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INFLUENCE OF HEAT TREATMENT TECHNOLOGY ON THE STRUCTURE AND PROPERTIES OF THICK SHEET STEEL ASTMS14 DEGREE F

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ABSTRACT

In this paper, based on the researches carried out a heat treatment technology can be determined which further lead to an optimum set of mechanical properties according to the technical conditions: A. Annealing (austenite at temperature 920 °C, exposure 2 minutes/mm, water cooling) and B. Tempering (heating at temperature 680 °C, exposure 4 minutes/mm, air cooling). The micro-structural analysis showed the structural modifications which takes place when tempering within 580 – 700 °C. Upon heating, the martensite out of balance structural tend to get transformed. To be able to characterize steels in terms of their physical and mechanical properties, a significant role is played by the pull tests. The following mechanical characteristics was determined: ultimate strength (R_m), yielding point standing ($R_{p0,2}$), breaking elongation (A_5) and the resilience test (KV_L).

KEYWORDS: annealing, tempering, structure, properties, martensite

1. Introduction

Based on the researches carried out a heat treatment technology can be determined which further lead to an optimum set of mechanical properties according to the technical conditions: *annealing* (austenite at temperature 920 °C, exposure, 2 minutes/mm, water cooling); *tempering* (heating at temperature 680 °C, exposure 4 minutes/mm, air cooling) [1-3].

To be able to characterize steels in terms of their physical and mechanical properties, a significant role is played by the pull tests: ultimate strength (R_m), yielding point standing ($R_{p0,2}$), breaking elongation (A_5) and the resilience test [4-6].

Upon heating, the martensite out of balance structural tend to get transformed. The process is based on diffusion whose amplitude is higher when the temperature is higher too [7-9].

The micro-structural analysis showed the structural modifications which takes place when tempering within 580 – 700 °C.

2. Experimental researches and results

The following research schedule was designed to determine the heat treatment parameters:

- austenite at 900 °C, 920 °C, exposure time 2 minutes/mm;
- water cooling;
- tempering temperatures: 580 °C, 600 °C, 620 °C, 640 °C, 660 °C, 680 °C, 700 °C, exposure time 4 minutes/mm.

The heat treatment research schedule is given in Table no. 1.

***Table 1.** Experimental conditions*

Austenite temperature [°C]	Exposure time [min]	Cooling agent	Tempering temperature [°C]	Exposure time [min]	Tempering agent
920	40	water	580 600 620 640 660 680 700	80	still air

To be able to characterize steels in terms of their physical and mechanical properties, a significant role is played by the pull tests.

For this purpose, samples were taken transversally with respect to the rolling direction to make STAS 200 – 75 samples.

The test consists in applying slow smooth loads in ambient environment.

The following mechanical characteristics are determined:

- yielding point standing for the ratio of the load where the length is increasing and the initial cross section area of the blank;
- ultimate strength which is the ratio of the max load and initial cross section area of the sample;
- breaking elongation: A_5
- breaking throttle: $\Psi = \frac{S_o - S_u}{S_0} \cdot 100$

The resilience test is actually a bending test by shock and serves the purpose of assessing the material tenacity.

Table 2. *Mechanical properties*

No	Austenite temperature [°C]	Tempering temperature [°C]	Mechanical properties under annealed and tempered conditions			
			R_m [N/mm^2]	$Rp_{0,2}$ [N/mm^2]	A_5 [%]	$KV_{L\text{-}46^oC}$ [J]
1	900	580	1092	1005	15	54;52;53
2		600	1075	1000	16	61;62;63
3		620	1058	995	16.5	66;67;68
4		640	1030	972	16.5	74;75;73
5		660	995	944	18	93.5;95;96.5
6		680	920	848	20	112.5;115;117.5
7		700	786	786	22.5	123;125;124
8	920	580	1105	1011	15.5	51;50;52
9		600	1068	998	16.5	58;58;58
10		620	1061	990	16.5	63;62;64
11		640	1035	965	17	72;70;68
12		660	989	937	17.5	95;94;93
13		680	923	873	21	102;100;101
14		700	782	791	22	115.5;115;114.5

The test consists in breaking by one strong hit with a pendulum hammer Charpy, a sample fitted with a V – shaped groove in the middle which freely leans against two seats to determine the breaking energy.

The samples are cooled in systems made of heat insulated recipients. Cooling agents are ethyl alcohol and carbon snow.

The results obtained are given in Table 2 for the annealed and tempered samples.

The value of the mechanical characteristics obtained further to the heat treatments applied have been statistically processed and illustrated vs. heat treatment parameters, in Fig. 1; 2; 3 and 4.

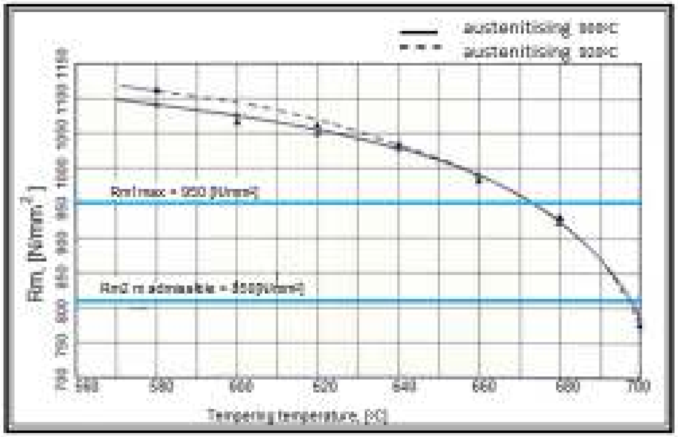


Fig. 1. *Effect of tempering temperature the ultimate strength, R_m [N/mm^2]*

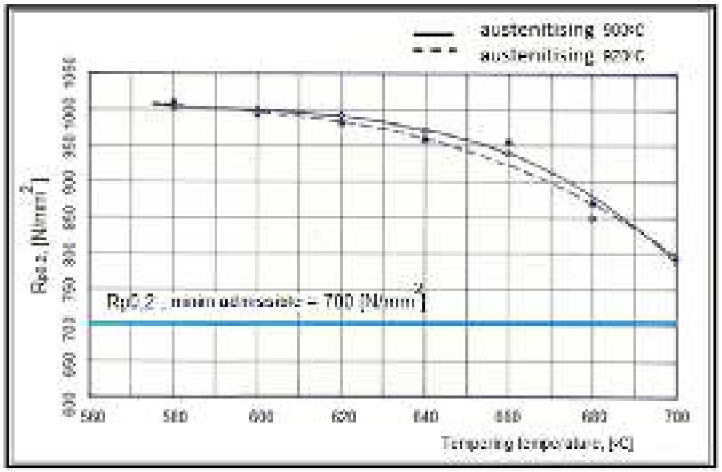


Fig. 2. *Effect of tempering temperature the yielding, R_{p02} [N/mm^2]*

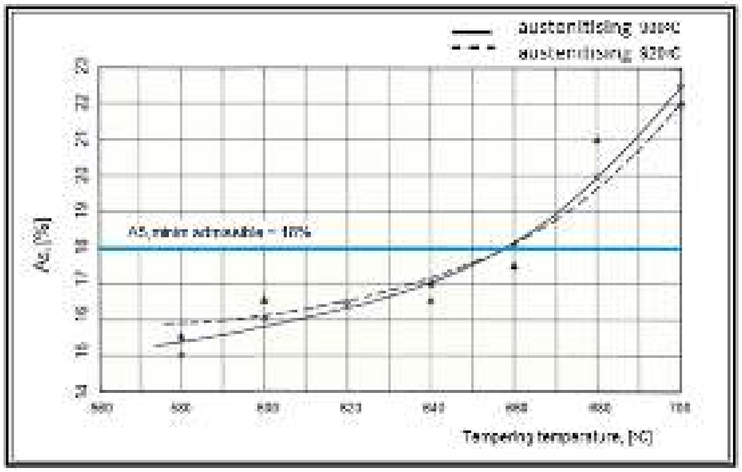


Fig. 3. *Effect of tempering temperature on the breaking elongation, A_5 [%]*

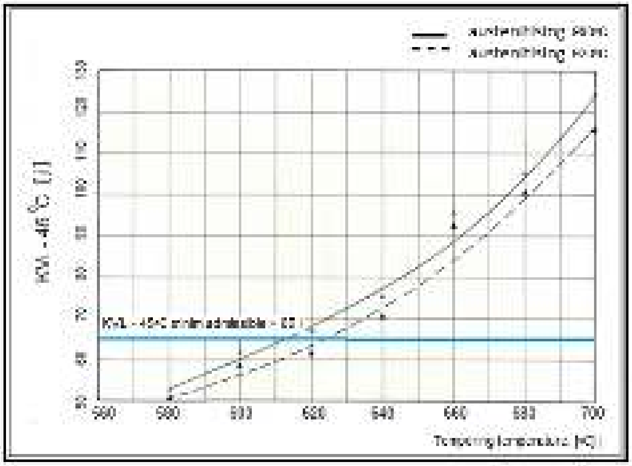
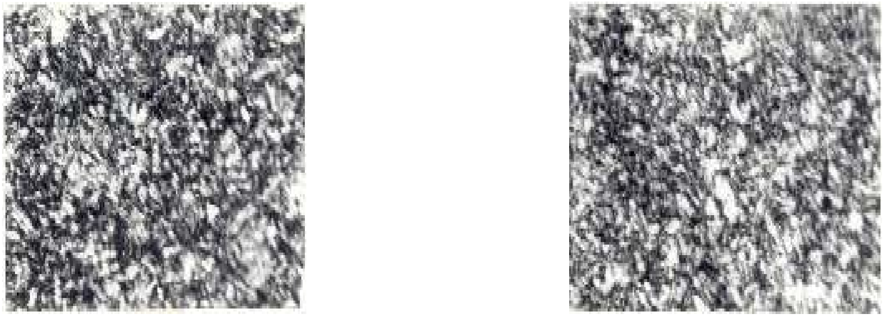
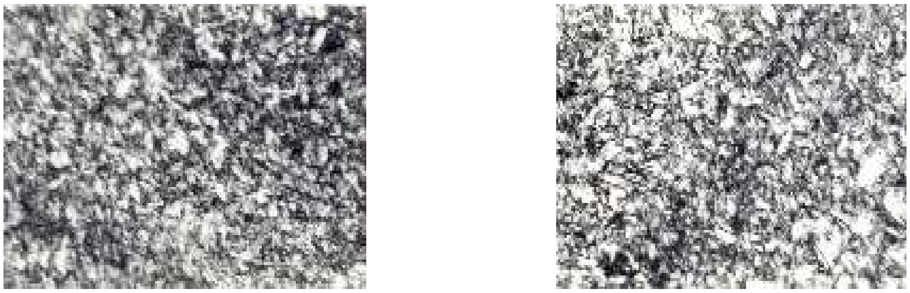


Fig. 4. *Effect of tempering temperature on cross resilience, KV_L [J]*

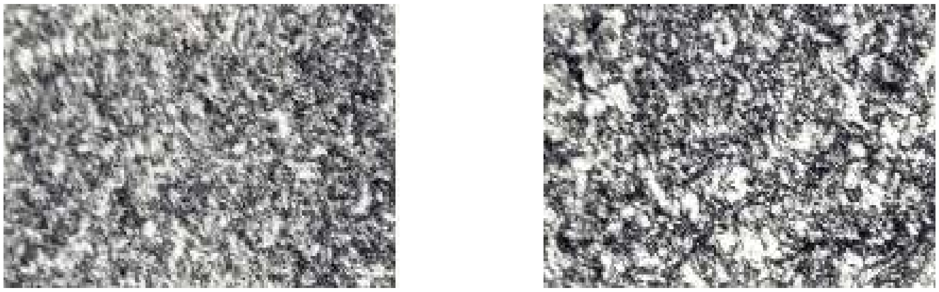
From the heat treated materials, according to the research schedule, metallographic samples were taken. The micro-structural analysis revealed the structural transformations occurring during tempering at various temperatures within 580 – 700 °C interval. The results obtained the microstructures corresponding to the tempering temperature in the above mentioned interval are given in the Figure 5 bellow.



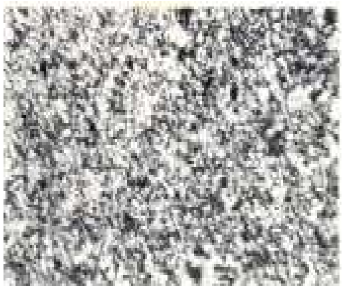
T_{rev} = 580 °C T_{rev} = 600 °C



T_{rev} = 620 °C T_{rev} = 640 °C



T_{rev} = 660 °C T_{rev} = 680 °C



T_{rev}=700 °C

Fig. 5. *Microstructures corresponding to the tempering temperature at various temperatures within 580 – 700 °C interval*

4. Conclusions

The ultimate strength and the yielding point decrease while the tempering temperature increases within 580 – 700 °C.

Plasticity characteristic, A_5 % and tenacity KV_L increase when the tempering temperature increases. An optimum assembly of strength and tenacity properties can be obtained for austenite temperatures when tempering takes place.

The micro-structural analysis showed the structural modifications which take place, upon heating, the martensite out of balance structured tend to get transformed. The process is based on diffusion whose amplitude is higher when the temperature is higher too, with smaller tempering temperatures, the martensite needles gets segmented.

High temperature heating causes a more acute fragmentation process, the fragments turns into globes and the globe carbons keep on increasing so that at tempering temperature, the structure is made up of a feritic matrix and globular perlite.

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BEHAVIOUR OF THE MOBILE PHONES OWNERS RELATING TO THE MANAGEMENT OF THEYR DEVICES

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ABSTRACT

Today mobile phones have become apparently indispensable. They are the most used electronic devices in the world. The useful life of a mobile handset is decreasing; life cycle is diminished as a result of the speed of technological innovation. Unlike other appliances for personal use, mobile phones are often replaced due more technological moral wear than their malfunction. Another particularity in the evolution of mobile phones is the number of devices utilized. In the case of mobile phones, along the years, the total number of devices used increased extraordinary. As a result, the amount of wastes equipment is in constantly growing and is increasingly higher. This situation calls their environmentally sound management and economically advantageous for recovery of valuable materials. In this respect an important role has the equipment's consumers, this aspect being analysed in the paper. The paper presents the study based on responses of the people to a questionnaire regarding their behaviour and awareness relating to the management of own used or unusable mobile phones.

KEYWORDS: mobile phones wastes, recycling, consumers, behaviour

1. Introduction

Romania's alignment with EU legislation on waste management involves the organization of specific flows for ensuring the achievement of the accurate targets for collection and recycling imposed at Community level. Romania, like other countries from Central and Eastern Europe benefits from a transition period, translated by performing in the first stage (2016-2019) a collection rates between of 40 and 45% and by delaying the achievement of the collection rate of 65% (applicable in the EU in 2019) until a date decided by Romania, but no later than 2021 [1, 2]. The collection target for which our country is accountable to the European Commission can be achieved with optimum operating costs through a sound management of wastes [3-5]. In Romania the organizing of management system for mobile phones wastes is in early phase, the collection and recycling activities are conducted still slow [6-8]. The developing and implement of the sustainable waste management system (which also requires a long time) are hampered by a number of factors specific to our country. For the management system of mobile phones can be identified some weaknesses [6, 9, 10].

In collection phase the behaviour of mobile phones owners and the consumer's awareness represent some of them. These are a major barrier to reuse and recycling their used or inoperative equipment in a proper manner. This paper presents a survey focused on the following objectives: identify the behaviour of mobile phone owners to their old or damaged equipment; perceived motivations at the population level for sound management of equipment that reached at their end of life stage or that are not utilized by owners.

2. Experimental method

The research method used was the survey. Questions were formulated in accordance with the dimension, strengths and of WEEE management system in other states and in Romania [6, 9, 11]. Some of these have been utilised in other studies [7, 12].

The target population was represented by people from urban areas, women (70%) and men (30%). The lot interviewed was represented by people aged 18-65 years, the majority being young people aged between 18 and 30 years (65%), between 30 and 45 years (30%) and very few aged between 46 and 65 (5%). Most of those who were interviewed have university degrees (50%) or middle school (45%), the rest having less school like professional studies, respectively ten classes (5%). The technique for data collection has consisted of face interviews. The sample size was 100 respondents. Data collection period was from 20.01.2015 to 01.04.2015.

3. Results and discussions

The particularity regarding the mobile phone utilization of people surveyed is the rate of penetration and possession shape of the population. All those questioned (*How many mobile phones are in your home?*) had responded that they had in use mobile phones: one device (70%) or more devices (20% two, 5% three and 5% four or more). As a result of constant desire to use high performance equipment, a new technology more efficient, and also as a result of intensive marketing promoted by manufacturers these devices were often changed. Most respondents (65%) use the equipment between 1 and 2 years and after this time replacing it. Into equal percentage are those that changes less than 1 year (5% to 6 months, 15% between 7 and 12 months) and those using the equipment between 3 and 5 years (15%). Those who gave as response between 3 and 5 years probably use this equipment until it becomes inoperative. Unlike other appliances for personal use, mobile phones are most often replaced due to technological obsolescence. So 35% of respondents have motivated the phone change by the appearance of another model (*What are the reasons for that you have purchased another phone?*).

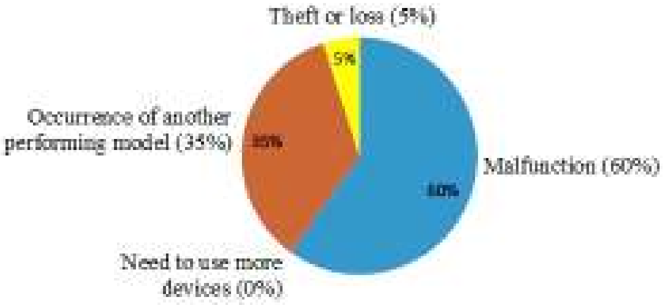

Fig. 1. *Answers to the question: What are the reasons for that you have purchased another phone?*

For recycling of mobile phones wastes under controlled conditions is essential the collection rate of used equipment. In the first step in the recycling process the consumer plays an important role. Its behaviour is crucial.

Regarding keeping, transmission or returning equipment that users cease to use them. Most people surveyed have kept its old cell phone as functional device (45%) (the question was *What happens with your old mobile phones?*). A fairly large number of people have kept the old phone as spare equipment (10%). Others have given the old phone to your family members or friends (20%).

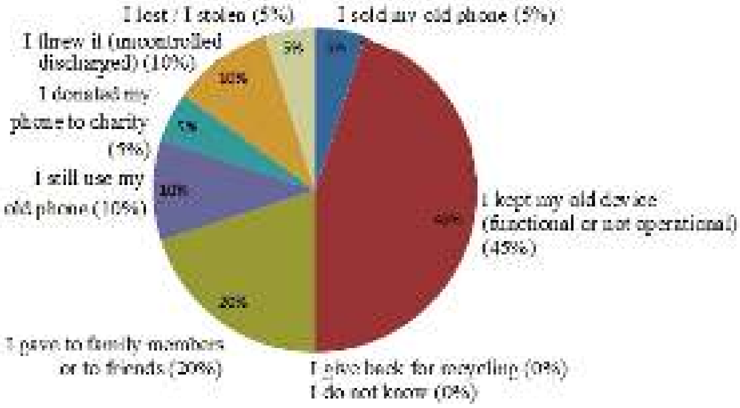

Fig. 2. *Answers to the question: What happens with your old mobile phone?*

The survey on the behaviour and attitude of consumers on recycling has revealed a very serious problem. Zero used phones were returned for recycling by owners after their not being utilised (0%). Moreover, many people have abandoned uncontrolled or discarded your devices (10%). Others were concerned to obtain a sum of money on their old phone, selling it to someone else (5%).

In many cases there is a tendency for users to temporarily store the equipment inoperable. These form so called the "hibernating equipment stocks" or "drawer equipment stocks" [9]. The answers to the question: *Currently you have broken phones at home?* show that 85% of target group members have responded positively. This behaviour represents a serious barrier in the functioning of recycling system to the extent possible that must achieve. The desire to keep the old mobile phones with the intention to repair or as spare parts is other weaknesses of wastes management system. A share of 25% from respondents cited this option to motivate their indifference to the benefits of recycling (answers to the question: *Which of the following situations best describes the reason for keeping the inoperative phones?*). The convenience is another reason of people in the way of recycling: 25% of respondents said that they not have time to deal with it. Lack of information and absence of collection locations near are other obstacles for poor collection and recycling of used equipment. 20% of those questioned replied that they do not know what to do with they. Also 10% said that in the proximity not exist they are not points of take over for mobile phone wastes or disposal centres. The study showed that people surveyed do not encourage the return of inoperable phones at recycling centres. Many of old devices remain stored at home; even if their owners could get recompense when give back the old equipment. Some incentive is necessary to get people more involved to the recycling program.

