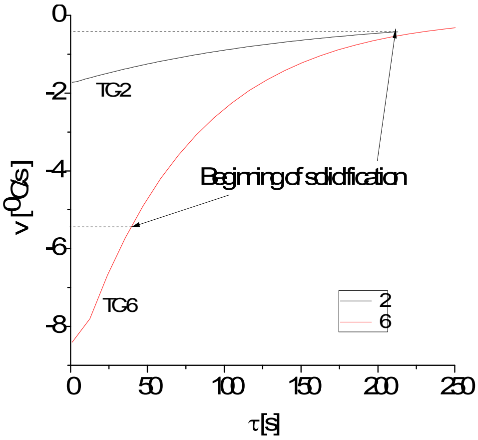


***Fig. 6.** Variation of cooling rates versus time*

The completed computations revealed that during cooling the temperature gradient in the liquidus and the eutectoid transformation area, respectively, varied within the ranges of 0.6-4.6^{o}C/mm and 1.2-6.4 ^{o}C/mm, respectively.

The cast bar was cut by the segments corresponding to the thermocouples and samples were taken for structural, DSC, dilatometric, microhardness and wear strength analyses.

Fig. 7 presents the macrostructures obtained in the longitudinal section along the entire height of the cast bar.

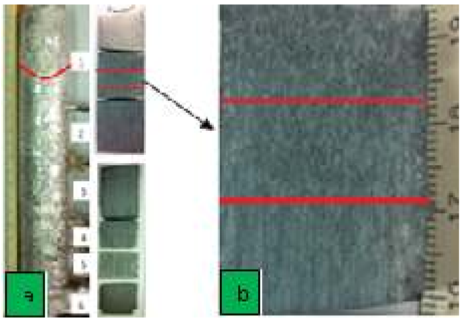


***Fig.** 7. Macrostructure of the cast bar: a) in longitudinal section; b) transition area, columnar – equiaxial crystals*

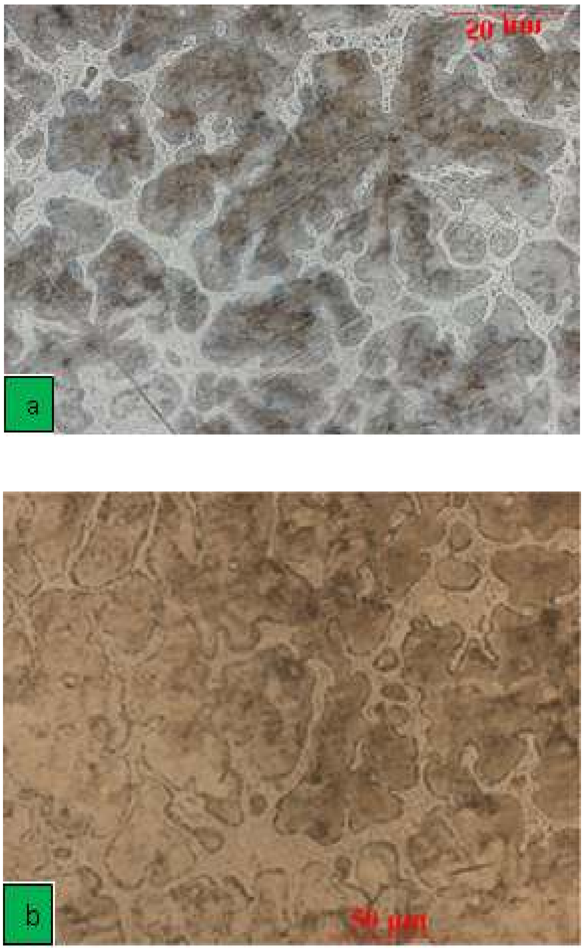
The area of columnar crystals covers nearly the entire height of the test piece.

The transition from the area of columnar crystals to that of equiaxial ones occurs approximately at the centre of area 1, at 170 - 180 mm distance from the cooled end of the bar, whose limit is marked on the cast bar, Fig. 7.

At the inferior end of the bar, area 6, the columnar crystals are thin, and their diameter increases along the height of the bar from 0.5 mm to 2-3 mm in area 1. The length of these crystals exceeds 20-30 mm. In area 1 the diameter of the equiaxial crystals is 2-4 mm.