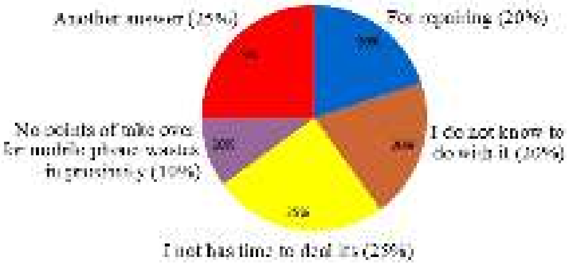

Fig. 3. *Answers to the question: What incentive would motivate you more to give back the old phone to collection centres?*

The answers to next question *What incentive would motivate you more to give back the old phone to collection centres?* showed what rewards they would like receive to promoting the device return and thereby the storage time of equipment unusable can be reduced. The interviewees said they prefer the reductions when they purchase a new phone and also the providing of additional call minutes: 45% of respondents chosen to encourage the return by applying discounts at purchase another phone; 15% want to receive additional minutes; 30% would prefer to receive a voucher.

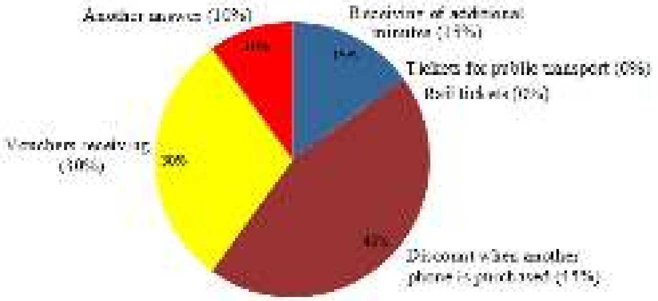

Fig. 4. *Answers to the question: What incentive would motivate you more to give back the old phone to collection centres?*

In Romania, the collection is performed by mobile phone service providers and retailers and this based on the return of old equipment when is buying a new one. These applying the return by discounts system (*buy-back* scheme) or free return (*take-back* scheme). To free return scheme has not made use any of the interviewed. The other was used by many of those who bought a new device from a retail centre.

More waste collection points must be organized as take back locations. This conclusion results from answers to question: *How would more convenient for you to operate the collection of mobile phones wastes?* 50% of people surveyed prefer the direct return to specialized stores. In the same proportion (25%) they want to return directly to the collection points specialized for phones wastes or they have opted for special events designed to collect mobile phones in a certain day and with a certain periodicity.

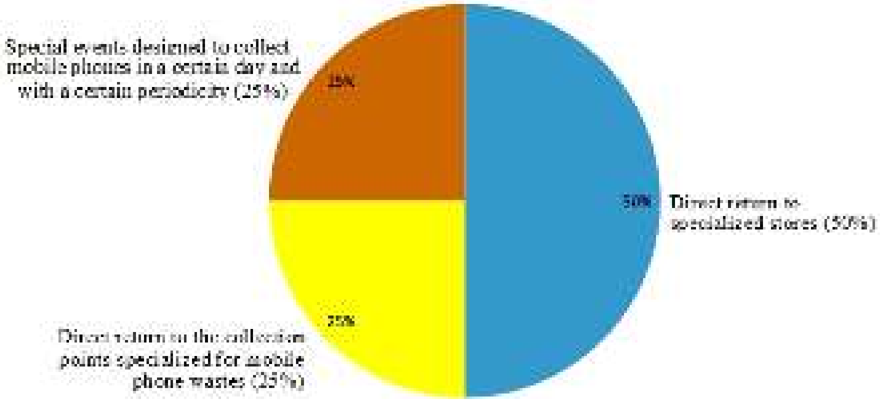

Fig. 5. *Answers to the question: How would more convenient for you to operate the collection of mobile phones wastes?*

For the majority of the consumers the positive effects of this wastes recycling on the environment are not clear. 40% of respondents have negatively responded to the following question *Did you know that the abandonment or uncontrolled discharging of mobile phones wastes have negative impact on the environment and human health?*

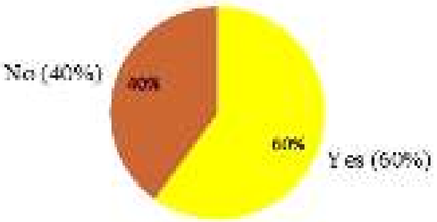

Fig. 6. *Answers to the question: Did you know that the abandonment or uncontrolled discharging of mobile phones wastes have negative impact on the environment and human health?*

Most respondents have not seen the special collection systems called *"green recycling machines"* even if they have heard of their existence (60% according to the answers to question *Have you seen or used the so-called "green recycling point"?*). Only 5% of them have used these locations in large shopping centres.

5. Conclusions

In the mobile phone management system from Romania are obviously a number of weaknesses. Most analysed in this work is linked to the development of recycling culture in the population of Romania.

The study revealed that most of the Romanian consumers do not have a responsible attitude and an appropriate behaviour towards the fate of the mobile phone. Lack of education and responsibility makes the collection of phones sold in Romania to carry out hard. These weaknesses can be rehabilitated by increasing of awareness and involvement regarding WEEE recycling activity.

The local authorities should be more responsible for collection activities. According to the legislation they must organize collection points, to equip them and to ensure their functionality. Currently, they can organise periodically the campaigns for collection used mobile phones (as example periodically a special day for collecting them). Also the collection centres organized by municipalities and other organizations are less specialised to take over direct from consumers the old mobile phones. In the

Romania, as in other European countries, this form of waste collection is typical only for different types of WEEE (*"white goods"* wastes as refrigerators, stoves, washers, televisions, etc.).

In Romania, the special collection locations for old phones began to be organized timidly. They could be placed in institutions, schools, universities or densely populated places (large shopping centres). The most suitable alternative for localization is in a shop (or mall). As mobile phones have a residual economic value special collection machines (so-called *"green recycling machines"*) for public use can be an adequate method. In these anyone can deposit its old mobile phone or other electrical and electronic appliance.

The desire to be stimulated at give-back of old equipment was observed to all respondents: by additional minutes and by discounts at buying of new phone; by urban public transport tickets in compensation for returned old phone; by receiving a voucher for the purchase of other products.

The mobile phone owners are not aware of the importance of the collection and recycling benefits. Also do not know the effects of waste on the environment.

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INFLUENCE OF ALLOYING ELEMENTS ON CORROSION RESISTANCE OF SOME IRON - BASED SINTERED P/M ALLOYS

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ABSTRACT

In this paper is described the influence of alloying elements on corrosion behavior of sintered iron parts. The compacts were sintered at 1,150 °C and the sintering time was 60 minutes. After microstructural studies, the electrochemical tests were carried out. The corrosion behavior of samples was evaluated using potentiodinamic polarization technique in 3.5% NaCl solution. Different parameters like i_{corr}, *cathodic (*βc*) and anodic (*βa*) slopes derived after the extrapolation of the Tafel plots were obtained. The results reveal that the alloying elements can improve significantly corrosion resistance of iron based sintered P/M alloys.*

KEYWORDS: alloying elements, powder metallurgy, sintering, corrosion resistance

1. Introduction

In Powder Metallurgy (P/M), the produced parts are of complex shapes and closed to final form, and are widely used, especially in the automotive industry [1, 2]. But the main problem of these products is the presence of the pores, which can act as potential cracks initiation, and also can propagate cracks through the material. The properties of the sintered powder metallurgy alloys can be improved by reducing the pore size [3-5], increasing the density [6, 7], by adding some alloying elements [8-17] or by additional operations [18-20]. The most common alloying elements added in the mixing powders are copper, nickel, molybdenum, manganese and phosphorus because of low cost and their ability to improve the properties of the alloys. Cu increases the density of the alloys by filling the pores due to its melting point during the sintering time (1,083 °C). Ni can also increase strength, ductility and impact properties. In the literature, Hong et al. [21] have investigated the effect of copper addition to low alloy steels on their corrosion response in sulphuric acid have found that the rate of corrosion is reduced by the addition of Cu due to higher hydrogen over potential and prevention of the active dissolution. Addition of higher percentage of alloying elements such as Cu, Ni, Cr, P, S, Si, Mn is reported to enhance the corrosion resistance of the steels in aqueous solutions. It is concluded that the addition of higher percentage of chromium could act as a passivating agent [22].

In this paper, the influence of alloying elements on corrosion resistance of iron based sintered P/M alloys is analyzed. The anti-corrosion performances of the sintered specimens in 3.5% NaCl solutions were studied.

2. Experimental procedure

The starting materials studied in this paper are represented by atomized iron powder and pre-alloyed iron base powder. The chemical composition of the powders, pure iron and iron-based prealloyed powder with Cu, Ni and Mo is presented in Table 1. The powders were blended with 1% zinc stearate and then were uniaxially compacted into specimens, using a universal mechanical testing machine at ambient temperature. After blending, the samples were compressed in a mold using uniaxial pressing and the applied pressure was 600 MPa. The disc specimens have the dimensions of $\phi 8 \times 6$ mm. After compacting, the green samples were subjected to sintering, the temperature was approximately 1,150 °C and the sintering time was 60 minutes and then air-cooled to room temperature. In order to evaluate the effect of alloying elements, the sintered specimens were subjected to corrosion resistance tests and electrochemical characterization. The corrosion behavior of the sintered specimens was investigated by potentiodymanic polarization technique. The polarization curves were obtained using a Voltalab PGP 201 Potentiostat at a scan rate of 2 mV/s. A conventional three electrode electrochemical cell consisting of the saturated calomel electrode (SCE) as the reference, the platinum plate as the counter electrode and the specimen was used as working electrode. The test area (0.5 cm^2) was obtained by embedding the specimens. After 40 minutes of exposure to an open circuit potential, the measurements were carried out. The tests were carried out in a 3.5% NaCl electrolyte solution. All electrochemical experiments were performed at room temperature.

Table 1. *Chemical composition of analyzed powders*

Powder type	**Cu**	**Mo**	**Ni**	**C**
P_1	0.10	0.01	0.05	<0.01
P_2	1.50	0.53	4.01	<0.01

The microhardness Vickers values were used to correlate the influence of alloying elements on corrosion resistance. The results show that an increase in microhardness leads to an increase of corrosion resistance.

3. Results and discussions

3.1. *Microstructural characterization*

The microstructural characterization was carried out using an optical microscopy (Olympus BX 50). Optical micrographs of sintered samples are presented in Figure 1 and indicates a basic ferritic structure. The copper and nickel have diffused with the iron, the copper melted and moved throughout the pore network. Mo is known as a ferrite stabilizer element and a carbide former also. In combination with Ni, the presence of Mo in this alloy has conducted to a ferritic microstructure with distributed molybdenum carbide. Also, the Mo particles are combined with diffused carbon during sintering; forming molybdenum carbide, their presence in the alloys may improve the strength. As can be seen in microstructure, the sample P_1 has the higher porosity.

3.2. *Mechanical properties*

The microhardness Vickers of the sintered specimens was investigated by using a microhardness tester. The test parameters are: the penetrator is a diamond pyramid diameter and load of 100 g. The sample P_1 has the microhardness Vickers value of 152 daN/mm^2, comparintg with sample P_2 with a value of 181 daN/mm^2.

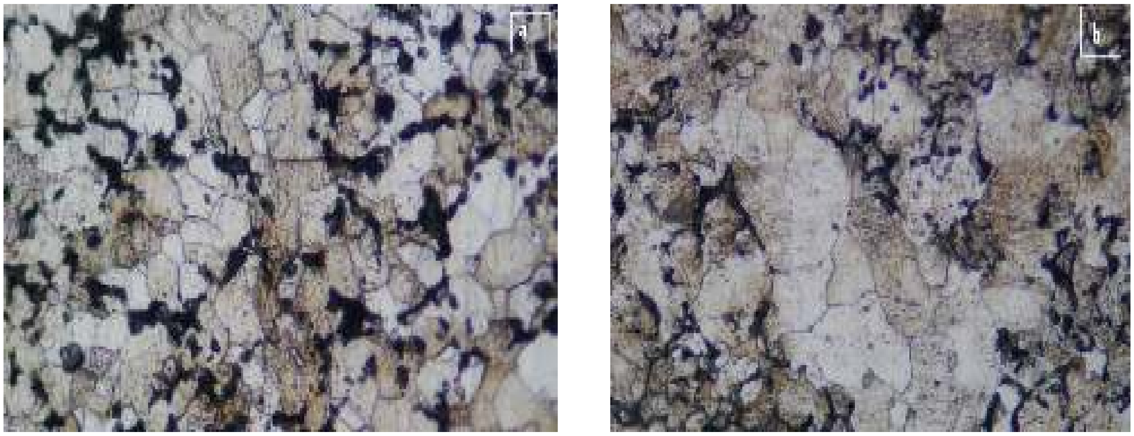


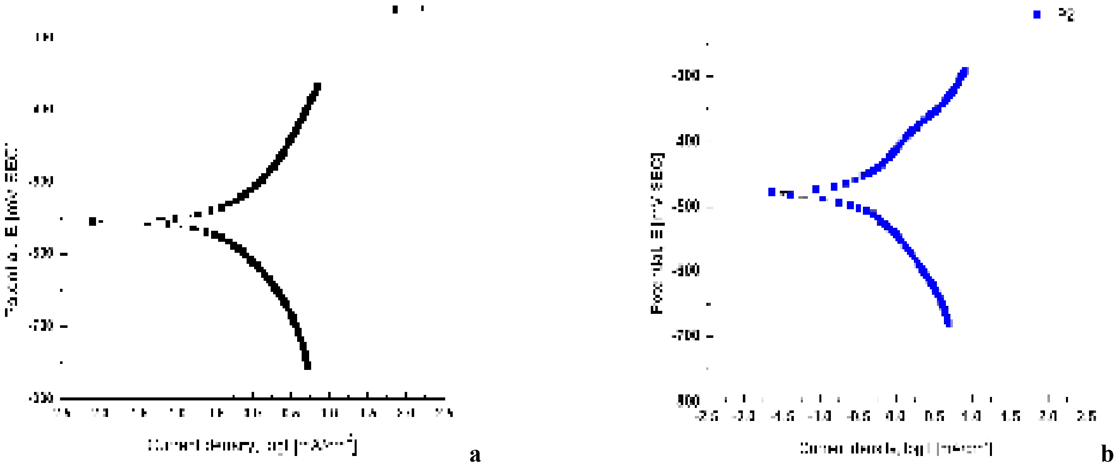
Fig. 1. *Image of the microstructure of sintered samples, 2% Nital etched, 200x: a) P_1, b) P_2*

3.3. *Corrosion test results*

The corrosion resistance of the sintered samples was evaluated by electrochemical measurements in 100 mL of unstirred 3.5% NaCl solution. The corrosion potential and the corrosion current density were obtained through Tafel approximation. Figure 2 shows the potentiondynamic polarization curves in 3.5% NaCl solution for sintered specimens (Tafel plots) and it can be seen that the corrosion potential of sample P_2 is higher than the unalloyed P_1 sample.

This is attributed to the alloying elements, 4% Ni, 1.5% Cu and 0.5% Mo and less porosity. Comparing polarization curves of the sintered samples, the results show that corrosion resistance is enhanced by the alloying elements. The least corrosion resistant result was subjected to series P_1, which has the highest porosity.

The potentiodynamic polarization parameters like corrosion current (i_{corr}), anodic and cathodic slopes (β_a and β_c) and corrosion rate (v_{corr}) were calculated from Tafel plots and are presented in Table 2. The electrochemical parameters obtained by Tafel extrapolation method shoed that the prealloyed sample P_2 with Cu, Ni and Mo had an improved in corrosion resistance compared to unalloyed sample P_1.



a b

Fig. 2. Potentiodymanic polarization curves in 3.5% NaCl

***Table 2.** Different electrochemical parameters obtained by Tafel extrapolation method*

Sample	$\beta_{a,}$ (mV dec $^{-1}$)	$\beta_{c,}$ (mV dec $^{-1}$)	$i_{corr,}$ mA/cm^2	Corrosion rate (mm year $^{-1}$)
P_1	220.1	-248.4	0.98	10.49
P_2	142.5	171.4	0.45	6.31

4. Conclusions

The results reveal that the corrosion resistance in P/M parts is correlated to processing parameters such as alloying elements, porosity and mechanical properties. The prealloyed sample P_2 with Cu, Ni and Mo can improve corrosion resistance of sintered steels.

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RESEARCH ON RISK ASSESSMENT OF THE WORKPLACE IN AN EMERGENCY COUNTY HOSPITAL

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ABSTRACT

In hospitals crisis conditions, in Romania, it is necessary along with the implementation of a correctly medical act, applied to patients and security measures relating to the employment for staff involved. The work shall be reviewed at all risks to which complexity is exposed a medical assistant when practicing in a hospital emergency department in infectious diseases. Assessment of the risk of workplace division of infectious diseases, for workers involves analysis of all factors and conditions in accordance with their respective internal rules and European ones.

KEYWORDS: emergency county hospital, medical assistant, work risk

1. Introduction

Emergency hospitals are equipped with materials and medical staff which should satisfy most types of medical emergencies which may arise. Specialist medical staff shall carry out their activity inside of the emergency County Hospital. The main components of the system work: equipment for primarly imedical investigation (Electronic tensometru, stethoscope, syringe, sterile bandages, disinfectant, antibiotics), electric shock unit, adjustable beds lounge, computer and printer, desktop, locker for acts.

1.1. Analysis of risk factors for occupational illness

Risk factors acting on the performer by two main components: gravity consequence/event) and probability of occurrence (events/time unit). Combining these components determine the level of risk itself.

Risk factors are all components of the system's own job.

The risk factors are classified as follows:

a. Physical risk factors include: excessive air temperature (high/low); improper air humidity (high/low); high speed air currents, they define the microclimate and the working environment; excessive air pressure (high/low); inadequate lighting; noise; radiation, vibration, electrostatic potential, natural disasters, aggression to aggression in the workplace.

b. Risk factors of chemical which include: gas, vapours, aerosol dust and toxic, pneumoconiogene. Between the contractor and the collectivity and within which they operate to create links, dependencies and interference that varies depending on the level of integration in the communit and which exerts a decisive influence on his behavior. Concepts and habits within a unit, as well as how that group appreciates the risk, determines in a very large measure behavior in terms of safety at work.

Risk factors (potential causes) of system components that form the basis of accidents at work and occupational diseases as well as preventive measures, schematic, are presented in Fig. 1.

Complete presentation of all the risk factors on the 4 components of the system is given in Table 1.

Risk factors are all factors likely work system to act on the health or integrity of injuries to workers. It's about what the majority of people in the current parlance, they are considered hazards or dangerous situations. In this respect the European norm EN 292-1 defines danger [1], dangerous situations or events related to hazardous work (risk factors) as being a "reason capable of causing an injury or a sickness attack". This definition is a qualitative risk assessment commonly used in its identification.

Security is defined as the fact of being sheltered from any danger. Risk and security are closely interrelated and mutually exclusive.

Risk is defined in accordance with the European standard EN 292-1, [2] as "the combination of the probability and severity of an injury or sickness attack that can occur in a dangerous situation". This is a quantitative definition of risk that can be used in prioritizing risks. In other words, the risk is the likelihood of a specific gravity of damage during exposure to the risk factor.

Consequently, professional risk associated with a particular situation or a particular technique from combining the following elements:

- foreseeable consequence severity (severity of the most likely consequence);
- the likelihood of such consequences.

Thus defined, the risk can be assessed quantitatively, if severity and probability have been quantified themselves. Quantitative assessment (evaluation) can be used to compare different risks within a system and to determine the priorities of intervention or to compare risk levels before and after the implementation of measures to prevent the manifestation of him.

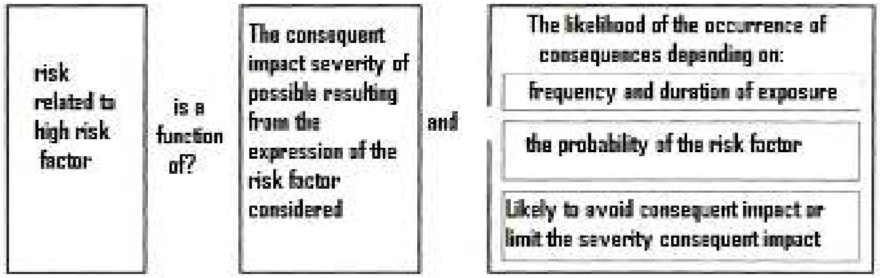


Fig. 1. *Defining the risk according to severity and probability of work place* [1]

The absence of a system of review, a small number of accidents or occupational diseases, low severity of consequences of accidents should not be automatically regarded as a presumption of a low risk.

1.2. Severity

Shall be assessed in accordance with MIL-STD-882 C by evaluating the consequences of the most serious accident that could have caused the risk factor.

Consequence severity (severity of the damage possible) can be estimated by considering the following:

- the nature of the protected object (persons, property, environment);
- severity of injuries or damage to health (easy - normally reversible serious - normally irreversible, death);
- the magnitude of manifestation the consequent impact (a person, more than one person).