The effect of the directed cooling, under the conditions of the experiment, extends over a height of 170-180 mm. The microstructural analyses were conducted by means of a NIKON Eclipse MA100 microscope endowed with an *OMNIMET-BUEHLER* image analyser.

Fig. 8 shows the microstructure of the bar obtained by directed solidification in various cooling areas and in cross-sections, perpendicular to the direction of solidification (T) and longitudinal (L).



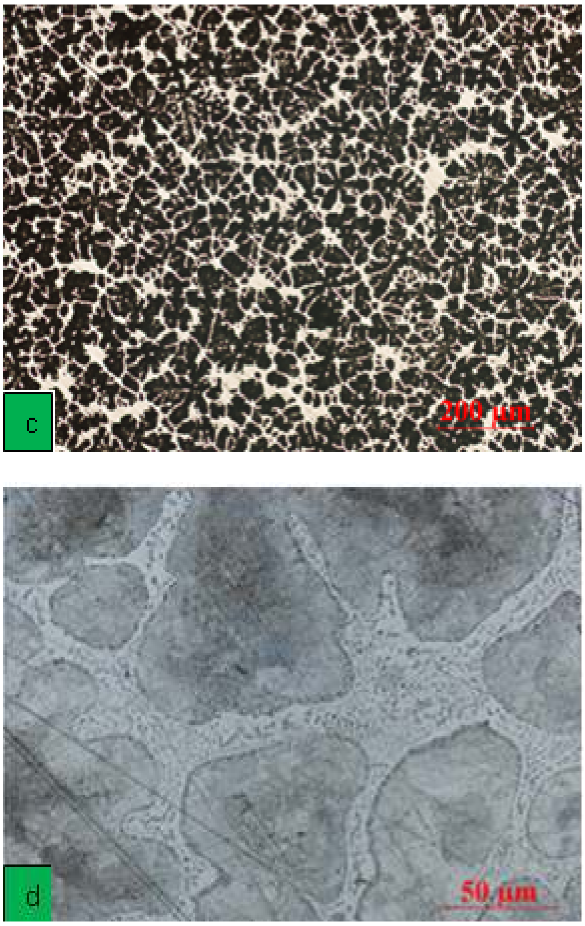
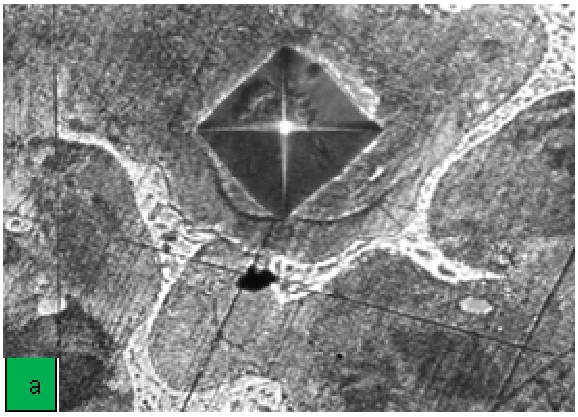


__Fig. 8.__ Microstructure of the bar obtained by directed solidification in various areas: a) 6 - L; b) 5 - L; c) 5 - T and d) 1 - L

Microhardness was determined by means of an FM-700 AHOTEC device. The results are given in Fig. 9 and Table 1.

The values in the Table are the arithmetic mean of at least 3 measurements.



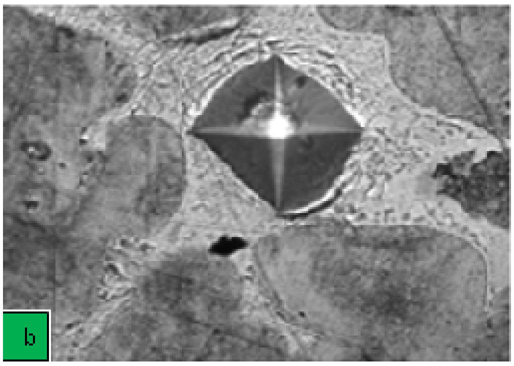


__Fig. 9.__ Microhardness of the Zn-Al alloy obtained by directed solidification: a) dendrites and b) eutectic

__Table 1.__ Microhardness of the Zn-Al alloy obtained by directed solidification

Crystalline area	dendrites	eutectic
5 - longitudinal	99.5	91
2 - transversal	89	80

Because of the high cooling rate, in area 5, the hardness of both dendrites and the eutectic is greater than the alloy solidified at smaller cooling rates, in area 2. The hardness of dendrites is greater than in inter-dendritic areas, which were enriched in zinc due to structural transformations during cooling. A LINSEIS L75PT/1400 °C dilatometer and a DSC 200 F3 – Maia - Netzsch differential scanning calorimeter were used for the analysis of microstructure modifications determined by phase transformations as well as by the diffusion processes brought about by the thermodynamic tendency of restoring the state of equilibrium. The diagram in Fig. 10 presents the results of the dilatometric analyses conducted on various cooling areas and for various states.

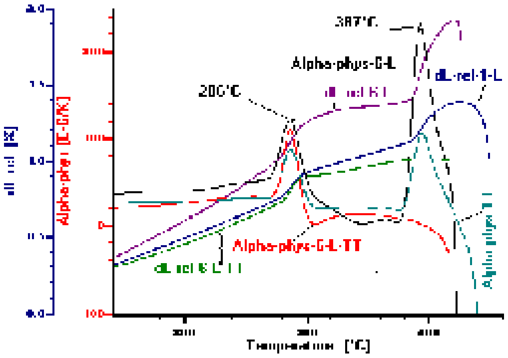


__Fig. 10.__ Dilatation curves (dl-rel) and the variation of the dilatation coefficient versus temperature

In the case of the heat treated test piece, 6 – L - TT, the treatment entailed heating up to 420 ^{o}C. Both heating and cooling were carried out at a rate of 10^{o}C/min. There are significant differences between the dilatation of the test pieces in the area of columnar and that of equiaxial crystals.

DIL analysis results reveal the intensity of the segregation processes during solidification. This finding is in agreement with the observations published in [9] that indicate the presence of eutectic also in compositions with 8% aluminium content. The results of the differential calorimetric analysis shown in Fig. 11 confirm the presence of the phase transformations revealed by dilatometric analysis. In the calorimetric analyses as well as in the dilatometric ones the heating and cooling rates were of 10 ^{o}C/min.

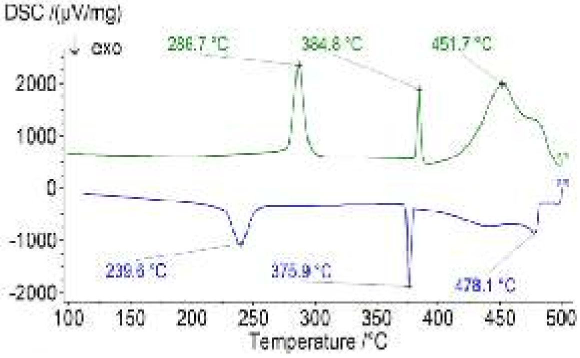


Fig. 11. *DSC curves for the heating and the cooling of the test piece in area 6*

The DSC curves indicate the presence of eutectoid, eutectic and peritectic transformations during both heating and cooling. It needs be pointed out that the 3 transformations occur with different intensities during heating and cooling, respectively, what is explained by the thermodynamic tendency of restoring the equilibrium structure.

3. Conclusions

By the directed solidification of the slightly hypereutectoid Zn-Al alloy, the area of columnar crystals extends over a very wide range.

With a decrease in local cooling rate the thickness of the columnar crystals increases.

In the case of directed cooling, the equiaxial crystals start forming at cooling rates smaller than 0.4^{o}C/s.

The completed analyses reveal significant differences in structure and properties between the areas formed of columnar and equiaxial crystals, respectively.

Because of segregation phenomena the eutectic transformation is present also in slightly hypereutectoid compositions.

Acknowledgements

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STUDIES AND RESEARCH ON TREATMENT OF TITANIUM ALLOYS

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ABSTRACT

Titanium and its alloys have an extended use due to special properties. The paper highlights the TiZr alloy intended to manufacture prostheses, the influence of plastic deformation on the properties and structure. Applied research and technology have shown good deformation behavior of the alloy, good plasticity and a reduced hardening trend. The plastic deformation provides a fine structure and a 50% increase in hardness and strength properties.

KEYWORDS: titanium alloys, direct extrusion, degree of deformation, structure, hardness

1. Introduction

Titanium is a very common element, the ninth in descending order, representing about 0.6% of the Earth's crust. More than 95% of titanium is used in the form of TiO_2 and other compounds in the manufacture of white paints, coating rutile titanium electrodes, etc. Only 5% is used as a pure metal, for micro-alloying of steels or alloy with high strength and low specific weight. The percentage is growing.