Categories of severity of consequences allow assigning a qualitative size potential accidents due to human error, environmental conditions, non-compliance project, procedural deficiencies or damage and organ dysfunction product, sub-assemblies or its components.

The product manager, the manager the quality assurance program of safety of the product and the one who carried out the product should be able to lay down exactly what is meant by destroy the product, by major consequences/minor to product/environment and by occupational disease or serious injury. Gravity can be defined on the basis of criteria such as:

- temporary incapacity (ITM), permanent work incapacity (disability), death;
- health effects, reversible or not, for risk factors likely to have psychological effects;
- interference with the comfort, satisfaction, worker motivation for social risk factors and organizational.

1.3. Probability

Probability means in accordance with MIL-STD-882 C frequency of occurrence of the event unwanted and can be described as potential occurrence in the unit time or reported from the population, item or situation [2].

Probability is conditional on even terms of work processes: reliability of technical equipment, materials, organization of work, time constraints, etc.As with the severity of the consequences for estimating the probability of occurrence of consequences can use multiple grids of appreciation. For a more accurate estimate of the probability of occurrence of consequences is recommended to be taken into consideration:

a) the frequency and durationof exposure that are determined by:

- need access to the danger zone (normal operation, maintenance or repairs);
- nature of access (eg manual feed materials);
- time spent in the danger zone;
- the number of people who register;
- frequency of access.

b) probability of occurrence dangerous due to:

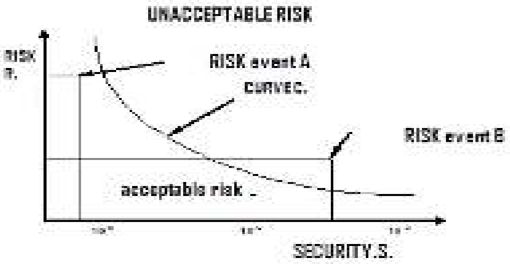
- technical equipment reliability and other statistical data;
- statistical data related to the frequency of accidents and occupational diseases;
- comparing the risks of system already accepted analyzed risks of systems.

c) the possibilities to avoid or limit the consequence of a hazardous event by:

- executing (which can be qualified or unqualified person can perform the task supervised work or not, etc.);
- rate of occurrence of the event estimated dangerous (sharp, fast, slow);
- any form of risk awareness (through general information by direct observation, by means of warning and indicating devices),
- possibilities to avoid or limit performer consequence (eg reflexes, the skill saving opportunities that make the chances contractor to avoid or limit the result to be possible in certain circumstances possible, impossible);
- practical experience and knowledge of the performer (on the job examined, on a similar work process or inexperienced).

1.4. Level of risks

The level of risk [3] is an indicator quantity absolutely once rated allow knowing to what extent the security of a system, in terms of the possibility of accidents and occupational diseases, it is acceptable or not. In practice it is considered that a system is secure, if having a non-zero risk, but small enough, known as residual risk or acceptable.In the absence of corrective interventions while the residual risk increases as the work degrade and age under the law of increasing entropy.Notions of security and risk are opposites being connected by a hyperbolic equation R = (S Security R - risk), like in Fig. 2.



y = f(x)

Fig. 2. *Relationship Risk – Security* [2]

Where the risk cannot be null (infinite security) must be determined which couples probability of occurrence/consequences can provide an acceptable level of risk.

Graphic representing acceptable risk in the form of rectangles with areas equal to F1 = F2 = F3. gravity/probability, data in Fig. 3 the curve that show the variation in the severity of consequences with the probability of occurrence what unites top right corners of the quadrilaters areas under the curve for the acceptability of the risk, according to CEN 812/85. (The Farmer) [3].

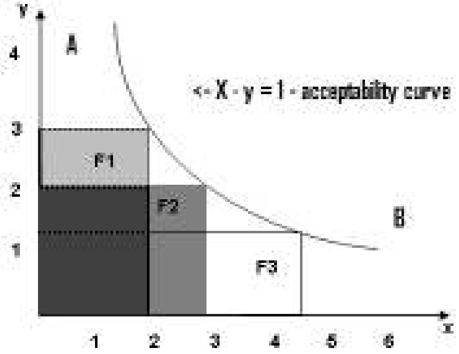


Fig. 3. *The depending between risk at work place and severity of consequences of risk factors on the human. A-acceptable risk; B-unacceptable risk* [3]

Under the curve (A) the risks are acceptable, and above the curve (B) the risks are unacceptable. The curve in Fig. 3 called risk acceptability curve and corresponding function p hyperbole. g = const. In Romania currently accepted value of this constant is to be 3.5.

The main objective of the evaluation is to establish acceptable risk and bringing in acceptability.An acceptable risk may be characterized by a probability of occurrence (frequence), but the seriousness of the consequences (F1) - nuclear accidents, or vice versa-a high frequency with low severity of consequences (F3) - traffic accidents. Risk level assessment method and its classification as acceptable or unacceptable risk has the advantage that it can be applied both to existing employment systems and those in construction-design phase.Establish risk acceptability curve (delineating acceptable risks) is a difficult issue. This is done through a strategic decision be based on the cost of human life, whether from the comparison with other risks already accepted.

1.5. Exposure

Exposure to risk factors, represents the duration in the time or frequency in time at which the contractor is exposed to a risk factor and the level to which it is exposed. Assessment of exposure may be carried out, in some cases, in terms of quantitative metrics. Needs analysis can choose diverse exposure assessment rubrics. Exposure is often integrated into the concept of probability, the assessment of risk, taking into account the duration or frequency of exposure. Consideration of exposure, in a separate probability is subtle and it requires a complex approach for assessing occupational risks.

2. Work environment and identified risk factors for place of work named main medical assistance

The risk factors are divided in: mechanical, electrical, physical factors, biological factors, factors shuffle, factors of the work task.

2.1 Mechanic risk factors

F.1. - pedestrian movement on the access roads inside the unit by means of transport (supply, delegate, service providers etc.);

F.2. - Bumping, or crushing grip in traffic accident at the movement in the interests of the service (for action);

F.3. - Defect-parts and mechanisms, the deviation from the normal trajectory of movement, impact, overthrow;

2.2. Electric risk factors

F.4. - Electrocution by direct accidental unprotected pathways voltage at the venue of the activity: plugs damaged makeshift cables stripped portion, makeshift electrical connections, etc.;

2.3. Physical risk factors

F.5. - Alternate interior exterior temperature;

F.6.- Air current on corridors or rooms, or the simultaneous opening of doors and windows;

F.7. - drop at the same level, through the slip, due to the condition of the roadway, the climate conditions (ice), wet floors, etc.;

2.4. Biological risk factors

F.8.-Contamination caused by the presence of patients carriers of viruses, bacteria, etc.;

2.5. Shuffle risk factors

Wrong actions:

F.9. - Moving, staying in hazardous areas, in the vicinity of access roads, roadway in access of the gauge;

Omissions:

F.10. - Skip taking measures to prevent traffic accidents at pedestrian movement (insurance, diminished, crossing through illegal places, meaning failure indicators, etc.);

2.6. Risk factors of the work task

F.11. - Psychic stress due to this solicitation of patients, relatives, media;

F.12. - Failure to take measures to prevent the movement of pedestrian traffic accidents (insurance, diminished attention, crossing the forbidden places, etc.);

F.13. - Due to this mental stress of patients, relatives, media;

F.14. - Stress caused by the intense pace of work, quick decisions in a short time and negotiation.

Table 1.

Work system components	**Identified risk**	**Actual form of risk factors (description, parameters)**	**Maximum predictable consequence**	**Severity class**	**Class of probability**	**Partial risk level**
0	1	**2**	**3**	**4**	**5**	6
Means of production	Mechanical risk factors	F.1. - Pedestrian movement on the Impact of access roads inside the unit by means of transport (supply, delegate, service providers etc.);	Lethal	**7**	**1**	3
		F.2. - Bumping, or crushing grip in traffic accident at the movement in the	Lethal	**7**	**1**	3

		interests of the service (for action);				
		F.3. - Defect-parts and mechanisms, the deviation from the normal trajectory of movement, impact, overthrow;	ITM 3-45 days	**2**	**4**	2
	Electric risk factors	F.4. - Electrocution by direct accidental unprotected pathways voltage at the venue of the activity: plugs damaged makeshift cables stripped portion, makeshift electrical connections etc.	Lethal	**7**	**1**	3
	Physical risk factors	F.5. - Alternate interior exterior temperature	Negligible	**1**	**5**	1
Own environmental risk factors of work	Physical risk factors	F.6. - Currents of air corridors or rooms, or the simultaneous opening of doors and windows;	ITM 3-45 days	2	2	2
		F.7. - Drop at the same level, through the slip, due to the condition of the roadway, the climate conditions (ice), wet floors, etc.	ITM 3-45 days	2	5	3
		F.8. - Contamination caused by the presence of patients carriers of viruses, bacteria, etc.	ITM 3-45 days	2	4	2
	Biological risk factors	F.9. - Moving, staying in hazardous areas, in the vicinity of access roads, roadway in access of the gauge;	ITM 3-45 days	2	4	2
Contractor's own risk factors	Wrong actions	F.10. - Skip taking measures to prevent traffic accidents at pedestrian movement (insurance, diminished, crossing through illegal places, meaning failure indicators, etc.);	Lethal	7	1	3
		F.11. - Psychic due to this solicitation of patients, relatives, media;	ITM 3-45 days	2	4	2
	Omissions	F.12. - Failure to take measures to prevent the movement of pedestrian	Lethal	7	1	3

		traffic accidents (insurance, diminished attention, crossing the forbidden places, etc.);				
Risk work factors task	Psychic stress	F.13. - Due to this mental stress of patients, relatives, media;	ITM 3-45 days	2	2	2
		F.14. - Stress caused by the intense pace of work, quick decisions in a short time and negotiation.	ITM 3-45 days	2	2	2

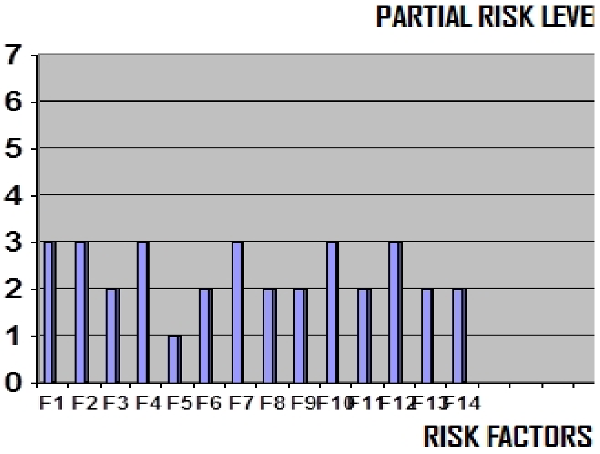


Fig. 4. Partial risk levels on risk factors

For calculus of **global risk level** "*Nrg*" is used the formula:

$$N_{rg} = \frac{\sum_{i=1}^{14} r_i \cdot R_i}{\sum_{i=1}^{14} r_i} = \frac{6(3 \times 3) + 7(2 \times 2) + 1(1 \times 1)}{6 \times 3 + 7 \times 2 + 1 \times 1} = 2.51$$

The global risk level has the value 2.51.

By using the scale of severity of quotation probability consequences of risk factors on the human body for the place of work named „main medical assistance" we see in the Table 2 the framing that corresponding at value of 2.51.

Table 2.

Probability classes		**The probability of consequences**
Class	**Events**	
1	Extremely rare	Probability of producing extremely small P-1 10 </year

2	Very rare	Probability of occurrence of the consequences of the very small 10-1 < 5-1 P </year
3	Rare	Probability of occurrence of the consequences of short 5-1 < 2-1 P </year
4	Uncommon	Probability of occurrence of the consequences of an average 2-1 P-1 << 1/year
5	Frequently	Probability of occurrence of the consequences mean 11 P < F1 </year
6	Very common	Probability of producing very large consequences > l-1 P/month

In conclusion the severity of consequences for the place work named "main medical assistance" is framing between small and average.

3. Conclusions and measures to avoid the work risk

Table 3.

Nr. crt.	**Indicated risk factors**	**Risk level**	**Nomination proposed measures to prevent**
1.	F.1. - Pedestrian movement on the impact or access roads inside the unit by means of transport (supply, delegate, service providers etc.);	3	*Technical measures:* - Maximum speed control vehicle access inside the unit by placing limit signs at the entrance to the establishment; - Restrict access of vehicles depending on unit needs; *Organizational measures* - Training of workers on safety consequences of failure to movement restrictions inside the unit; - Preparation of instructions / procedures on the conduct domestic workers (general obligations, and pedestrian travel by car, etc.);
2.	F.2. - Bumping, or crushing grip in traffic accident at the movement in the interests of the service (for action);	3	*Organizational measures* - While moving on road traffic routes shall comply with road traffic regulations - Rules of the Road; - Thematic training plan will include provisions of traffic law section *Other road users.*
3.	F.4. - Electrocution by direct accidental unprotected pathways voltage at the venue of the activity: plugs damaged makeshift cables stripped portion, makeshift electrical connections etc.	3	*Technical measures* - Maintaining electrical work equipment by specialized and authorized personnel; *Organizational measures* - Daily visual check of the integrity of the casing cord electrical work equipment, the condition of the outer casing and power plug; - The use of extension cords provided with protective null; - Supply of equipment for electrical work and will be only effectuated with extension cords from outlet provided with protective null;
4.	F.10. - Skip taking measures to prevent traffic accidents at pedestrian movement	3	*Organizational measures* - While moving on road traffic routes shall comply with road traffic regulations (insurance, diminished, crossing through illegal places, meaning failure indicators, etc.);

5.	F.12. - Failure to take measures to prevent the movement of pedestrian traffic accidents (insurance, diminished attention).	3	*Organizational measures* - While moving on road traffic routes shall comply with road traffic regulations - Rules of the Road; - Thematic training plan will include provisions of law traffic section other road users.

References

[1]. ***, *European norm EN 292-1.*
[2]. ***, *Eurostandard occupational ilness work MIL-STD-882 C.*
[3]. ***, *Directive 2000/39/EC establishing a first list of indicative limit values for occupational exposure in implementation of Council Directive 98/24/EC on the protection of the health and work safety against the risks related to chemical agents at work.*
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RESEARCH ON INFLUENCE OF METALLURGY FACTORS ON THE QUALITY OF METAL COMPONENTS IN METAL-CERAMIC PROSTHETIC RESTORATIONS

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ABSTRACT

The paper summarizes the characteristics of the metal component in the structure of metal-ceramic fixed prostheses and the technological conditions for obtaining it. The paper presents partial results of an experimental study on identifying the causes that favor the generation of defects during the stages of metal melting-casting, defects which in turn may be causes of failure in metal-ceramic restorations. The type of defect identified elucidates both the cause of and effects on the quality of metal-ceramic bond. The study was conducted by light and electron microscopy analysis of samples from two non-noble dental alloys (Co-Cr and Ni-Cr), samples taken from casting network, supply channels and metal crown. Results of the analysis performed with a scanning electron microscope SEM fitted with an energy spectrometer EDAX revealed the presence of oxide inclusions, chemical and structural heterogeneity, alloy solidification shrinkage voids and discontinuities caused by lack of technological discipline in the steps of metallurgical alloy processing, particularly the lack of rigorous assessment of temperature and optimum casting time and exposure of the molten alloy into contact with the atmosphere for a long time.

KEYWORDS: alloy, melting, casting, metal - ceramic, metal parts, impurities, chemical non-homogeneity

1. Introduction

Prosthetic treatments commonly used in solving partial edentulous are fixed metal ceramic restorations, partly or wholly physiognomic. Fixed metal-ceramic prostheses made of a metallic component and a ceramic part combine the aesthetics of the ceramic crown through natural physiognomic effect, mechanical strength and marginal adaptation of the metal (casting) component [1-5]. A particular problem raised by the metal-ceramic crown or bridge restoration is the alloy compatibility with the ceramic material to ensure a proper connection [6, 8-10]. It is undoubtful that a successful metal-ceramic restoration depends essentially on the compatibility of the two components which in the long run determine the firmness of the bond between the metal component and ceramic mass. The strong bond between ceramic and alloy surface is a condition for metal-ceramic prosthetic work to keep their integrity in any situation. Given the strong bond between metal and ceramic, the strain (tension) acting on ceramic is transmitted to the metal substructure. This connection is based on the chemical interaction of metal and ceramic and the ionic bond between oxides (Al_2O_3 and SiO_2) from the ceramic phase and the oxides on the metal surface. The oxide layer formed by the addition of alloy elements is usually closely linked to the alloy surface and achieving good chemical adhesion between metal and ceramic is determined by optimal wetting of the metal surface by the ceramic mass. This requires maximum contact surface between metal and ceramic, i.e. lack of macromechanic retentions on the metal surface, fluidity of the ceramic when applying it onto the metal and lack of porosity, obtained from burning ceramic in vacuum which favors the elimination of porosity in the interface area. Also to achieve a good connection between metal and ceramic involves conditions related to the metal structure which must be sufficiently rigid so as to prevent the occurrence of bending forces in the ceramic plating and therefore in the interface. Generally failures in obtaining adhesion of the ceramic to the alloy range from the design and casting conditions of the metal component, but they can also occur in any of the stages of the physiognomy composition, such as the paste, depositing and burning the ceramic layers, preparation of the teeth when contact is made uneven between the abutment tooth and the metal component, carrying out the working arch impression with gaps at cervical level, or when making an incorrect occlusal adaptation. In the production technology of metal-ceramic bridges, several versions are known, as follows: bridged with metallic infrastructure obtained by single molding, bridge with body deck infrastructure and aggregation elements poured independently and then bonded together, large bridges consisting of several segments to be subsequently put together by gluing or sliding systems.

The metal construction of the intermediate elements must be designed so as to obtain a uniform layer of ceramic mass to fit the outer contour of the final prosthetic parts. This requires strict control of the cast metal component (without casting defects that will affect adhesion of the superjacent ceramic mass after sintering).

Achieving a homogenous metal component depends on how the casting rods (channels) of the molten alloy flowing are fixed. Also important is the layout and positioning of the model packaged into the cast plug and the insertion direction of the molten alloy [5-7, 12]. The pattern must be filled as rapidly as possible with the molten alloy without hot crystallization -phases in the plug. Dental practice shows that the flow channels which have a spherical profile tank (5mm in diameter) are very effective because the layout of the junction place of the cast channel (rod) with the denture model is in spots. Along with the casting rod shape, position and number of junctions between the cast channels layout and metal component model can be particularly important to achieve the final denture. A wrong position can cause pores or stress concentrations in regions with variable thicknesses of the future metal structure. Some experts recommend setting an oversized channel as tank for the molten alloy. If a correct location of the casting rods is complied with it can be obtained a homogeneous metal structure that is favorable to the ceramic mass coating.

The alloys used in metal-ceramic technology are gold and palladium -based noble alloys and non-noble alloys [20, 22].

Noble alloys were developed as an alternative to noble alloys that became expensive and inaccessible. They were first used for casting metal on the prostheses partial skeleton, but the benefits in terms of their characteristics (higher mechanical properties, low density, low cost) have imposed them in other technologies as well, such as casting dental crowns and bridges. Among these alloys the most commonly used in metal-ceramic technology are: alloys Ni-Cr (50-80% Ni; 20-25% Cr), alloys Ni-Cr-Fe (48-66% Ni; 14-27% Cr; 8-27% Fe), alloys Ni-Cr-Co (40-62%Ni; 10-21%Cr; 5-34%Co), alloys Co-Cr-Ni and Ti-base alloys.

Non-noble alloys meet superior characteristics in terms of tensile modulus and ultimate strength compared to the noble ones, which means that it requires minimum thickness of the metal frame compared to the noble alloys. To improve the properties of these alloys, additions should be made of elements like Mo, Al, Mn, Si, Be, Cu, Co, Ga, Fe, such as modern Ni-Cr alloys (Ni - 60-70% and Cr - 15-20%).

Corrosion and oxidation resistance of these alloys is due to the formation of the protective chromium oxide microlayer on the surface of the ingot or cast.

These advantages, however, are overshadowed by certain disadvantages such as: casting is much more difficult and solidification shrinkage coefficient can create big problems in the marginal adapting of the metal substructure.

There are studies that demonstrate significant differences in terms of quality of the metal-ceramic bond between the various commercial Ni-Cr alloys. These differences occur for reasons such as variations in the mechanical properties of these alloys, the method used for melting and the design of the metal structure.

Titanium and titanium-based alloys are an interesting alternative due to their excellent biocompatibility, low specific weight and a cost price lower than that of noble alloys. However, titanium alloys also feature a number of disadvantages of the metal-ceramic technique. The oxide layer formed on the surface of titanium alloys during casting is extremely thick and it may grow during the heating to sinter the ceramic. To avoid these problems various solutions have been proposed, from sanding to the use of CAD-CAM system for producing metal components.