Pure titanium has a strength of 434MPa. Commercial purity titanium is 99.2%. In the form alloyed titanium is a very high resistance up to over 1400MPa. Stressed metal reduces its strength when heated to over 430^{o}C. Titanium has two allotropic states: hex to 882^{o}C and the body-centered cubic above this temperature. These structures are found in the case of zirconium with titanium alloy well forming solid solutions with complete solution as shown in the diagram Ti - Zr equilibrium, Figure 1.

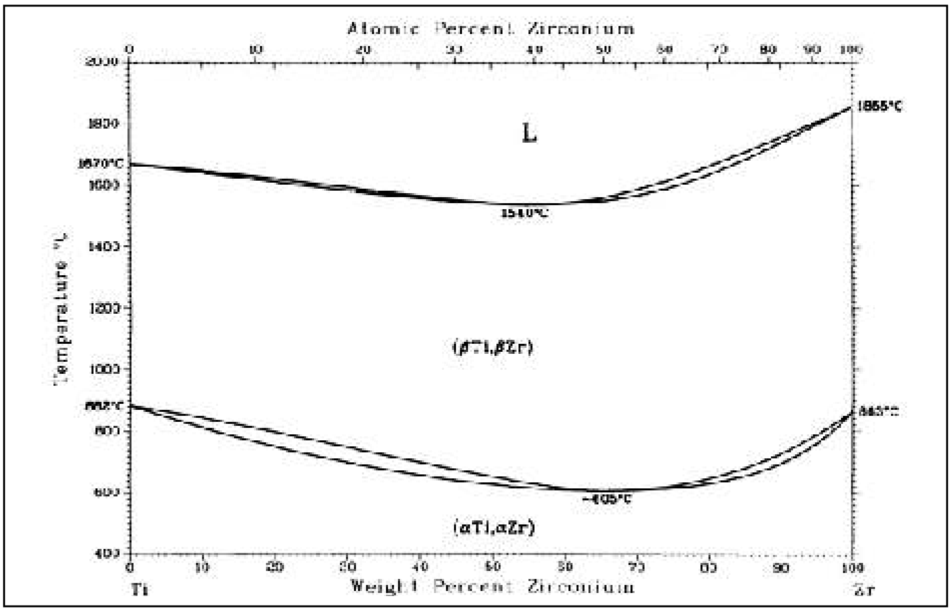

Fig. 1. The diagram Ti-Zr equilibrium

A special feature of titanium and its alloys is corrosion resistance. From this point of view it is comparable to platinum. Titanium better resist the attack of acids, solutions of chlorine in water, it is soluble in concentrated acids. Although titanium Pourbaix diagram, Figure 2, shows that it is a very reactive metal, its reaction with water and air are very slow.

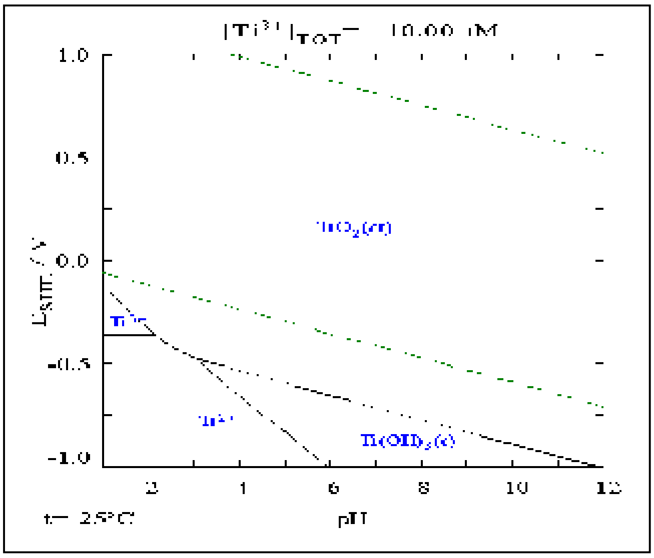

***Fig. 2.** Titanium Pourbaix diagram*

At ambient temperature, in spite of the oxidation resistant titanium has a loss of gloss; formed TiO2 layer thickness of about 2nm. Air temperature increase it was estimated that TiO_2 layer can grow up to 25nm in about four years, enhancing the corrosion resistance of the metal.

Heating to above 1200^{o}C in air causes spontaneous combustion of titanium, so melting, production and casting of titanium and its alloys should be performed in an inert atmosphere or vacuum.

In addition to over 800^{0}C merge seamlessly with nitrogen to form titanium nitride TiN. It is extremely hard and lowers the ductility of the metal or alloy. Titanium is not toxic, even in large amounts and has no impact on tissues or organs of the human body. It was found that it is tolerated by the tissues and also if ingested, its excreted without being absorbed. In power plants, it is found in very small amounts 2ppm, exception being the horse tail and nettle, about 80ppm.

2. Current applications of titanium and its alloys

As a result of its qualities, titanium will become one of the most used metals, the third in terms of global importance.

The growth in the production of titanium, exceeds the growth rate of the world economy and other industries. Initially, titanium has been used in the aerospace industry with spectacular results. Therefore, the enhanced production of titanium explored other potential applications.

Today we distinguish a wide variety of uses such as:

- in the aerospace industry : frames and panels fuselage structure strength, braking, jet engine components, fire walls, etc. Titanium is also used to achieve: turbine blades, compressor blades and disks, hot air pipes, bearings, rotors of helicopters, etc.
- applications that involve the use of titanium due to its outstanding resistance to corrosion, such as: chemical technology, paper manufacturing industry, energy industry, water applications;
- biomedical applications that exploit the inertia of the metal in the human body (biocompatibility): implants dental;
- special applications that appeal to the properties of superconductivity (niobium alloys) or shape memory effect (nickel alloys)
- applications that operate mostly with high specific strength: the automotive industry, vehicles in general;
- applications in consumer goods: cameras, jewelry, musical instruments, sports equipment etc.

3. Aspects of producing Ti

World production of titanium metal is around 100 000 tonnes annually. The most part is produced by the Kroll process that uses TiO_2 and ore concentrates, involving the following reaction sequence:

a) obtaining titanium tetrachloride:

$TiO_2 + 2CI_2 + 2C <-> TiCI_4 + 2CO$

b) reduction of magnesium:

$TiCI_4 + Mg <-> 2MgCI_2 + Ti$

Magnezotermic titanium tetrachloride is reduced in a reactor under an atmosphere of argon. Magnesium chloride is formed and the excess of magnesium is washed with water and dilute hydrochloric acid, resulting in the "titanium foam". This was purified by van Arkel - De Boer process played by the reaction:

$TiJ_4 <–> Ti + 2J_2$.

By replacing magnesium with sodium, Degussa method, one can get a pure " titanium sponge ".

Then titanium sponge is melted in a special insullations, such as the electric arc under vacuum. In these furnaces, electric arc generated between a consumable cathode of sponge titanium and copper crucible in a current of 15-40 kA and a vacuum level of 10^{-2} mbar.

In industrial technologies protective atmospheres are used for different heat processing (melting, sintering, plastic deformation, welding, heat treatment, etc.), inert gases such as argon and helium or some controlled atmospheres.

A significant amount of titanium is obtained by recycling waste materials. Recycling waste requires prior preparation, which consists of sorting, cutting, grinding, degreasing and pickling, washing and drying. Degreasing wastes is made alkaline and acid etching. Degreasing wastes is made with alkaline solutions and etching with acid solutions. Operations must preserve the physico- mechanical and chemical properties of the metal or alloy.

Flowsheet melting waste includes the following:

- Obtaining electrodes by compacting waste;
- Melting of the electrode of titanium or alloys waste titanium in the vacuum arc furnaces, or electron beam. In some cases is applied alloy remelting for composition uniformity throughout the length of the ingot;
- Heat treatment and plastic deformation processes;
- Characterization of the products obtained.

Waste titanium and titanium alloys generally have high concentrations of impurities compared to sponge titanium source in the preparation. The reason is that, although the melting takes place in vacuum or in an inert gas atmosphere in the atmosphere of the oven where melting occurs, there is always a certain amount of oxygen and hydrogen, as a result of freeing the waste gases adsorbed on the electrode, or oven walls. These gases are almost entirely related to the melted titanium and therefore the amount of impurities in the remelted ingot is always higher than that of primary sponge. These impurities will be found in pieces and manufactures cast, which will add other impurities absorbed during plastic deformation.