The Co-Cr alloys have advantages over the Ni-Cr alloys due to their biocompatibility (highly resistant to corrosion due to chromium which forms a protective oxide layer on the surface) and the lack of allergic reactions that they can develop. The corrosion resistance of the alloy is extremely important in avoiding crevicular corrosion that will undermine the plating ceramic. That is why it is indicated to use gold-based alloys or those of high corrosion resistance. Non-noble alloys show a lower resistance to corrosion than noble alloys, but they feature higher hardness and higher elastic modulus. The alloys that possess elastic modulus and therefore high elastic resistance are rigid thereby preventing the transmission of excessive occlusal stress onto the ceramic. At the same time the metal structural rigidity is maintained even while reducing its size to achieve a proper aesthetic effect (thicker ceramic layer).

2. Materials and experimental conditions

The investigations were conducted on samples from two kinds of non-noble alloys commonly used in metal-ceramic restorations or Ni-Cr (NIADUR) alloy and Co-Cr (ADORON LX) alloy, samples taken from the alloy delivered, samples cut from the casting network, supply channels/rods and crowns.

The study of the samples was performed by microscopic analysis (optical and electron scanning spectrometer equipped with a diffraction energy EDAX) able to reveal defects in material or those occurred while processing the alloy to make the prosthesis.

Table 1 illustrates the chemical composition of the alloys studied in their marketing phase.

Casting network was sectioned by cutting. The sample thus obtained was embedded into resin to be prepared by paper metallographic grinding and felt polishing, followed by the chemical attack for subsequent microscope analysis. The metallographic attack was made with the reagent: 50 ml HCl + 1-3 ml H_2O_2 (for Ni-Cr alloy) and electrolytic attack in solution of 10 ml of HCl in 200 ml ethanol at 2V DC and a temperature of 200 °C for 10 seconds (for the Co-Cr alloy), followed by sample washing and drying. To highlight any changes that may occur during processing by alloy melting and casting in the dental laboratory, first it was analyzed the structure and composition of the samples before their processing (marketing alloys).

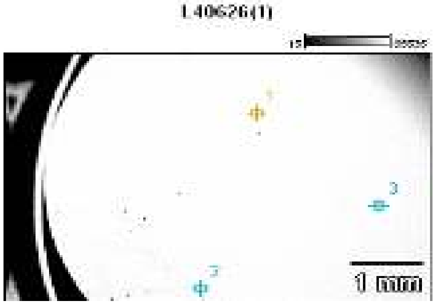
Table 1. *Chemical composition of the alloys studied*

Alloys/Elements	Co	Ni	Cr	Mo	Si	Nb	Al	Mn, C, N
Co-Cr	62.5	-	29.5	5.5	1.4	-	-	up to 1%
Ni -Cr	-	75.5	11.5	0.608	3.5	4.25	2.25	-

3. Experimental Results and Discussion

Microstructural aspects are shown in Figure 1, along with X-ray spectroscopy analysis of the chemical composition.

Fig. 1. *Microscopic appearance (optical microscopy without metallographic attack, magnification X50) of the Co-Cr alloy samples (ADORON LX40626) delivery/marketing state of alloy* [5]



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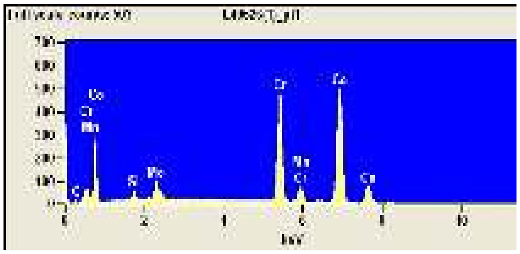

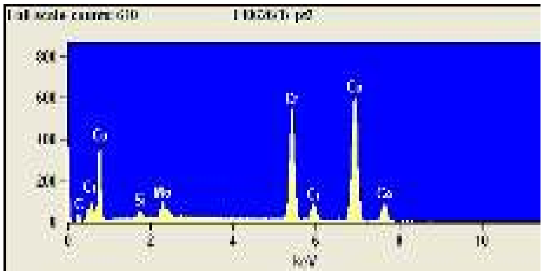

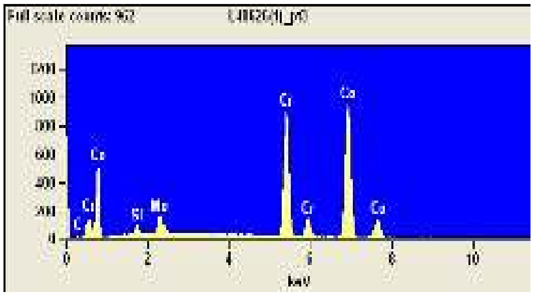

***Fig. 2.** X-ray spectroscopic analysis of chemical composition of samples of Co-Cr alloy (ADORON LX40626) delivery/marketing state of alloy* [5]

The analysis results for the marketing samples, before their processing indicates an alloy of chemical composition according to the bulletin indicated by the manufacturer. It is found a high purity alloy, absence of inclusions, porosity and other defects.

The research conducted on samples from the same alloy after their processing, namely Co-Cr alloy samples taken from the casting network indicates the presence of oxide inclusions. A comprehensive analysis providing information on the nature of the inclusions was performed by spectroscopy EDAX, the analysis indicating high oxygen content along with silicon and aluminum, the proportion of the basic elements (Cr and Co) decreasing significantly in these areas (Figure 3). It may be noted that determinations in the basic mass indicate the initial composition of the alloy within the limits prescribed by the manufacturer.

***Table 2.** The chemical composition of the alloy Co-Cr (ADORON LX40626) %, delivery/marketing state of alloy* [5]

	C-K	Si-K	Cr-K	Mn-K	Co-K	Mo-L
L40626(1)_pt1	2.23	0.94	29.11	1.26	62.13	4.33
L40626(1)_pt2	5.47	0.77	27.53		62.64	3.59
L40626(1)_pt3	1.94	0.93	30.03		63.02	4.09

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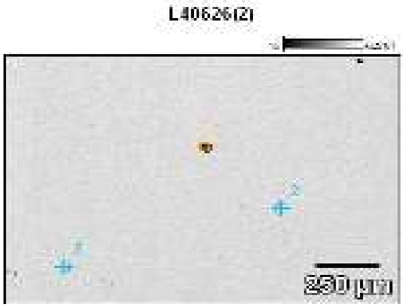

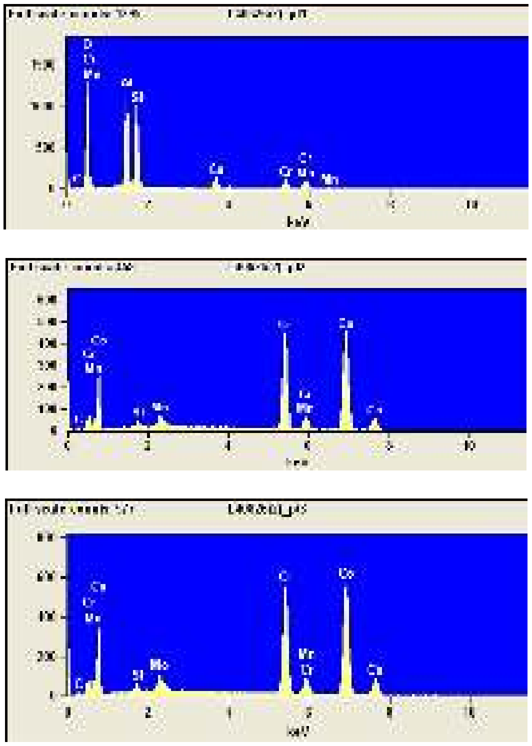

***Fig. 3.** X-ray spectroscopic analysis of chemical composition of samples of Co-Cr alloy (ADORON LX40626), the sample taken from casting network* [5]

Table 3. *Chemical composition (%) of the alloy Co-Cr (ADORON LX40626), samples taken from the casting network* [5]

	C-K	*O-K*	*Al-K*	*Si-K*	*Ca-K*	*Cr-K*	*Mn-K*	*Co-K*	*Mo-L*
L40626(2)_pt1	3.58	61.18	11.43	12.32	2.76	4.49	4.25		
L40626(2)_pt2	3.02			1.01		28.74	0.83	62.44	3.95
L40626(2)_pt3	2.30			0.96		29.33	1.00	61.63	4.78

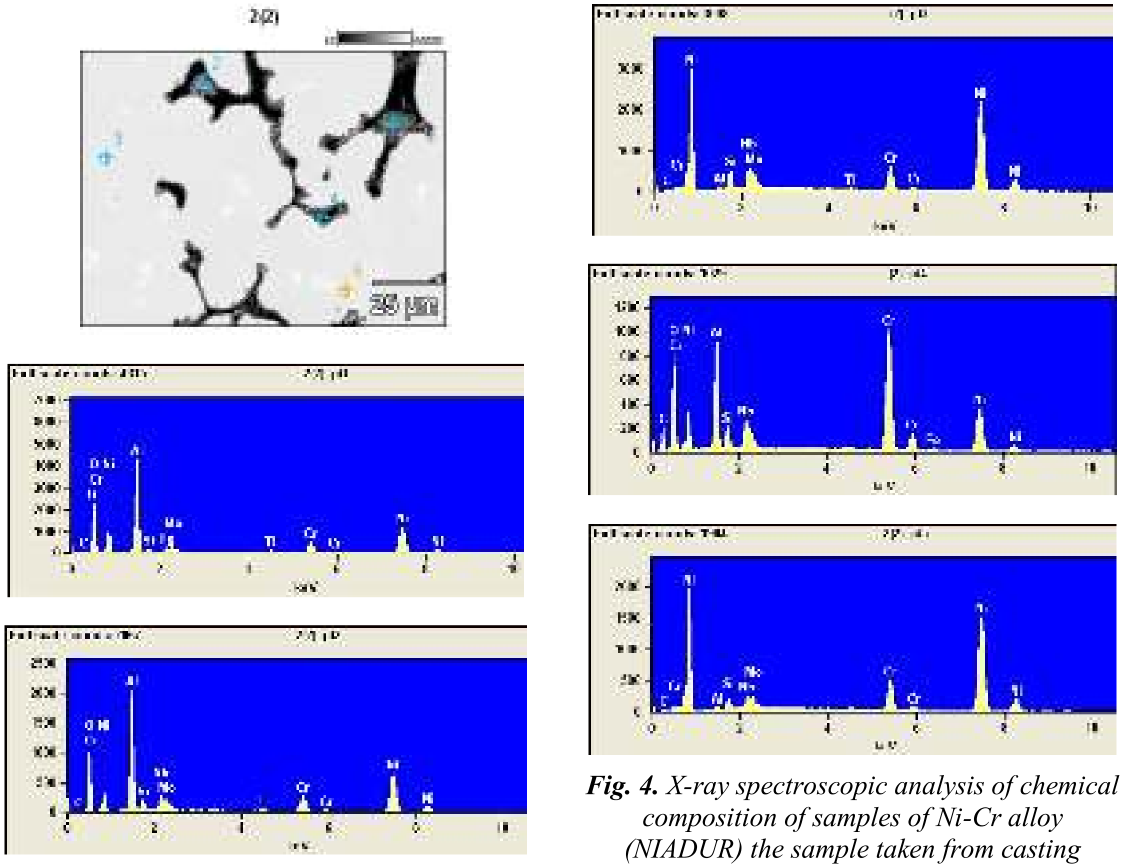

Fig. 4. *X-ray spectroscopic analysis of chemical composition of samples of Ni-Cr alloy (NIADUR) the sample taken from casting network*

Tabel 4. *Chemical composition (%) of the alloy Ni-Cr (NIADUR), samples taken from the casting network*

	C-K	O-K	Al-K	Si-K	Ti-K	Cr-K	Fe-K	Ni-K	Nb-L	Mo-L	Hg-L
TURNATE 1-PLIC 2(2)_pt1	2.78	37.55	19.57	0.50	0.88	5.71		30.85		1.69	0.46
TURNATE 1-PLIC 2(2)_pt2	2.66	35.30	17.18	1.64	0.71	5.70		30.10	4.99	1.71	
TURNATE 1-PLIC 2(2)_pt3	3.17		0.62	3.21	0.32	8.65		72.17	8.32	3.54	
TURNATE 1-PLIC 2(2)_pt4	12.45	30.09	7.85	1.69		23.98	0.44	18.56	4.94		
TURNATE 1-PLIC 2(2)_pt5	3.02		0.61	1.81		11.01		76.11	4.21	3.22	

The high content of oxygen and the presence of inclusions indicate that the alloy was oxidized during the casting in contact with the atmosphere for a long time. With Ni-Cr alloy samples (Figure 4) oxide inclusions are highlighted.

EDAX analysis reveals, in addition to the basic elements (Ni and Cr), the presence of a high content of Si and other elements such as C, O, Al, Fe. The presence of oxygen in the inclusions suggests that the material studied oxidized for a long time during casting. The presence of carbon is explained as having come from the metallographic sample preparation process (particles of diamond paste). The predominant component is nickel as alloying element, to be found in a constant amount in the solid solution and in the eutectic, with an increase in the mass of the base metal (above 70%) and reduced inclusions (about 30%).

The analysis of the samples at different resolutions highlights the typical structure of dendritic casting aspect (Fig. 5 and Fig. 6).

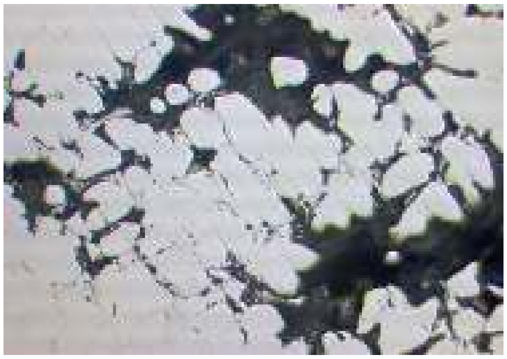

Fig. 5. *Microscopic appearance (optical microscopy, magnification X400) of the Co-Cr (ADORON LX40626), Samples from the casting alloy network* [5]

Fig. 6. *Microscopic appearance (optical microscopy without metallographic attack, magnification X100) of the Co-Cr alloy samples (ADORON LX40626), Samples from metal crown* [5]

Highlighting the chemical inhomogeneity in the studied samples reveals the existence of manufacturing processes at temperatures noncompliant with the specific alloy melting and casting ones. Also there are material discontinuities (alloy solidification shrinkage voids) and some areas of material overheating. The optical microscopy analysis of the metallic sub layer of metal-ceramic restoration reveals a cell-appearance dendritic structure and compound interdendritic separations. The presence of cell appearance is determined by the corresponding reduction in the thickness of the casting part, which further increase the solidification speed. In this situation, the solidification of the melt occurs quickly enough so that dendrites have no time to develop and the supersaturated interdendritic liquid precipitates intensely the intermetallic compound. The electron microscope examination of the metallic sub layer of the metal-ceramic crown highlights the same interdendritic inhomogeneities originated in the mold. The alloying elements are distributed unevenly. In terms of chemical composition, they have noticeable losses decreasing with respect to the gross alloy used, losses that take place in the melt. It is noted the presence of heterogeneous dendritic eutectic structure. The material was cast at a low temperature, which resulted the appearance of restoration.

4. Conclusions

Defects arising from failure to comply with the technological alloy foundry- casting conditions in the mold/pattern are generated on the one hand by not meeting the casting temperature requirements, causing either overheating (high temperature) or decreased fluidity and occurrence of the alloy solidification shrinkage voids (low temperature) and on the other hand there are defects caused by improper network design, incorrect sizing of the rods or supply channels which should provide a sufficient amount of metal into the mold cavity.

It is necessary to correctly size the system of rods to provide a quantity of molten metal in the mold prior to rapid quenching of the alloy. The channels will be wide and short to increase the pressure of the metal in the mold and its absorption from the metal tank.

Lack of rigorous assessment of the melt temperature and optimal timing of casting is possible because this is assessed only visually by loss of the geometric shape of the tablets and their collapse into the mold cone. Failure to comply with specific alloy melting range (as specified by the manufacturer) is another possible cause of occurrence of casting defects. Usually alloy melting is achieved with a high flame nozzle with many holes to quickly reach the melting point of the alloy.

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USE OF ALTERNATIVE FUELS IN ROAD TRANSPORT AND ITS ENVIRONMENTAL EFFECTS. A LITERATURE REVIEW

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ABSTRACT

This paper presents a literature review on use of alternative fuels in road transport, in respect of their performance and emission in diesel engines/vehicles. The major limitations of vegetable oils as fuel in diesel engines are their high viscosity and poor volatility, which lead to severe engine deposits, injector coking, and piston ring sticking. Transesterification reaction reduces the viscosity of vegetable oils, and the result of this reaction is biodiesel. In general, engine power dropped due to the lower heating value of biodiesel. A proper injection timing, by advancing the start of fuel injection by 1-2°BTDC, determined that all changes in engine emission are according to chemical and physical properties of the tested fuels.

KEYWORDS: diesel engine, vegetable oils, biodiesel, emission

1. Introduction

Our society is highly dependent on petroleum for its activities, about 90% of it being used as an energy source for transportation, heat and electricity generation [1].

The extensive use of fossil resources and especially of petroleum and its derivatives as fuel has given rise to serious environmental concerns related mainly to the production of harmful gases like SO_x, NO_x, and CO_x, which are mainly held responsible for several environmental problems [2]. Conventional diesel fuel originating from crude oil is responsible for greenhouse gas (GHG) emissions that contribute to global warming; around ¼ of the GHG emissions in Europe are caused by the transport sector, including passenger cars [3].

Diesel engines are more efficient than gasoline engines of the same power [4] and vehicles powered by a diesel engine are considered one of the primary sources of air pollution, especially in metropolitan areas [5]. The problem associated with the emissions of smoke, PM, sulfur oxide (SO_x), PAHs, and odor from the exhaust of diesel engines has been widely been a concern in many countries [6].

The use of renewable energies is considered as a viable solution for a sustainable transport future [7]. An increased usage of biofuels can contribute to reduce CO_2 emissions in road traffic. Directive 2009/28/EC on the promotion of renewable energy set a mandatory 10% minimum target to be achieved by all Member States for the share of biofuels in transport petrol and diesel consumption by 2020 [8].

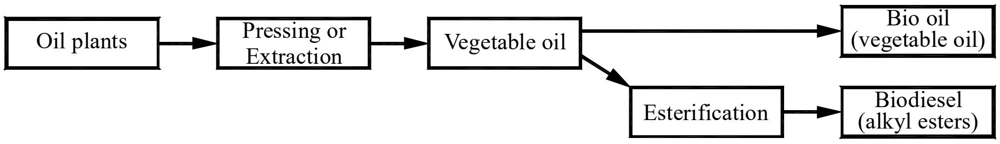


***Fig. 1.** Conversion route from oil plants to biofuels (adapted from [10])*

This paper aims to present a literature review on use of alternative fuels in road transport, in respect of their performance and emission in diesel engines/ vehicles.

Currently, transportation fuels based on biomass (i.e., biofuels) are identified as first and second generation biofuels [9]. Among the most common types of first generation biofuels for diesel engines are biodiesel and straight vegetable oils. Figure 1 presents the main routes to produce vegetable oil and biodiesel [10]. Biofuels are favorable choice of fuel consumption due to their renewability, biodegradability and generating acceptable exhaust gases [11].

2. Vegetable oil as diesel fuel

Many researchers have concluded that vegetable oils hold promise as alternative fuels for diesel engines [12]. Vegetable oils have [13, 14]:

- high biodegradability;
- high calorific value: high energy density;
- ready availability and renewability;
- are neither harmful nor toxic to humans, animals, soil nor water;
- are neither flammable nor explosive, and do not release toxic gases;
- reduced emission, particularly CO_2, SO_x, soot and aromatic compounds.

The major limitations of vegetable oils for their use as fuel in diesel engines are their high viscosity and poor volatility, which deteriorate the atomization, evaporation and air-fuel mixture formation leading to improper combustion and higher smoke emission [15]. The increased viscosity and low volatility of vegetable oils lead also to severe engine deposits, injector coking, and piston ring sticking [12].