Technological scheme for obtaining plastic deformation elements include the following:

- pre-treatment consisting of a homogenizing annealing at about 1000^{o}C and may be followed by a quenching of sample to eliminate the grain boundaries of the eutectic formed with some accompanying parts ;
- hot plastic deformation which can consist of a rolling at temperatures of 800 - 850^{o}C or forging or extrusion. Hot plastic deformation will be in controlled atmosphere furnace or vacuum;
- plastic deformation by cold rolling;
- final treatment comprising recrystallization annealing at 800°C and stress relief annealing at a temperature of 570 ^{o}C . Heating the thermal treatment should be performed under vacuum or in a controlled atmosphere, the duration of the treatment and several days depending on the size of the blanks.

Application of thermomechanical treatments, which combines the various thermal treatments to the plastic deformation, has a high potential for improving the mechanical properties of titanium alloys, and as a results it can be taken into account.

4. Deformation of titanium alloy semi-products laboratory

The blank was originally a cast titanium alloy bar with 10% zirconium, machined by turning. It has a diameter of 18mm and length of 35mm. It has been subjected to heating at 850^{0}C, in the electrical resistance furnace with maintaining equalization for 10 minutes. The temperature was chosen in view of the equilibrium diagram such as Ti-Zr alloy has a solid solution structure of the beta crystalline crystal structure solid solution centered cubic system with a better plasticity.

The blank/semi-product was subjected to heating hot extrusion to a diameter of 10 mm into a mold preheated to about 400°C to avoid cooling of the blank during deformation. Also in this regard, we performed a valuable rapid transfer of the blank from the furnace in the extrusion die container. After forming, the preform was cooled in air.

The second extrusion blank was cut to a length of 35mm, consistent with the increased dimensions.

The Φ10x35mm new blank was subjected to heating at 850^{o}C and was hot extruded to a diameter of Φ5mm and cooled in air.

Finally Φ5mm extruded preform was cold rolled to a diameter of Φ3mm sizes.

For evaluation of materials, all stages of research in all the blanks were sampled by cutting by milling.

Sample preparation and analysis of the structure and hardness.

Titanium alloy samples at each stage of processing: molding, 1 extrusion 1, 2 extrusion 2, cold rolling, were embedded in an acrylic solution.

Sample preparation was done by metallographic grinding paper to very fine grained, scoring 1200 and then fine polishing felt or velvet, with fine alumina paste with high humidity and moderate pressure. To highlight the microstructure of the samples they were attacked with Kroll solution, and 1.5ml HF, HNO_3, 4ml, 94.5ml H_2O.

To determine the Vickers hardness, a test was applied with small tasks HV_{100}. The values obtained as the average of at least three tests were as follows: 212daN/mm^2 for cast, 290daN/mm^2 for extrusion 1, 306daN/mm^2 for extrusion 2 and 320 daN/mm^2 for cold rolled. They show as expected a significant improvement of the properties after deformation. This is confirmed by microstructural analysis. The cast sample has an inhomogeneous structure, consisting of large grains aspect of dendritic cells, Figure 3. Improvying this structure can be achieved by applying a homogenization treatment or hot plastic deformation.

In the research we have done hot plastic deformation by direct extrusion in two stages: extrusion 1 from Φ18mm to Φ10mm and extrusion 2 from Φ10mm to Φ5mm. Metallographic analysis shows a gradual completion of the structure and its uniformity and homogenization.

It also highlighted the lines of flow of the material during deformation, Figure 4 and Figure 5. Moreover, the effect of hot plastic deformation was highlighted as shown by hardness increase from 212 to 306 daN/mm^2. Deformation by cold rolling marked the same trend finishing and smoothing of the structure (figure 6) and increasing hardness from about 320 daN/mm^2. With relatively small increase in cold rolling, the alloy showed good plasticity and a reduced hardening trend. Table 1 and Figure 7 show the trend of hardening of titanium alloy and influence of the degree of deformation expressed by coroiaj C_T on hardness HV_{100}.