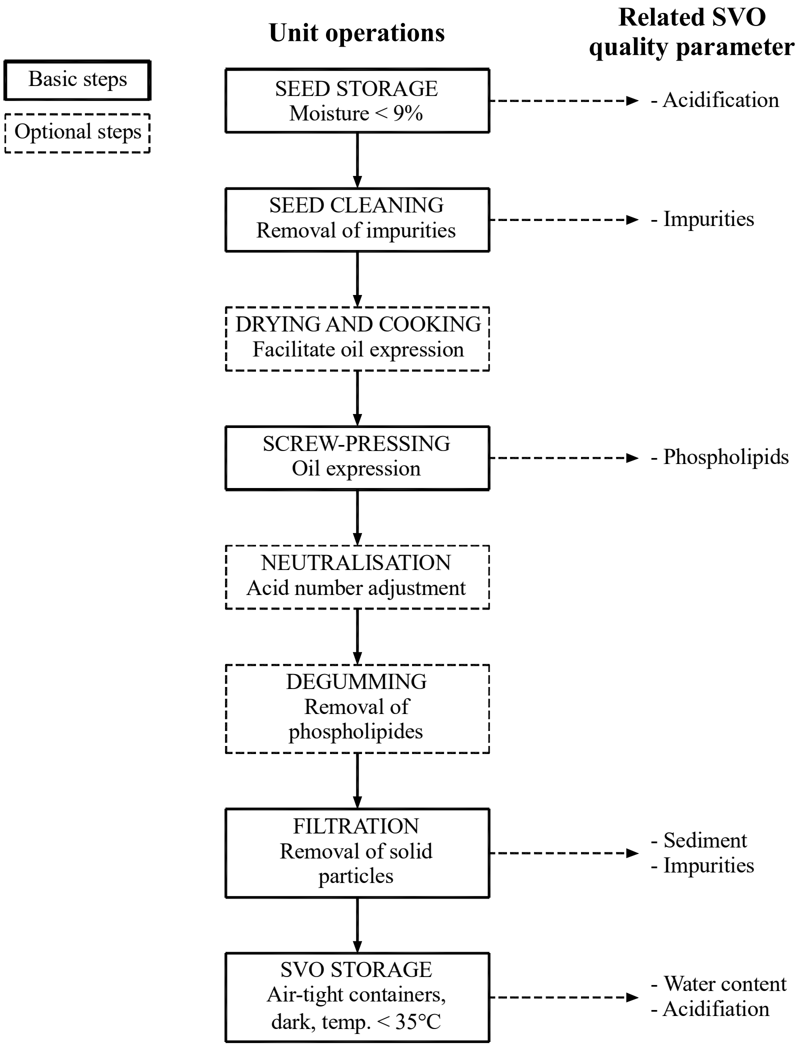


Fig. 2. *Straight vegetable oils quality in relation to the production process* [16]

Straight vegetable oils (SVO) are usually produced by mechanical extraction of oil from an oil-bearing biomass as feedstock [16]. The quality of SVO for fuel use is strongly influenced by both the quality of the feedstock and the processing conditions. Oilseeds come usually from dedicated crops (sunflower, rapeseed, oil palm, Jatropha curcas, etc.). There are five main operations in the SVO production process that govern fuel quality and which need to be carefully managed (Fig. 1).

In order to use vegetable oil as fuel, a professional engine conversion is strongly recommended [17]. This conversion often includes installing a second fuel tank, allowing the engine to start and shut down on biodiesel or diesel fuel. The basic idea is to use only preheated vegetable oil to at least 60 °C in order to reduce the oil viscosity (Fig. 2).

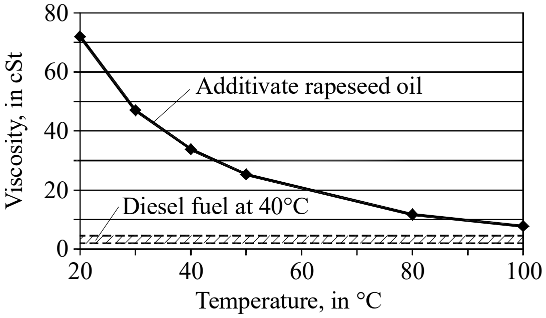


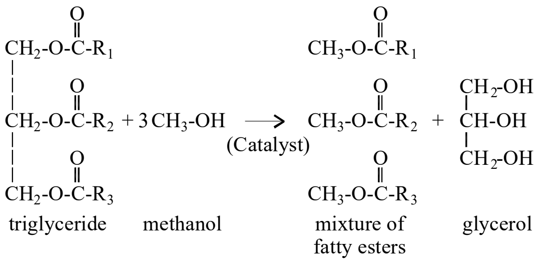
Fig. 2. *Viscosity of rapeseed oil versus temperature (adapted from [18])*

Current interest in the use of pure plant oils is growing, that can be used in pure form but can also be blended into diesel up to 25%vol [19]. These blends can in principle be used in unmodified direct injection diesel engines. Also higher percentages blends and blends with different oils and e.g. ethanol are possible. Table 1 presents an overview regarding the effects of pure plant oils (pure and blends) on the diesel engine emissions, according to the literature cited in [19].

3. Biodiesel

Crude vegetable oils are inferior as fuel in terms of viscosity, heating value, freezing point, etc. [20]. In order to reduce viscosity, vegetable oils are converted into esters by transesterification reaction [1]. The result of transesterification reaction (Fig. 3) is biodiesel, as a fuel comprised of mono-alkyl esters of long chain fatty acids derived esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100 [22].

Because the biodiesel viscosity is almost twice higher than the diesel fuel viscosity (according to Standard EN 14214:2003, the biodiesel viscosity at 40 °C is 3.5-5.0 mm^2/s [23]), biodiesel is currently used in blends with diesel fuel.



$$CH_2\text{-O-}\overset{\overset{O}{\|}}{C}\text{-}R_1,\ CH_2\text{-O-}\overset{\overset{O}{\|}}{C}\text{-}R_2,\ CH_2\text{-O-}\overset{\overset{O}{\|}}{C}\text{-}R_3 + 3\,CH_3\text{-OH} \xrightarrow[\text{(Catalyst)}]{} CH_3\text{-O-}\overset{\overset{O}{\|}}{C}\text{-}R_1,\ CH_3\text{-O-}\overset{\overset{O}{\|}}{C}\text{-}R_2,\ CH_3\text{-O-}\overset{\overset{O}{\|}}{C}\text{-}R_3 + CH_2\text{-OH},\ CH\text{-OH},\ CH_2\text{-OH}$$

Fig. 3. *Transesterification reaction* [21]

Biodiesel can be produced from various vegetable oils, waste cooking oils or animal fats. The fuel properties of biodiesel may be changed when different feedstocks are used [24]. However, biodiesel production is highly dependent on many local variables such as feedstock and land availability, costs associated with feedstock procurement, government subsidies and tax reductions as well as interactions with the food industry [25].

Table 1. *Effects of virgin plant oil (pure & blends) on diesel engine emissions* [19]

Blend, %	**Regulated emissions**				**References cited in [19]**
	CO	**HC**	**NO$_x$**	**PM**	
100	–	–	+	–	Lance 2004 (LDV)
100	+	+	+&–	+ $^{3)}$	Aberson 2004 $^{2)}$
30			–	+	Senda 2004 (HDV)
100	–	–	+	+ $^{1)}$	Kumar 2001
100	+		+	+ $^{1)}$	Niemi 1997
50/100	–	+	+	+ $^{1)}$	Ziejewski 1992
100	–	–	+	–	Hammerlein 1991 (DI)

1) Smoke; 2) Unclear whether this information is based on test data; 3) Soot
+ = positive/yes; – = negative/no
LDV - Light Duty Vehicle; HDV - Heavy Duty Vehicle; DI - Direct Injection diesel engine

The main stages of the fuel systems for biodiesel from vegetable oil and waste cooking oil are shown in Figure 4.

A survey on 27 literatures [26] to study the effect of pure biodiesel on engine power, showed that 70.4% of them agreed that, with biodiesel (especially with pure biodiesel), engine power will drop due to the loss of heating value of biodiesel (Table 2). However, the results reported show some fluctuation. Some authors found that the power loss was lower than expected (the loss of heating value of biodiesel compared to diesel) because of power recovery.

Table 2. *Statistics of effects of pure biodiesel on engine performances (adapted from [26])*

	Total number of references	Increase	%	Similar	%	Decrease	%
		Number		Number		Number	
Power performance	27	2	7.4	6	22.2	19	70.4
Economy performance	62	54	87.1	2	3.2	6	9.7

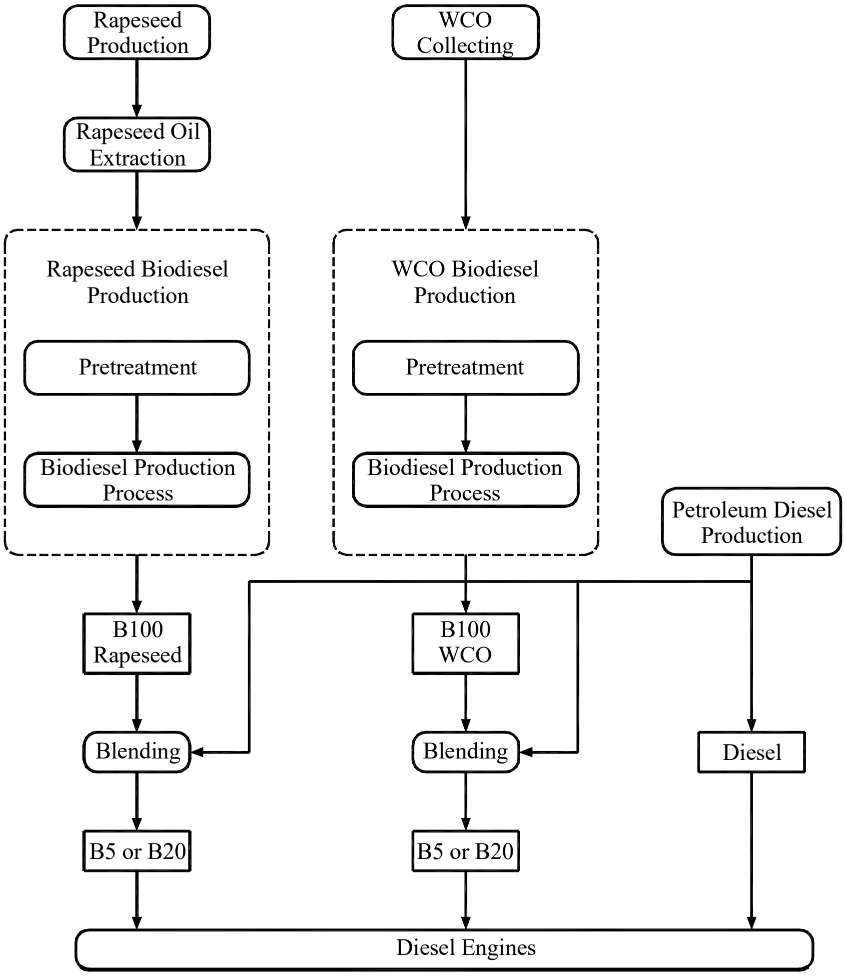


Fig. 4. *Fuel systems for biodiesel from vegetable oil (rapeseed oil) and waste cooking oil (WCO) (adapted from [25])*

Table 3 summarizes some available results of Light-Duty diesel vehicle test data for some rapeseed biodiesel blends (a minimum of 20 measurements of a particular blend were required to assess the significance of the effect) that allow one to explore the differences in the effects on emissions of the different biodiesel feedstock [27]. The emission data from Table 3 could be discussed as follows:

- HC lower for B20 and B100, but no correlation between biodiesel content in the blend and level of HC emission;
- NO_x higher than for diesel fuel for all blends, the higher content of biodiesel, the higher NO_x emission;
- CO emission is random, lower for B20, but higher for B30;
- Particulate matter (PM) emission is not significant versus diesel fuel. However, a very slight increase of PM for biodiesel blends is observed.

The heterogeneous and uncorrelated data from the Table 3 could be due to the use of biodiesel and biodiesel blends on diesel engines tuned only for pure diesel fuel or for B5-B7 blends. Using higher percentage biodiesel blends, or even B100 fuel, on existing unmodified engines, could cause an inappropriate response of the engine in respect of torque (power) and emission.

In their experimental work, Canakci and Van Gerpen [28] found that to provide the same torque as with diesel fuel, it was necessary to inject 13 to 14% more biodiesel and for that, the injection timing was advanced between one and two degrees. The combustion characteristics of the fuels used, according to the physical properties of the fuels, self-timing of the injection pump, and injector nozzle opening pressure (20.7 MPa), are presented in Table 4.

According to Van Gerpen [29], the cetane number (CN) for biodiesel blends is calculated using the following linear regressions:

- for 20% SME

$$CN = 0.089 \cdot (\%\ \text{blend}) + 42.6 \tag{1}$$

- for 20% YGME

$$CN = 0.2 \cdot (\%\ \text{blend}) + 42.6 \tag{2}$$

Table 3. *Effects and significance of rapeseed biodiesel blends on the relative vehicle emissions for chassis dynamometer data with light-duty vehicles (adapted from [27])*

Emission	Biodiesel blend	Effect ± 95% confidence interval	Number of measurements	Significant effect *
HC	B10	+4.9 ± 5.0%	27	NS
HC	B20	-10.6 ± 7.9%	28	Lower
HC	B30	+3.1 ± 5.7%	26	NS
HC	B50	+1.2 ± 15.7%	29	NS
HC	B100	-20.9 ± 19.3%	32	Lower
NO_x	B10	+0.9 ± 1.8%	27	NS
NO_x	B20	+3.2 ± 4.8%	28	NS
NO_x	B30	+4.5 ± 2.2%	26	Higher
NO_x	B50	+5.2 ± 4.3%	29	Higher
NOx	B100	+5.7 ± 5.5%	33	Higher
CO	B20	-9.6 ± 6.5%	28	Lower
CO	B30	+11.6 ± 6.4%	23	Higher
CO	B50	+2.3 ± 16.6%	26	NS
CO	B100	-4.3 ± 19.3%	32	NS
PM	B20	-0.8 ± 9.5%	21	NS
PM	B50	+6.4 ± 18.7%	20	NS
PM	B100	+4.5 ± 11.0%	26	NS

* NS – not significant

Table 4. *Combustion characteristics of the fuels (adapted from [28])*

Fuel	Start of fuel injection (°BTDC)	Start of combustion (°BTDC)	Ignition delay (°)	Cetane number	Kinematic viscosity at 40 °C (cSt)
No. 2 Diesel	13.50	7.42	6.09	42.6 *	2.8271
20% SME	14.40	8.33	6.07	44.38 **	3.1071 **
20% YGME	14.60	8.50	6.10	46.6 **	3.2871 **
SME	16.18	10.83	5.34	51.5 *	4.2691
YGME	17.05	11.58	5.46	62.6 *	5.1643

SME – soybean oil methyl ester; YGME – yellow grease methyl ester
* Cetane number determined according to ASTM D613 [28]; ** Calculated using linear regression

Table 5. *Average percent changes in the engine emissions with Tukey grouping statistical results (adapted from [28])*

Fuel type	Change in CO %	Change in CO_2 %	Change in HC %	Change in NO_x %	Change in SN %
20% SME	-7.5	-0.04	-3.1	+1.5	-15.8
20% YGME	-7.0	-0.06	-2.3	+1.1	-16.8
SME	-18.2	+1.8	-42.5	+13.1	-61.1
YGME	-17.8	+1.2	-46.3	+11.6	-64.2

SN – Bosch smoke number

According to data from [30], for methyl ester of soybean oil, the kinematic viscosity for biodiesel blends may also be calculated using linear regression. Thus, the linear regressions, to estimate the kinematic viscosity (KV), at 40 °C, for the biodiesel blends from [28], are as follows:

- for 20% SME

$$KV = 0.014 \cdot (\%\ \text{blend}) + 2.8271 \qquad (3)$$

- for 20% YGME

$$KV = 0.023 \cdot (\%\ \text{blend}) + 2.8271 \qquad (4)$$

The average percent changes in the engine emissions, at engine full load for peak torque condition (1400 rpm and 258 Nm), are shown in Table 5. It can be noticed that all changes in engine emission are according to chemical and physical properties of the tested fuels: the higher oxygen content (i.e. for the biofuels and their blends), the lower CO and SN emission and higher NO_x emission. These correlated results could be due to a proper injection timing by advancing the start of fuel injection by 1-2°BTDC.

4. Conclusions

Vehicles powered by a diesel engine are considered one of the primary sources of air pollution, and the use of alternative fuels is considered as a viable solution for a sustainable transport future.

Vegetable oils are a promising alternative fuel for diesel engines due to their high biodegradability, ready availability and renewability and their reduced emission. The major limitations of vegetable oils for their use as fuel in diesel engines are their high viscosity and poor volatility, which lead to severe engine deposits, injector coking, and piston ring sticking.

By the transesterification reaction, the viscosity of vegetable oils is reduced, and the result of this reaction is biodiesel.

A literature survey pointed out that in 70.4% of studied cases, engine power dropped due to the lower heating value of biodiesel. However, it was found that the power loss was lower than expected because of power recovery.

The emission data from some available literature results for Light-Duty diesel vehicle tests fuelled with rapeseed biodiesel blends showed that there is no correlation between biodiesel content in the blend and level of HC, CO and PM emission.

A proper injection timing, by advancing the start of fuel injection by 1-2°BTDC, determined that all changes in engine emission are according to chemical and physical properties of the tested fuels.

Acknowledgement

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RESEARCH ON THE CORROSION RESISTANCE, IN SALINE SOLUTION, OF STEEL SHEETS FOR INDUSTRIAL CONSTRUCTION, BY GRAVIMETRIC METHOD

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ABSTRACT

In this paper, it was presented a study on corrosion in saline medium, by gravimetric method, of the steel sheets for industrial construction. The corrosion rate was estimated by gravimetric method and evaluate based on corrosion indices, such as gravimetric index, the penetration index.

KEYWORDS: corrosion index, pitting, gravimetric index

1. Introduction

Corrosion of metallic materials consists in partial or total destruction through chemical reactions, electrochemical or biochemical, after spontaneous interaction between surface and ambient corrosive environment.

Corrosion is generally defined as an attack on a material environment, attack leading to a worsening of properties to destroy material. Corrosion is not limited to the destruction of metallic materials, it affects equally plastics, ceramic, concrete and even medium with which they interact.

The metals, under natural conditions, are not thermodynamically stable.

Local corrosion can be:

- The punctuate corrosion, which locates on small surfaces (corrosion points);
- Sub-surface corrosion, which starts at the surface but extends preferably in the metal surface causing swelling and peeling metal (corrosion bags);
- Pitting that is distributed on relatively large, but their depth is small;
- Inter-crystalline corrosion, which is characterized by the selective destruction of the metal on the edge of the crystal;
- The transcristalin corrosion, which is a typical case of local corrosion in corrosive destruction is determined by the direction of mechanical tension stress.

Characteristic of this type of corrosion is that cracks do not propagate only at the crystal but they actually crosses them [1, 3].

The steels studied are intended to construction in the marine industry and are exposed to corrosion in saline environments.

Quantitative criteria

Rate of the corrosion process can be estimated by laboratory tests or measurements based on corrosion index, such as gravimetric index, the penetration index.

Gravimetric index

It represents the variation in mass of the test specimen as a result of corrosion per unit area and time; frequently expressed in g/m^2 day, but can use and the other units. Measuring the mass variation of test specimens to determine the gravimetric index, is the most common way, of quantitative characterization in the corrosion testing.

Gravimetric index is denoted by K, then the variation in the loss of the metal mass, obtained after removal of the reaction products on the metal surface:

$$K = \frac{m_{cor}}{S.t} \text{ [g/m}^2\text{/day]} \qquad (1)$$

where:

S - surface area corroded (m^2);
t - time of corrosion (day);
m_{cor} - corrosion mass loss(g).

Penetration index

This index, characterizes the penetration corrosion, in metal mass.

In this form, who expressing the corrosion rate allows assessment of the duration of use of the equipment (pipes, columns, tanks, etc.) within a facility [2, 4].

The average depth of corrosion penetration is calculated from weight loss, the metal density and duration of exposure. The average depth of corrosive of the metal, in mm penetration per year is denoted by p (mm / year) and is calculated by the relationship:

$$I_p = \frac{K \cdot 24 \cdot 365}{1000 \cdot d} \qquad (2)$$

where:

K - is the gravimetric index, g/m^2day;

ρ - density, g/cm^3;

d is the density of the metal material, d = 7.85 [g/cm^3];

1000 represents the conversion factor.

Penetration, is most commonly expressed in mm/year, but can use the other units. Penetration index is determined by experiments, with limited time duration. It should therefore be avoided extrapolating laboratory data from longer interval of time [3].

2. Experimental research

Samples used were from steel sheet S355N and S355MC with chemical composition shown in Table 1 and 2. It was tested in 3.5% NaCl solution (Figure 1).

Table 1. *Chemical composition of S355N samples*

S355N	C [%]	Mn [%]	Si [%]	P [%]	S [%]	Al [%]	Nb [%]	Ti [%]
P1	0.168	1.42	0.23	0.013	0.002	0.045	0.038	0.019

Table 2. *Chemical composition of S355MC samples*

S355 MC	C [%]	Mn [%]	Si [%]	P [%]	S [%]	Al [%]	Nb [%]	Ti [%]
P2	0.098	1.18	0.34	0.011	0.005	0.031	0.019	0.015

Fig. 1. *Samples tested for corrosion in NaCl 3.5% saline solution*

To carry out the test, it was prepared, a solution of 3.5% sodium chloride. Weighing of the samples was performed at the 7, 14, 21 and at 30 days.

In order to determine the loss of mass after the attack, the samples were washed thoroughly at room temperature, first with distilled water, then with acetone and then dried. He attended weighing, Figure 2.

The variation of the corrosion rate of the steel samples is show in Fig. 3.

To evaluate the strength class of metallic materials, is used penetration index, which expresses the average decrease of the thickness of the metal material, under standard conditions [5, 6], per unit time [mm/year].

Fig. 2. *Weighing samples subjected to the corrosion test*

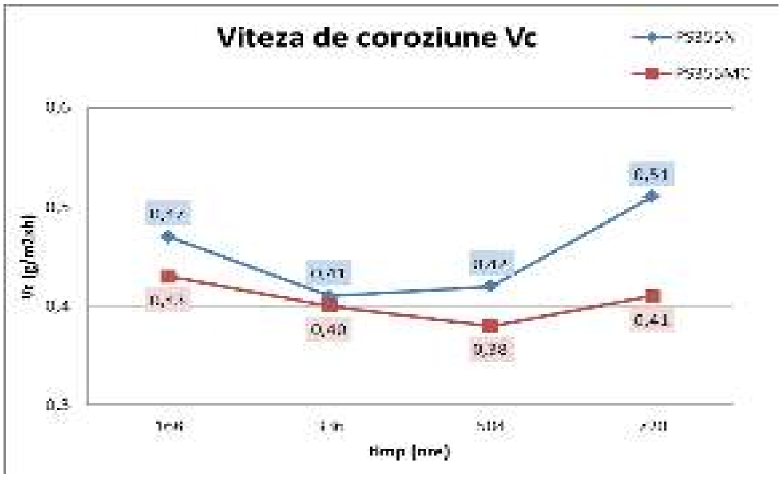


Fig. 3. *Variation of the corrosion rate of the steel samples*

Classes corrosion stability assessment used in the design are:

1. perfect stable: 1 * 10^{-3} mm year;
2. very stable 1 * 10^{-3} ÷1 * 10^{-2} mm/year;
3. stable 1 * 10^{-2} ÷1 * 10^{-1} mm/year.

Following the results obtained, the material falls into Class 3 Stability (stable).

The state of general corrosion assessment after penetration index values are given in Figure 4.

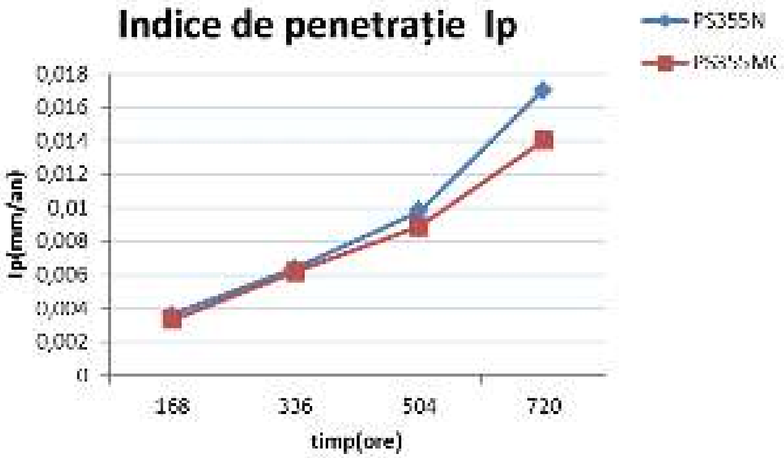
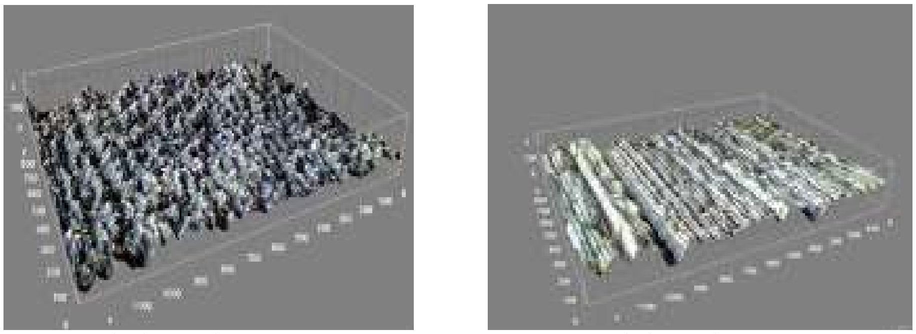


Fig. 4. *Penetration index variation*

3D Imaging

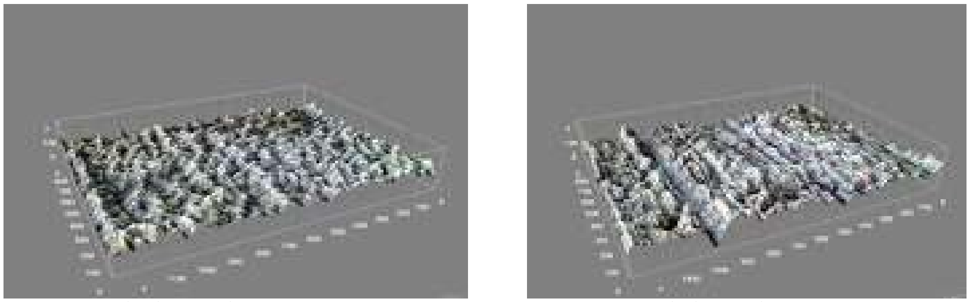
Changes in the structure of steel after corrosion have been studied in the Faculty of Engineering, surface engineering laboratory microscope NEOPHOT2, using software ImageJ.

3D images of the profile surfaces subject to corrosion from the two steel grades are shown in Figure 5.



Blank sample P1 S355N

Corroded sample P1 S355MC



Blank sample P2 S355N

Corroded sample P2 S355MC

Fig. 5. *3D images of the samples surface profile before and after corrosion*

Darker areas of 3D images show the place where the corroded material is, and where it had lost mass at weighing.

3. Conclusion

Following research on corrosion resistance in saline solution, at the steel sheets for industrial construction, we reached the following conclusions:

After the corrosion rate, the two steel grades S355N and S355MC are stable, under 0.10 mm/year due to:

- chemical composition (steel micro-alloyed with Nb);
- fine granulation.

Because the granulation structure, of the steel mark S355MC, is much finer, and amount of perlite is smaller, this sample was less corroded.

The sample S355MC of the steel, has a greater corrosion resistance, which is due to lower carbon content and finer structure.

Acknowledgement

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STUDIES AND RESEARCH ON OBTAINING BRONZE FILTERS USING POWDER METALLURGY METHODS

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ABSTRACT

The article presents how to obtain porous bronze products using copper - based powder by powder metallurgy methods. The formation of tablets was done by free pouring the spherical powder into the mould, followed by their sintering them in the range of 780 - 925°C, with an exposure time of 30 minutes. Characterization of the tablets thus obtained was done in terms of microstructure, microhardness, porosity and permeability.

KEYWORDS: powder metallurgy, microstructure, microhardness, porosity, permeability

1. Introduction

A main feature of the powder metallurgy is the possibility that this area offers to create porous materials whose working capacity and operating areas are determined by the characteristics of the porous structure.

Modern applications of powder metallurgy include obtaining special properties parts (permanent magnets, ferrite, electrical contacts, carbon brushes) for the electrical industry, the titanium and beryllium super alloys for the aerospace and nuclear industry, developing hard alloys for metal cutting, manufacturing products of predetermined porosity (filters - 25 - 90%, ball bearings - 8 - 25%) [1].

Porosity of filters must be associated with a high permeability for the filtered environment (gas or liquid) with as high mechanical strength as possible, shock resistance and sufficient corrosion resistance. Most recommended from these points of views are metal filters rather than ceramic or organic, except for corrosion resistance. But this aspect can be remedied by using bronze, nickel, stainless steels [1].

Thus metal filters show a number of advantages:

- ❖ Higher resistance to temperature variations;
- ❖ Possibility of relatively simple production, providing defined and uniform pore size;
- ❖ Goof reproducibility of the filtration properties;
- ❖ Easy cleaning in case of clogging.

The basic properties of metal filters are open porosity (passing), pore permeability and active size.

The structural characteristic of the highly porous materials is the intercommunicating porosity, associated with a constant pore size throughout the porous space. Pore sizes range from micron to millimeter order fractions. The method chosen for obtaining porous permeable material is a function of the initial raw material characteristics and determines the porosity, pore geometry and nature of the link between them. Within porous materials there are intercommunicating, sunken and closed pores [2].

The porosity is determined by the shape of the powder particles, the powder particle size distribution, the texture of its surface as well as the processing method [2].

Porous materials obtained by powder metallurgy technology are specified when necessary special features are required such as good mechanical properties, stiffness, corrosion resistance, uniform porosity and controlled permeability. For example, the porous bronze, stainless steel or nickel alloys are frequently selected for making parts operating in high temperature and pressure environments [1-3].

Researches undertaken in this paper are focused on the development of a technology to obtain porous powders products using copper based alloys and their characterization in terms of microstructure, micro hardness and permeability.

2. Experimental conditions

Within experimental research used was of bronze powder with the following chemical composition: 11% Sn; 89% Cu. The powder has a spherical shape determined by gas horizontal atomization. The average particle size of the powder is 400 μm. The appearance of the copper based powder is shown in Figure 1.

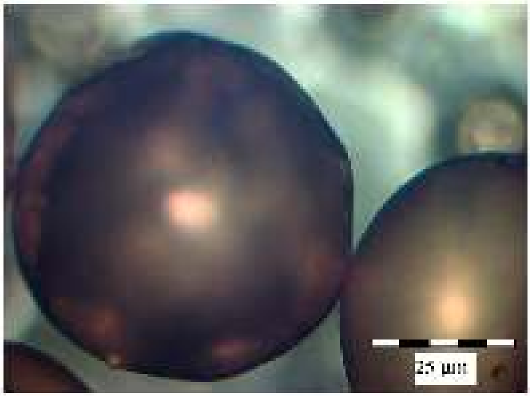


Fig. 1. *Appearance of Cu – Sn powder*

Formation of tablets was done by freely pouring the spherical powder into the mold and its slight compaction by shaking.

The mold used is made of graphite and is of cylindrical shape with the dimensions 23.9 X 9.8 X 18.5 mm.

The specific forming method chosen is specific for obtaining porous products such as filters, as it can give them various degrees of compaction regardless of the shape and size of the products and being at the same time an economical method.

Sintering of the powder tablets was made in a laboratory electrical furnace, and the regimes achieved are shown in Table 1.

Microscopic analysis of the powder and products obtained was performed using an optical microscope Neophot 2 with computerized data acquisition.

Table. 1. *Sintering regimes*

Sample code	**Sintering temperature [°C]**	**Sintering time [s]**	**Size of powder tablets**	
			Diameter [mm]	**Height [mm]**
P1	900 - 925	1800	3.85	6
P2	830 - 860		4.2	5.9
P3	800 - 830		4.2	5.6
P4	780 - 800		4.2	7.5

To study the influence of sintering on powders tablets, porosity of the samples was determined by the segments method.

Determination of hardness was performed using a micro hardness tester PMT 3.

Determination of the permeability of the obtained products was done using a lab plant, Fig. 2, wherein the fluid sample was air.

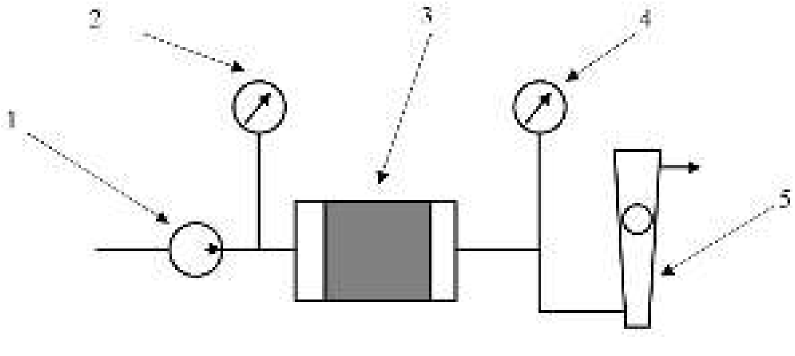


Fig. 2. *The lab plant for determination of the permeability: 1 - membrane pump; 2 - manometer 1; 3 - capsulated sample; 4 - manometer 2; 5 - flow-meter with floatable*

Permeability is the ability of a filter to be passed by a fluid when subjected to a pressure gradient. The permeability unit is 1 darcy which corresponds to the case where a fluid in laminar condition with a viscosity of 1 centipoise, has a rate of 1 cm^3/s through a cross section of 1 cm^2 of the filter under the influence of a pressure gradient of 1 at, over 1 cm thick material, (1 darcy = $0.9869 * 10^{-8}$ cm^2) [3].

The eq. used is:

$$\Phi = \frac{s \cdot \eta \cdot q}{A \cdot (p_1 - p_2)}$$

where:

Φ - permeability in darcy units;

s - material thickness, in cm;

η - test fluid viscosity, in centipoise (1 cp = 10^{-3} Pa∗s);

Q - flow rate of average pressure p, in cm^3/s;

p_1 - absolute pressure immediately upstream the fluid material, in at, 1at = 10^5 Pa = 100 kPa;

p_2 - downstream absolute pressure, in at;

A - effective surface of the filter in cm^2;

3. Results and discussions

For a metallographic study, the powder was incorporated into a cyanoacrylate adhesive and metallographic ally prepared by polishing and chemical attack with ferric chloride reagent (5 g ferric chloride, hydrochloric acid 30 ml, 100 ml water) and then examined under a microscope Neophot 2 with computer image acquisition.

***Fig. 3.** Microstructure of the Cu – Sn powder, attacked by ferric chloride reagent*

Microscopic analysis on particles embedded, polished and attacked with ferric chloride highlights their spherical shape and good compactness. It shows the microstructure of the Cu – Sn particles, resulting from the atomization process, consisting of a very fine dendritic solid solution α of Sn in copper as shown in Fig. 3.

Micro hardness determined on polished attacked section of the particles under load of 50 g was HV0.05 = 1600 MPa.

The metallographic analysis performed on powder tablets Fig. 4 suggests that the increase in temperature results in the reduction of porosity.

The sample P1 due to the high sintering temperature it was reported the presence of the liquid phase, which resulted in a stronger compaction.

At lower temperatures, corresponding to samples P3 and P4, sintering did not occur properly, which resulted in a low cohesion of the powder particles and their detachment during preparation of the samples.

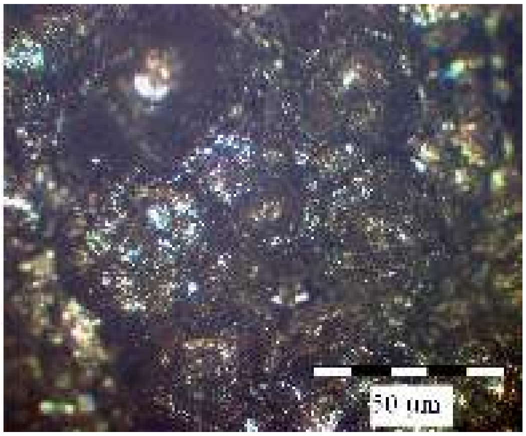
The optimum sintering regime is that corresponding to sample P2, which resulted in a proper porosity and good mechanical strength of the tablet.

Figure 5 - 8 illustrate 3D images, made with the software Image J, of the powder tablets after sintering [4-6].

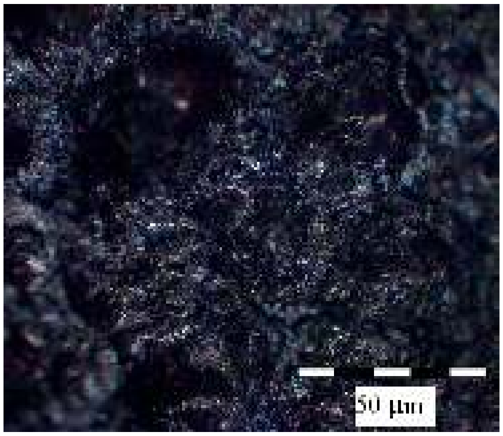
Looking at Fig. 5 - 8 it can be noticed the presence of a smoother surface of the sample P1 due to the occurrence of the liquid phase, with high toughness and low porosity.

Sample P2 has a homogeneous surface with a good bond between the powder particles.

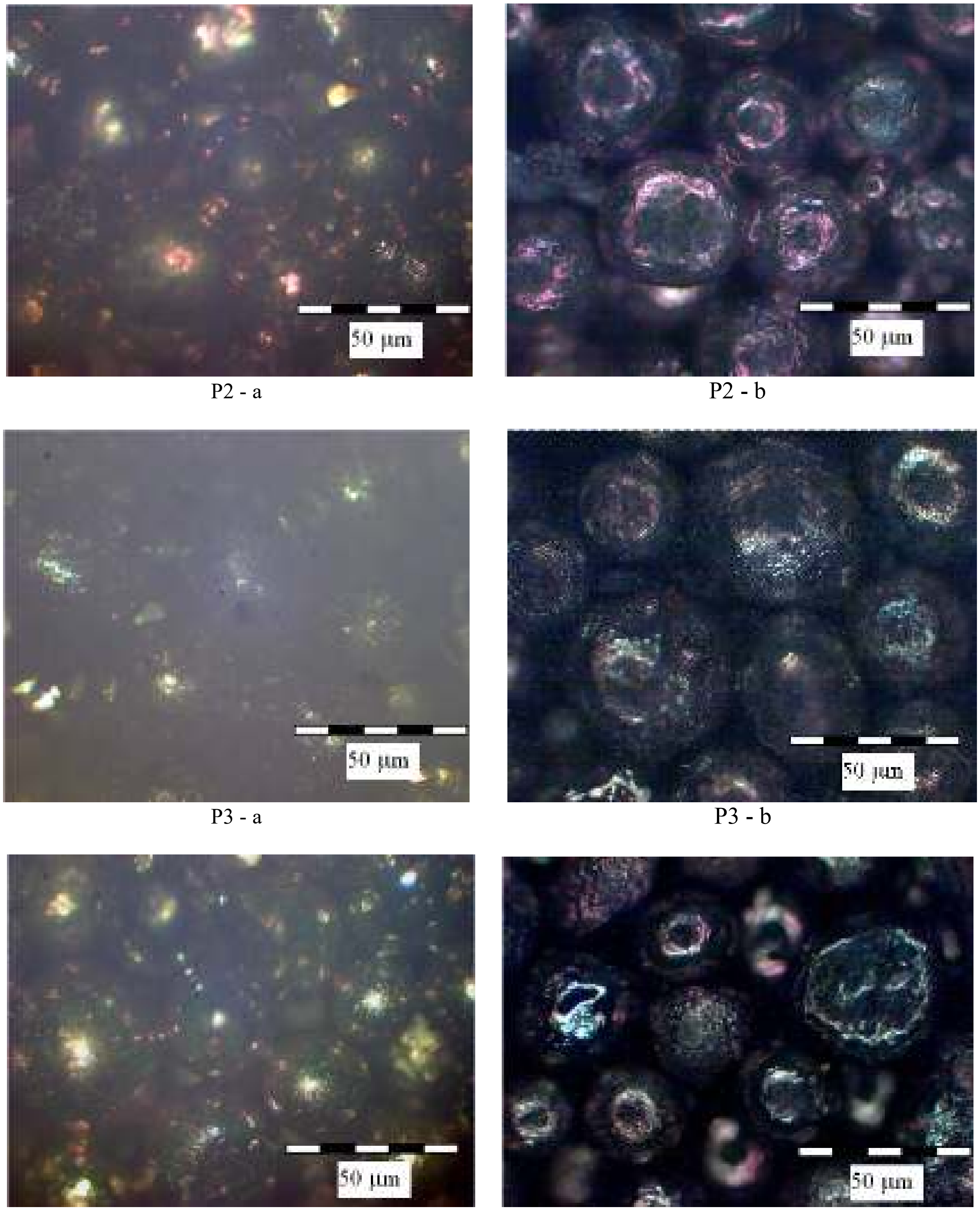
Samples P3 and P4 shows a heterogeneous surface with a weak bond between the powder particles.



P1 - a



P1 - b



P2 - a P2 - b

P3 - a P3 - b

P4 - a P4 - b

Fig. 4. *Imagine of powder tablets to different temperatures: a - bright field, b - dark field*

Decrease of temperature prevents the formation of contact-bridges between particles, which leads to low cohesion and poor strength of the powder tablets.

The microscopic analysis performed on the sintered samples with the microscope Neophot 2 revealed the existing porosity and their microstructure.