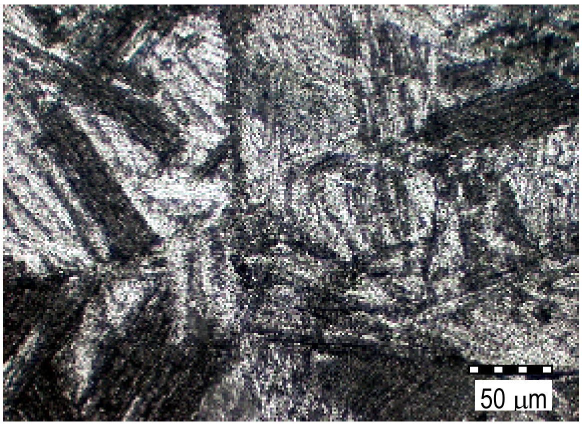

Fig. 3. *Castings microstructure of Φ18mm (X200)*

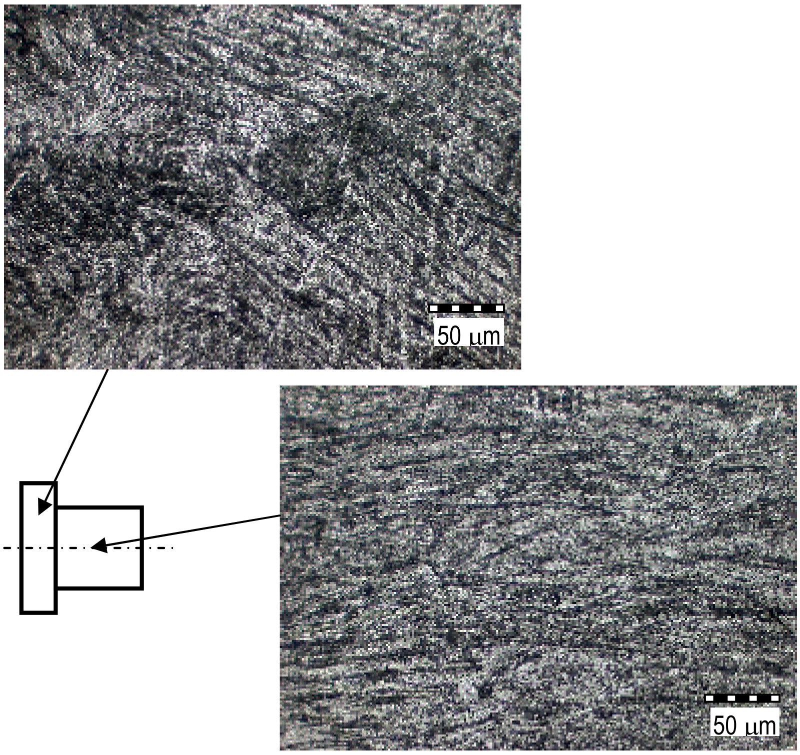

Fig. 4. *Microstructures no.1 extruded 1 from Φ18mm to Φ10mm (X200)*

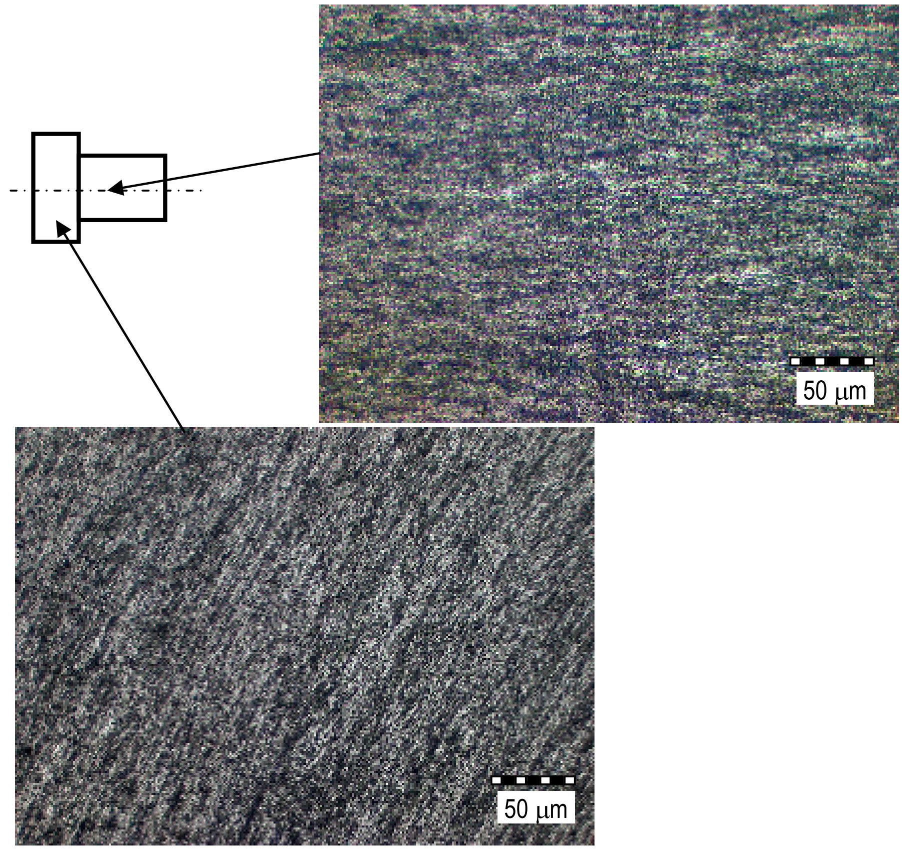

Fig. 5. *Microstructures no.2 extruded from Φ10mm to Φ5mm (X200)*

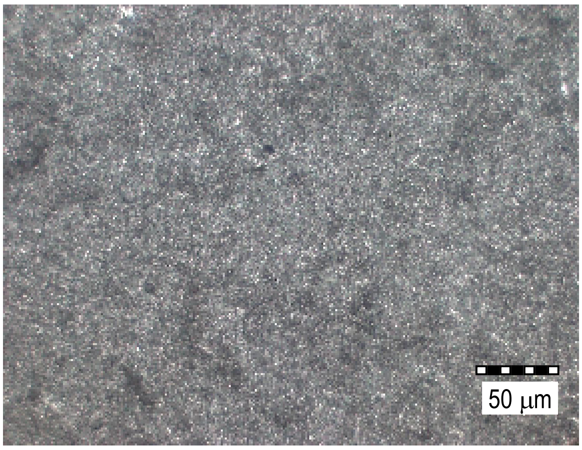

Fig. 6. *Cold rolled Microstructure from Φ5mm to Φ3mm (X200)*

Table 1

Nr.	**The blank Semi-product**	**Stage degree of deformation** $C=S_{i-1}/S_i$	**Total degree of deformation** $C_T=S_0/S_i$	**Hardness** HV_{100} **daN/mm^2**
1	Cast Φ18	0	0	212
2	Extruded Φ10	3.24	3.24	290
3	Extruded Φ5	4	12.96	306
4	Cold rolled Φ3	2.77	36	320