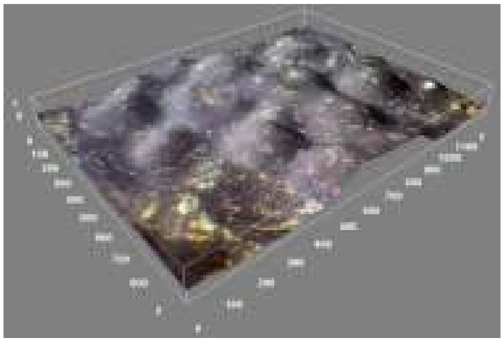


Fig. 5. *3D image of sample P1 surface after sintering*

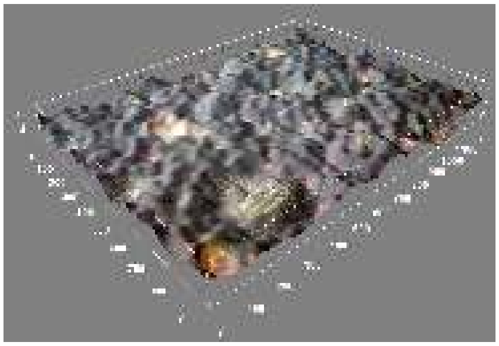


Fig. 6. *3D image of sample P2 surface after sintering*

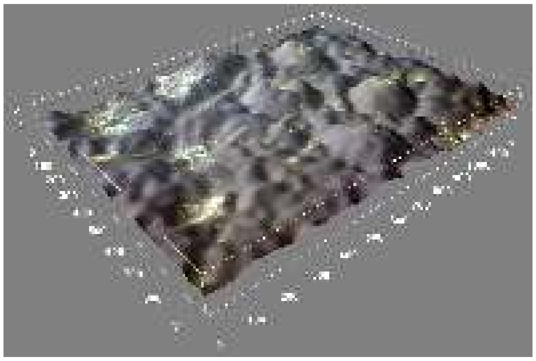


Fig. 7. *3D image of sample P3 surface after sintering*

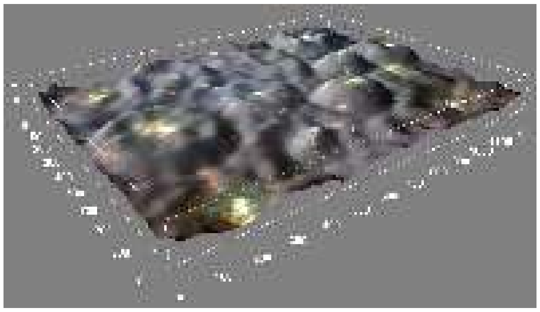
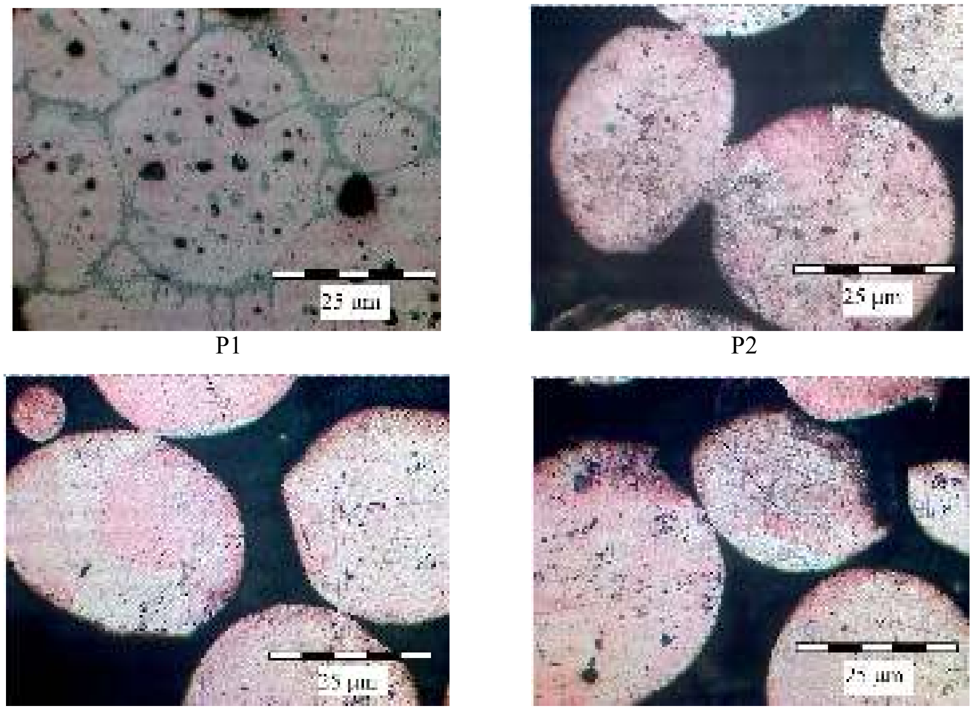


Fig. 8. *3D image of sample P4 surface after sintering*



P1 P2

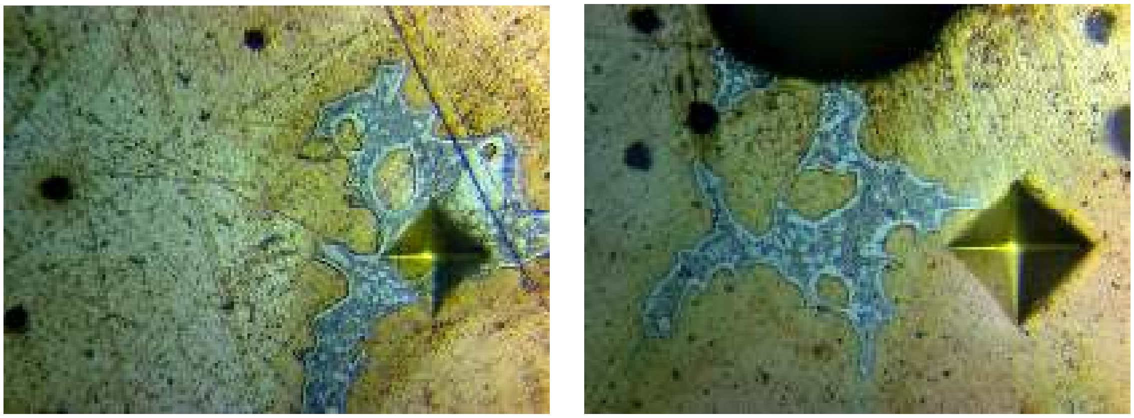
P3 P4

Fig. 9. *Microstructure of sintering samples, attacked by ferric chloride reagent*

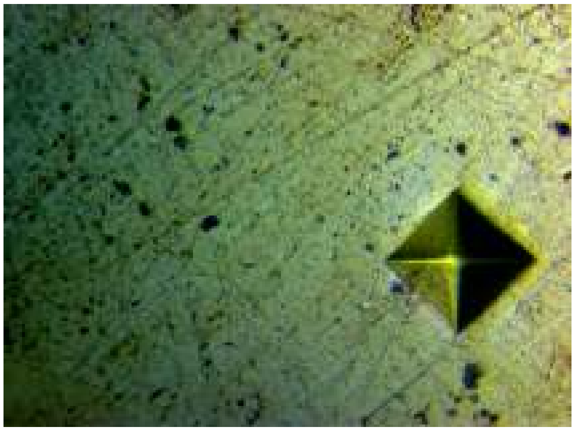
From Fig. 9 it is noted that sample P1 on which the sintering was carried out within the temperature range 900 – 925 °C, the structure consists of a solid solution α (HV 0.05 = 1060 MPa) and a mechanical mixture of the eutectoid phase composed of α and δ phases. The presence of eutectoid micro hardness of 1528 MPa increased the micro hardness in the immediate area consisting of solid solution α, this reaching HV 0.05 = 1368 MPa. These issues are highlighted in Fig. 10.

For the sample P2 sintered in the range of 830 – 860 °C the structure consists of macled solid solution α. It is found contact-bridges between powder particles which resulted in a high mechanical strength.

As the sintering temperature decreases, the formation of contact-bridges between the powder particles is reduced which results in reduced resistance of the powder tablets. Tablets structure is no longer altered consisting of macled solid solution α.



P1 - HV 0.05 = 1528 MPa P1 - HV 0.05 = 1368 MPa



P4 - HV 0.05 = 1028 MPa

***Fig. 10.** Determining powder tablets micro hardness*

It can be seen that for sample P1, the presence of eutectoid determines hardening of the powder tablets while for P2, P3, P4 tablets, hardness values are relatively close, respectively HV 0.05 = 1031 MPa, 1020 MPa, 1028 MPa.

Regarding the powder tablets porosity from the measurements made the following values were obtained: $P_{p2} = 44.4\%$, $P_{p3} = 50\%$, $P_{p4} = 49.2\%$.

With sample P1 due to the occurrence of the liquid phase porosity was more reduced, in the range 5-10%.

Permeability of powder tablets determined with a laboratory facility and using air as test fluid showed the following values: $\Phi_{p1} = 5.55$ darcy, $\Phi_{p2} = 42$ darcy, $\Phi_{p3} = 48$ darcy, $\Phi_{p4} = 54.86$ darcy.

It was thus found that, except for sample P1 where the high sintering temperature resulted in the formation of the liquid phase and thus the porosity was more reduced, all other samples showed a high porosity (greater than 25%), specific to filters and an adequate permeability of these products.

4. Conclusions

Obtaining porous sintered products revealed the following:

❖ tablet formation was achieved by free pouring of the spherical powder into the mold and its slight compaction by shaking it;

❖ powder tablets sintering was performed in the range 780 - 925 °C, exposure time 30 minutes; it was found that the increase in temperature leads to the reduction of porosity and increased compactness;

❖ Decrease of temperature prevents the formation of contact-bridges between particles, which leads to low cohesion and poor strength of the powder tablets;

❖ tablets powder microstructure consists of macled solid solution α of tin in copper;

❖ with sample P1 sintered in the range 900 - 925 °C it was found, in addition to the solid solution α, the presence of a mechanical mixture eutectoid phases consisting of α and δ which determined the hardening of the powder tablets;

❖ micro hardness HV 0.05 determined on the powder sintered tablets was within the range 1020 to 1060 MPa;

❖ 3D analysis of the tablets obtained, carried out by Image J software, highlights their surface appearance; it was found that the surface inhomogeneity increases with decreasing sintering temperature; this was due to the decreased cohesion between particles;

❖ porosity of powder tablets studied using the segments method showed the following values: P_{p2} = 44.4%, P_{p3} = 50%, P_{p4} = 49.2%; with sample P1, due to the occurrence of the liquid phase, porosity was more reduced in the range 5-10%;

❖ powder tablets permeability determined by a laboratory facility and using air as test fluid showed the following values: Φ_{p1} = 5.55darcy, Φ_{p2} = 42 darcy, Φ_{p3} = 48 darcy, Φ_{p4} = 54.86 darcy.

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THE INFLUENCE OF THE STEEL'S SURFACE QUALITY ON THE ELECTROLESS Ni-P COATINGS

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ABSTRACT

The method of autocatalytic reduction coating assures a precise reproduction of the coated surface. This is an advantage when the support surface has a complex geometry but also becomes a disadvantage because it requires a support without surface defects and without high roughness. Also the electroless method requires a special preparation of the support surface which should enhance its reactivity. This paper reveals the influence of different surface characteristics of the support on the quality of the coating.

Metallographic analysis has been done on the surface and transversal section of Ni-P coatings of different steel surfaces.

KEYWORDS: electroless method, Ni-P coatings, the morphology of the support, support steel

1. Introduction

Brenner and Riddel are known as the discoverers of the electroless nickel coating method, process first observed by Wurtz [1, 2] in 1844. Since Brenner and Riddel invention, the study of the electroless nickel coating method has continued to raise interest [3, 4]. The research has led to the development of the procedure first called by its inventors electrodeless, later electroless and now it is formally known as “autocatalytic reduction”. Bretean [5], Paal and Frederici [6], Scholder and Heckel [7], Scholder and Haken [8] are among the researchers who studied this method. Nowadays this method is used to coat with several metals like: Cu, Co, Sn, etc., and several alloys like: Ni-P, Ni-B, Ni-P-Sn, etc., and several composite and nano-composite materials.

Nickel coating is the most common application of electroless coating. Through this method it is possible to achieve nickel coatings with different phosphorus concentrations. The Ni-P coatings done in acid baths can be classified based on the phosphorus content in several classes:

- with low phosphorus content, 2-5 %P;
- with medium phosphorus content, 6-9% P;
- with high phosphorus content, 10-12 %P.

Low phosphorus content will lead to improved hardness, improved resistance to wear, improved high temperature resistance, improved corrosion resistance in alkaline environments. Medium phosphorus content coatings have a nice shiny aspect, good hardness and wear resistance, moderate corrosion resistance. High phosphorus content coatings have very good corrosion resistance and a total lack of magnetic response [9].

Research have shown obvious advantages of the electroless method. These are [10, 11]:

- thin coatings with constant thickness;
- selective coatings on metallic surfaces catalytically active;
- complex shape coatings;
- coatings on non-conductive and semiconductive materials;
- the possibility to control and modify the properties of the coating (for example by incorporating a nonmetal);
- the control of the residual stress.

It is also known from the professional literature that the autocatalytic coating with nickel assures a good reproduction of the surface profile, this method being recommended for highly complex surfaces. Good reproduction of the surface profile can however cause problems related to surface defects [12] or to the surface roughness. In this material we intend to show the way the preparation of the support material and the morphology of the support steel surface influences the Ni-P coating.

2. Experimental research

For the experiment thin low carbon steel (0.25 wt.%) strips 0.4 - 1.0 mm were coated with different degrees of surface finishing done through rolling and skin-passing with high to very low roughness.

The Ni-P coating has been done in a baths with 25 [g/L] nickel sulfate, 23 [g/L] sodium hypophosphite, 9% [g/L] sodium acetate and 1 [g/L] lead acetate. The pH control has been done with NaOH and acetic acid solution. The Ni-P coatings have been obtained at 80-81 ºC, pH = 4.5 and a bath spinning speed of 300 rpm, the immersion duration has been varied between 3 and 30 minutes.

The samples preparation for coating consisted of:

- chemical degreasing using a commercial product at 80-90 , followed by washing in hot water (80-90) and finally in cold water;
- pickling in hydrochloric acid 20% and washing in water at 90 to maintain constant the temperature of the coating bath when immersing the sample.

A large part of the nickel coating defects is caused by inadequate preparation of the surface of the support material. In Figure 1 (b, c and d) several macroscopic aspects of some coating defects are shown noticed on the surface of the steel strips caused by improper or insufficient surface preparation. The evaluation of the influence of the surface roughness on the Ni-P electroless coating has been done metallographically.

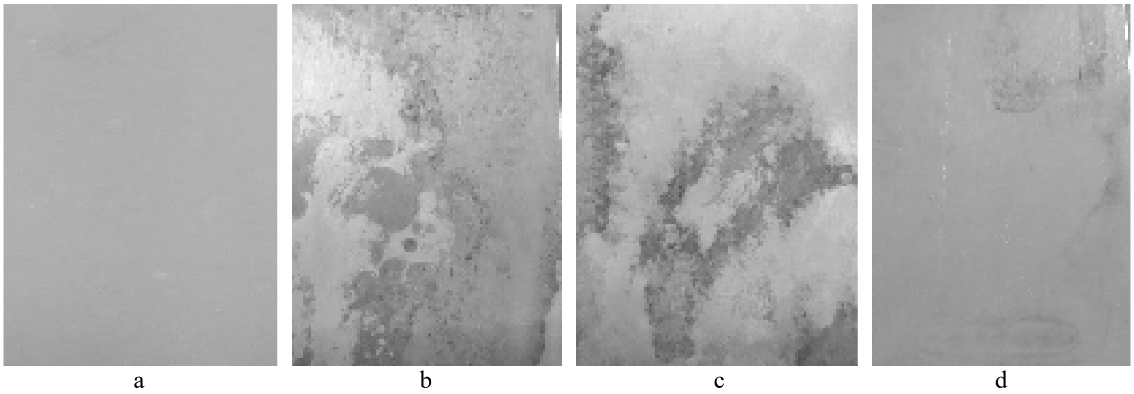


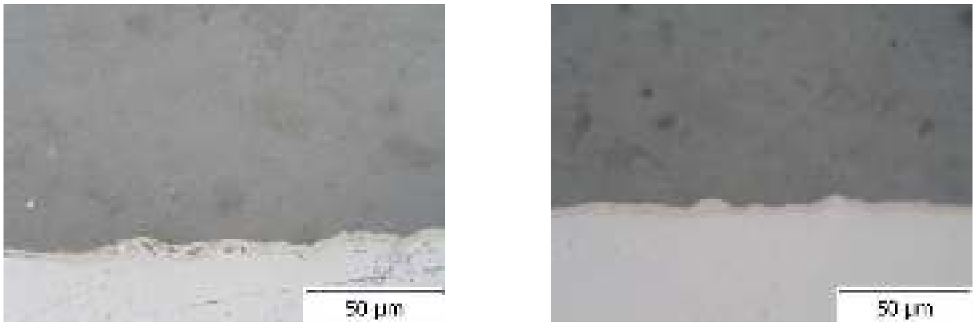
Fig. 1. *(a, b, c, d) Macroscopic aspects of some surface defects*
a - correctly prepared sample; b, c and d - defects caused by improper surface cleaning (1:2)

The coatings done on high roughness strips, obtained through cold rolling with 1.0 mm thickness, show at metallographic analysis (Figure 2) a difference in the aspect of the Ni-P layers depending on their thickness (caused by the different immersion durations).

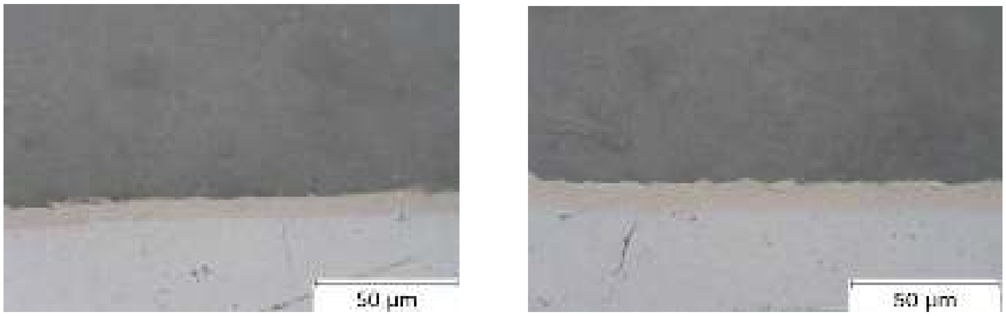
At low immersion durations (180 to 600 seconds) the coated layers are very thin and discontinuous (Figures 2.b and 2.c). Increasing the duration leads to continuous layers (Figure 2.d) which start to reduce the roughness of the support (Figure 2.e). At durations of 1800 seconds, the Ni-P layer covers the asperities of the substrate (Figure 2.f). For the thin layers it can be seen that the surface contour is reproduced with high fidelity while at thicker layers the roughness is suppressed, the layers become uniform.

On very thin steel strips (0.4 mm) with fine surface with low roughness even the thin layers, of 2 µm, are uniform as it can be observed from Fig. 3.a.

a. steel support, X 1000
b. 180 sec, X 1000



c. 600 sec, X 1000 d. 900sec, X 1000

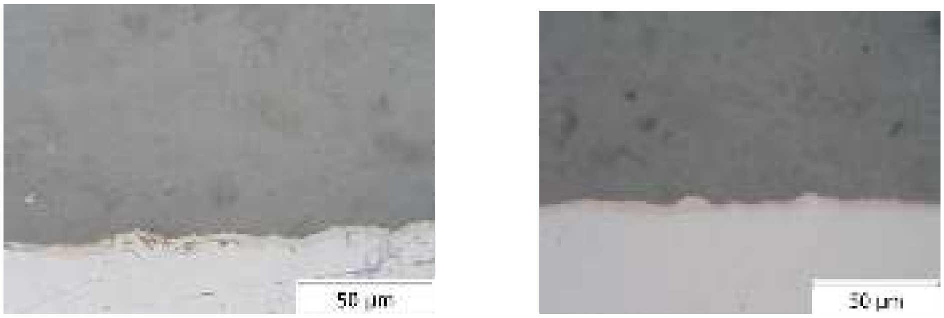


e. 1200sec, X 1000 f. 1800sec, X 1000

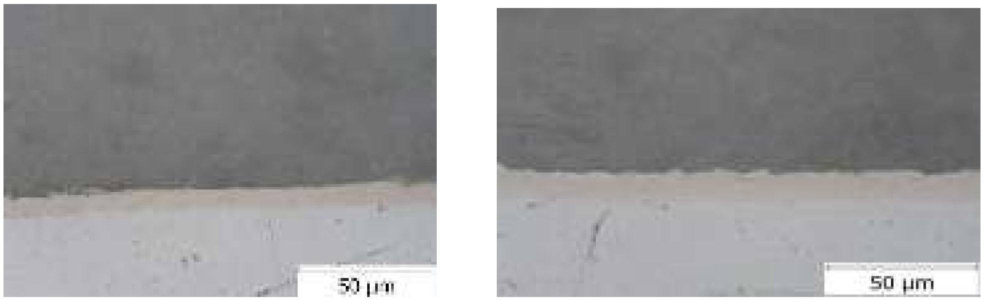
***Fig. 2.** The influence of the roughness of the surface on the coated layer at different immersion durations into the coating bath*

Increasing the immersion duration for these surfaces maintains the uniform aspect of the coating and can only be differentiated by their thickness (Figures 3. b, c and d).

a. steel support, X 1000 b. 180 sec, X 1000



c. 600 sec, X 1000 d. 900sec, X 1000



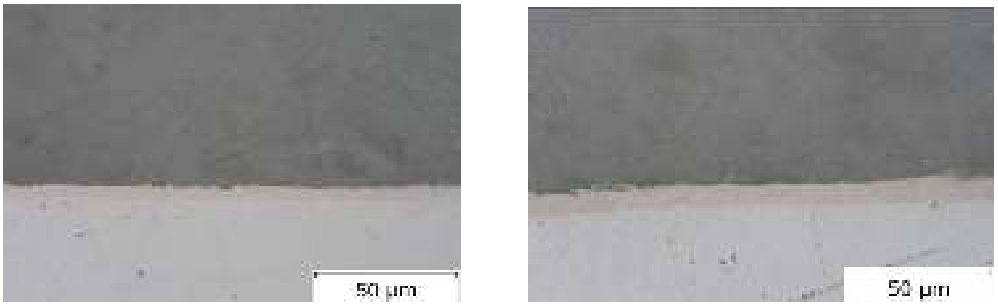
e. 1200sec, X 1000 f. 1800sec, X 1000

Fig. 3. *The influence of a smooth support surface on the coated layer at different immersion durations into the coating bath*

A good adherence of the coated layer is a quality requirement for any type of coating. A week adherence leads to detachment of the coating and this will no longer insures the protection role of the surface or the enhancement of other properties (wear resistance, hardness, etc.).