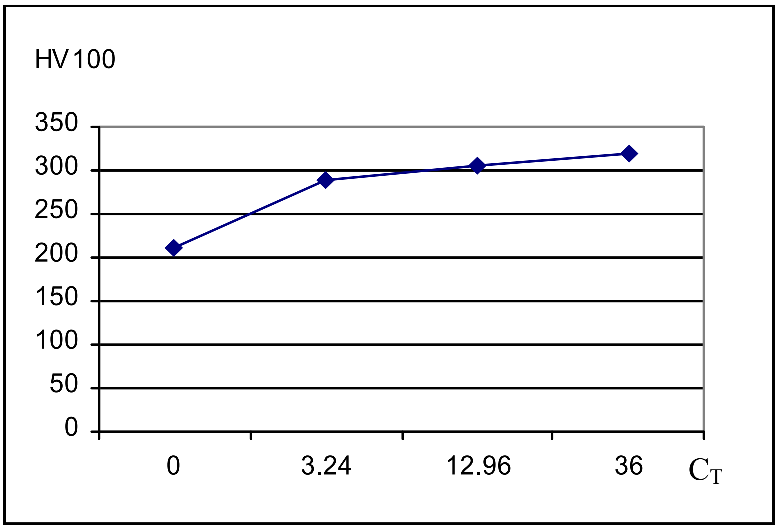

Fig. 7. *Total deformation influence on the hardness of the Ti Zr alloy*

4. Conclusions

The study and research highlight the importance of using titanium alloys both primary development and recovery of waste in the form of ingots of similar dimensions required. Improved performance of these alloys can be achieved by hot-plastic deformation and cold deformation by heat treatment. The applied technology applied to revealed smooth deformation behavior of the alloy, good plasticity and a reduced hardening trend. The deformation process ensures a fine structure and a 50% increase in hardness and strength properties.

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