The adherence can be tested through different standard methods, taking into consideration the novelty of these coating methods there are no specific testing techniques. In this context we chose to evaluate the adherence through microscopic analysis.

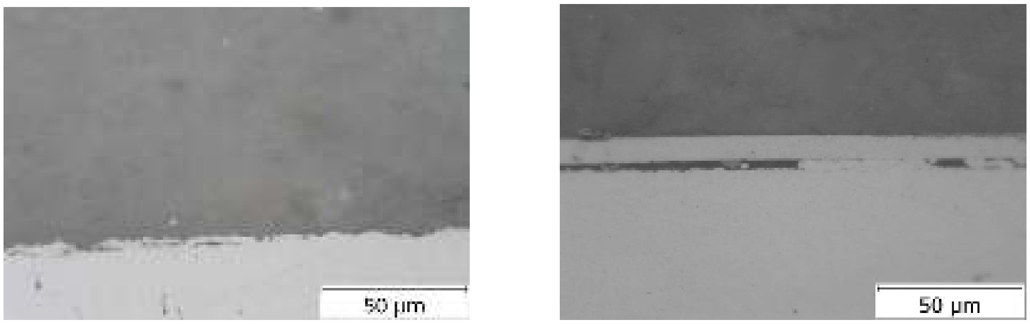
A very good adherence both for thick and thin layers has been noticed by observing the continuous interface between the coating and the support surface, as it can be seen in Figure 4.



a) b)

Fig. 4. *Good adherence of thin (a) and thick (b) layers demonstrated by the continuous interface between the coating and the support surface*

If the support surface has not been adequately prepared, between the support and the coating cavities and discontinuities appear which indicate weak adherence or total lack of adherence (Figure 5).



a) b)

Fig. 5. *Inadequate adherence of the layers, a - weak, b - total lac*

3. Conclusions

On very thin steel strips (0.4 mm) with fine surface and low roughness, even thin Ni-P protective coatings, 2 µm in thickness, are uniform. coatings on rough surfaces reproduce the surface of the support material with high fidelity. Increasing the immersion duration leads to continuous layers which start to reduce the roughness of the support.

A very good adherence of the layers has been noticed proven by the continuous interface between the coating and the support surface. The main factor which can affect the adherence is the surface preparation. If the samples’ surface has not been adequately prepared, between the Ni-P coating and the support cavities and discontinuities can be noticed which imply weak adherence or total lack of adherence.

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RECOVERY OF COPPER FROM WASTE CABLES USED IN ELECTRICAL APPLICATIONS

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ABSTRACT

The recycling of copper cables wastes has as main objective the recovery of copper. The effectiveness of this operation is guaranteed by the following factors: infrastructure able to collect, select and sort these wastes; a market capable to capitalize copper recovered from cables wastes to their true value; processors with equipment and technologies to achieve maximum recycling yields without negative effects on the environment. The most effective chains for wastes recycling may be considered those which use the copper recovered in wires and rods production. So is possible the design and operation of specialized flows for production of secondary copper with high purity. Contrary, a less efficient management of these wastes lead to the poor collection and mixed storage mixed with other types of copper scrap. In this case the copper wire can be recycled effectively to obtain copper-based alloys if special measures are applied at the recycling. The paper analyzes the driving forces that motivate the recycling of copper cables wastes. Also are presented the smelting experiments for obtaining high quality secondary copper and secondary brass from feed containing copper recovered from cables wastes into electric crucible furnace. The results are analyzed in terms of recovery yield and chemical composition.

KEYWORDS: secondary copper, recovery, electrical cables, smelting

1. Introduction

Copper is a highly recyclable material. Its potential recovery tends to infinity. The loss of performance can be insignificant for secondary copper processed with most accuracy from scrap. Recycling copper is very efficient way to reintroduce this valuable metal in the economy [1]. The use of secondary copper reduces the impact of primary copper production from ore on the environment. Recycling for metal recovery is also important from the perspective of saving energy. This energy saving leads to the conservation of valuable reserves of oil, gas or coal and reduces the amount of CO_2 released into the atmosphere [2].

The category of scrap copper recycled includes multiple grades of scrap copper and copper content materials. The sources of secondary copper are old scrap (from end of life products) and new scrap (from fabrication residues).

An important source of recyclable copper is wire scrap. It can be efficient recovered after its useful life in electrical applications and also from products reached at the end of their life of cycle.

In this paper is studied the recycling process of electric cables. The recovery of valuable metal copper as the main objective for recycling cable wastes is analysed. The efficiency of melting process in an electric crucible furnace of copper recovered from this typical waste is presented.

2. Driving forces for properly recycling of copper cables wastes

Copper ranks third in the world consumption of metals, after iron and aluminium. The recycling of copper cable wastes has economic and environmental implications. The recycling of copper cables wastes has as main objective the recovery of copper [3-5]. From the economic point of view, the industry for the preparation and utilisation of copper and copper alloys is dependent upon the recycling. About 40% of the total production of copper and its alloys is obtained from waste, for some products the proportion exceeding 90%. According to the report published by International Copper Study Group (ICSG) 41.5% of the copper used in Europe comes from recycling [1]. In the United States copper alloy scrap provides about half of the copper consumed each year [2].

The copper scrap can be recycled relatively simple, with low energy consumption and minimal losses. Costs are significantly reduced if only recycled copper can be recovered only by melting without further refining operations.

Recycling is an important economic activity, with important benefits for the environment. The valorisation of wastes copper leads to saving important natural resources and significant energy economy. The energy requirement for secondary copper production is between 35-85% of primary production. The benchmark energy requirements for the production of cathode copper metal from primary copper ore concentrate by pyrometallurgy, by hydrometallurgy and for secondary cathode copper metal from scrap and secondary sources are shown in Table 1.

Table 1. *Benchmark energy requirements from copper production* [6]

Copper recovery methods	Energy requirement (MJ/kg Cu)	Carbon footprint (t CO_2/t Cu)
Secondary production from scrap	6.3	0.44
Pyrometallurgy from ore concentrate	16.9	1.25
Hydrometallurgy from oxide ores	25.5	1.57
Source: The environmental benefits of recycling. BIR, Brussels. www.bir.org		

At the same time decreases the amount wastes which otherwise would be discharged into the environment.

Valorisation of copper from wastes is dependent on the efficiency of the collection system, a series of technological and economic factors, products design, social values and legislation.

In terms of legislation in the EU the management of waste scrap metal is currently under the waste regulations. The secondary copper production and the associated treatment of scrap metal on site are subject to the IPPC Directive [6]. In the United States since the passage of the Clean Air Act of 1970, numerous laws and regulations relating to improving human health and the environment have been promulgated by Congress and the federal and state agencies that enforce them [7].

Copper can be considered a resource „removable” because it can be recycled without loss of quality (chemical properties and physical). If the conditions of quality are respected can appreciate that the value of recycled copper can reach of ~ 95% from that of primary copper. Although for the use of secondary copper in electrical applications the most severe conditions are imposed on quality, increasing amounts are used in the manufacture of conductors. For this it is essential that the purity of secondary copper to be very high, thus ensuring the required physical properties: high conductivity; the possibility of obtaining the soft annealed wires; copper rods with plastic processing capacity in wires. In the case of using the feed from copper scrap in such applications, it is necessary the electrolytic refining. For non-electric applications, copper can be used in household installations as roofing sheets, heat exchangers and other products that are not so severe conditions imposed on quality. It can also be used for obtaining bronzes and brass.

Starting from quality conditions imposed at copper used to make conductors results that the most important source of high quality copper scrap are the copper cables wastes.

Choice of options for copper recovery from copper cables wastes should be based on: efficient use of energy and material resources; minimizing impacts from emissions and waste; comparative analysis of the economic aspects and ecological.

3. Experimental and discussion

Similar to the other metals, the recycling of copper scrap has three major steps: scrap collecting, dismantling and sorting. For recycling methods of copper wire the basic objective is the separate of metal from the rubber/plastic casing and extract the copper. The recycling stage is followed by secondary copper recovery to manufacture of new copper products.

The recovery of copper from scrap is possible following a technological flow sheet divided into 4 separate steps: scrap pre-treatment, smelting, alloying, and casting. Pre-treatment includes the cleaning and consolidation of scrap in preparation for smelting. Smelting consists of heating and treating the scrap for separation and purification of specific metals. Alloying involves the addition of one or more other metals to copper to obtain desirable qualities characteristic of the combination of metals [8].

The waste electrical cables with different shapes and diameters are used in laboratory experiments. These were in the form of uncoated wire and rod covered with varied insulations (Figure 1).

To melting the copper wire scrap was used an electric tilting crucible furnace (figure 2).


a.

b.

Fig. 1. *Original cables wastes subjected to experiments for copper recovery: a. cables with insulations; b. uncoated copper wires*

Fig. 2. *Electric crucible furnace for copper wire scrap melting*

Fig. 3. *Pouring of copper and copper alloy melted in graphite crucible*

There were two steps of experiments in which the components of feed were different: firstly, the copper wires scrap was melted to obtain copper with high purity; secondly the feed was composed from copper wires scrap and alloy scrap (brass) for obtaining a casting Cu-Zn alloy.

For each experiment the recovery yield was calculated with formula $\eta = \frac{m_i - m_f}{m_i} x100$ [%], when m_i is mass of scrap introduced as feed in crucible of furnace and m_f is the mass of copper or Cu-Zn alloy obtained after smelting.

In the first case the copper wires scrap with constant composition has been used in the feed of furnace. So was easy to obtain secondary copper with good quality. Only was necessary to apply the physical separation method for insulations removing. Also for reducing at melting the interaction of copper with oxygen from atmosphere the cleaned copper wires must be chopped and compressed in briquettes. The use of solid non-metallic flux is recommended for protecting the surface of melt [9]. The charcoal covers were used to add heat to the surface and to prevent the excessive oxidation losses by providing a reducing atmosphere. Also, to produce a refining action a metallic flux is introduced to the melt [9]. In laboratory experiments for deoxidizing was used the phosphor-copper alloy (15% P). The capacity of furnace crucible and the physical condition of de scrap allowed using a charge of 440g. At the end of the first set of experiments from uncoated copper wire was produced premium quality copper. The values of recovery yield were between 94.55 and 98.22%.

In second step the copper cable wastes have been utilized to obtain brass. Brass is usually made from a basic melt of scrap of similar composition adjusted by the addition of virgin copper or zinc [6, 9]. In our experiments brass scrap and copper wire scrap was together melted for obtaining the Cu-Zn alloy.

The chemical composition of brass scrap that was mixed with copper cables wastes is show in table 2.

Table. 2. *Chemical composition of Cu-Zn alloy scrap, (wt.%)*

Si	Al	Zn	Ni	Fe	Cu
0.8	3.51	34.90	0.11	0.18	60.41

Characteristic for melting of feed composed by mixture of untreated copper cables wastes is the burning of insulations from copper wire. Melting without cleaning operations result in higher pollutant emissions consisting of metal oxides and volatile compounds [10]. When brasses scrap is present in the charge, zinc is evaporated and fumed from the furnace. Other elements such as aluminium and silicon are oxidized and they pass into the slag. To minimize the oxidation losses of elements have been required a good control of bath temperature. Also for smelting process was necessary to use a larger amount of fluxes for protecting the surface of melt and for deoxidizing.

The chemical composition of copper alloy obtained is given in Table 3.

Table. 3. *Chemical composition of copper alloy obtained by melting copper wire and Cu-Zn alloy scrap, (wt.%)*

Si	Al	Zn	Ni	Fe	Cu
0.69	0.68	12.77	0.13	0.24	ball.

4. Conclusions

The valorisation of copper cables wastes is justified on the one hand by of profitability copper recovery as valuable metal and on the other hand is determined by conditionings imposed by legislation for environmental protection.

When the copper cables wastes are separately collected and cared stored the removing of insulations by stripping is easy to make. When copper cables wastes are mixed with other copper scrap the treatment operations for cleaning the scrap is clunky or is expensive through environmental measures that must be implemented. Burning of insulation from copper cables wastes generates large amounts of pollutant emissions as particulate matter and partially combusted organic compounds.

A large share of secondary copper or copper alloys is produced in crucible furnaces. In experiments an electric crucible furnace was used for melting clean the copper cables wastes and brass scrap. Non-metallic flux has been efficient used for a protective covering, and alloy flux has been added as a refining agent. By this mean were obtained high recovery yield and high quality for secondary copper or Cu-Zn alloy.

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EVALUATED WORK SYSTEM AND ENVIRONMENTAL RISK FOR A WORKER IN DRILLING FOR METHANE GAS

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ABSTRACT

Improving the safety and health at work is important not only in terms of human view, in order to reduce possibilities of accident to workers, but also as a way to ensure the success and durability work for a worker in drilling for methane gas.

Although considerable effort is undertaken, the number of working accidents and occupational diseases remains high. The cost that these involve for the society, businesses and individuals is high.

Accidents at work can have a major financial impact. Some costs are evident, for example loss of production and revenue, or the number of working days lost by taking medical leave. This loss can be expressed easily in financial terms.

KEYWORDS: worker in drilling for methane gas, safety work

1. Introduction

Enterprises should be aware of not only aspects of the costs involved in accidents at work, but also those relating to benefits on request may bring them a suitable management of safety and health at work.

Studies have made it clear that it was management efficiency of their safety and with employment is closely related to profitability and excellence in business. There is a direct relationship between a good working environment and a good performance of the undertaking. However, a large part of the consequences of occupational accidents on economic grounds are not visible immediately, or cannot be easily quantified.

The worker that drilling for methane gas need a lot of equipment like: drilling equipment, pipes, transport systems sealing systems, dig through drilling and efficiently quality control.

The daily work task for a worker is to drive drill equipment in mining area, to introduce pipes and seal-rings between them, to do not have leakage, to avoid open flames, to watch permanently pressure in the gases.

2. Identified risk factors

The risk factors for a worker in gas drilling are of such a nature as mechanical, physical, heating, electrical, biological like:

2.1. Mechanic risk factors

F1 - Cut, puncture contact with dangerous surfaces.

F2 - Adjusting of equipment parts that must be changed.

2.2. Heat risk factors

F3 - Flames, fire hazard.

F4 - High temperature materials because of frictions between diverse parts.

2.3. Electric risk factors

F5 - Electrocution through indirect touch or high voltage.

F6 - The occurrence of induced voltage.

2.4. Physical factors

F7 - High air temperature in warm weather.

F8 - Low air temperature in cold weather.

F9 - Air currents - especially when is storm.

F10 - Natural disasters: lightning, hail, blizzards, collapsing trees.

2.5. Biological factors

F11 - Airborne microorganisms from mining area.

F12 - Dangerous Animals and insects (rats, dogs, wasps).

2.6. Physical overload

F13 - Dynamic Effort (for introduction of new pipes).

F14 - Quick decisions in a short time, repetitive tasks in a short-cycle, stress caused by the high responsibility given and the intense work places.

2.7. Omissions

F15 - Failure to use protective means.

These risk factors and their magnitude we see in the Figure 1.

From the analysis of the evaluation form is found that 46.15% of identified risk factors can have irreversible consequences on the performer (death or disability).

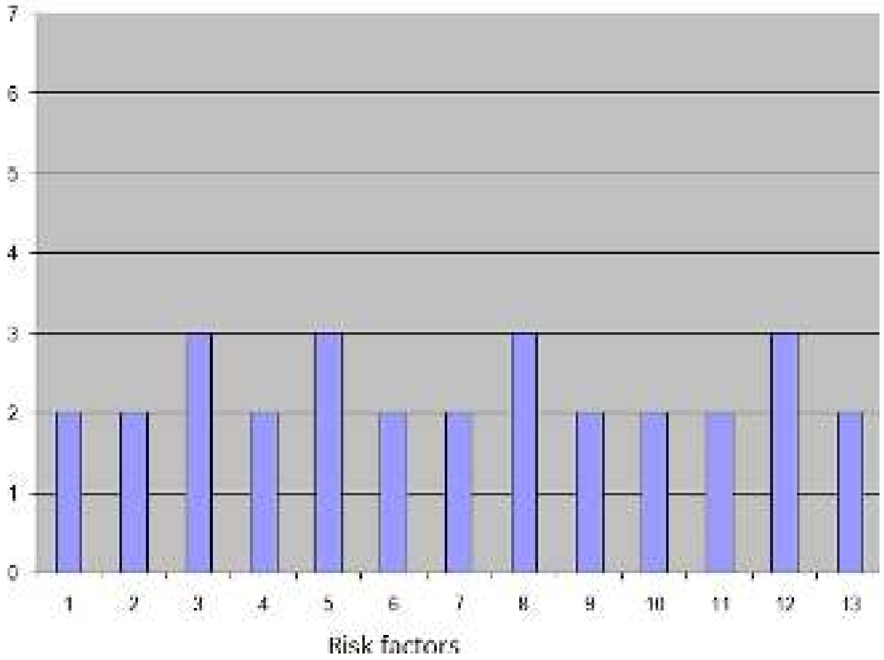

Fig. 1. *The magnitude of risk factors*

3. Calculus of global risk level at the workplace

For calculate the global risk coefficient (N_{rx}) we use the next formulas:

$$N_{rx} = \frac{\sum_{i=1}^{n} r_i \times R_i}{\sum_{i=1}^{n} r_i} = \frac{4(3 \times 3) + 9(2 \times 2)}{4 \times 3 + 9 \times 2} = \frac{72}{30} = 2.25$$

4. The results interpretation of workplace global risk coefficient

Assessment under beautician work led to a risk level equal to 2.25, a value that it falls into the category of jobs with acceptable risk level, the result is supported by the evaluation form which is observed as the total of 13 factors risk identified in Figure 1, only 4 factors indicate a partial risk of magnitude 3, representing 30.77%. The rest factors falling into the category of very low risk (magnitude 2).

Our research shows that the risk factors are in the range acceptable.

Regarding the distribution of risk factors on the sources generating the situation is as follows:

53.85% - own the means of production;
7.69% - the working environment factors;
23.08% - factors specific performer;
15.38% - factors work task.

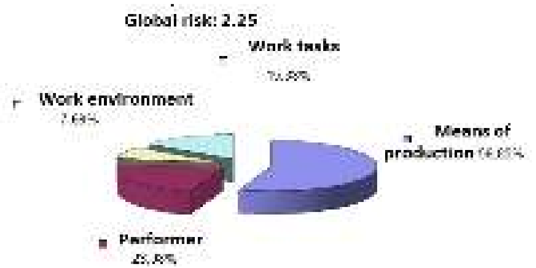

Fig. 2. *Elements of the work place named "worker in drilling for methane gas"*

In the next figure we see the percentage between work task, work environment, means of production and performer. The means of production occupied the first place (56.85%) and work environment (7.69%) is on the last place.

5. Evaluation of environment impact

Assessment of environmental impact shall be carried out using the matrix method (for index of quality) and V. Rojanschi method (calculation of global pollution index).

An assessment of the impact on the environment shall be based on:

- indices of quality on environmental factors (water, air, soil-sub soil, noise, human settlement, biodiversity, landscape) (I_C)
- index of global pollution (I_{PG} quality of an environment factors is falling within the allowed limits of STAS or reglementations Normative.

It is estimated effects „project” on the environment based on „factor size” which are to be analyzed taking into account the level of quality indicators that characterize its effects.

The formulas of environmental quality index is (I_c):

$$I_c = L_{project}/L_{reglementation} = E^{-1}$$

where:

$L_{project}$ – project actions;

$L_{reglementation}$ – reglementations of Normative actions;

E – environmental effects.

Interplay between actions project ($L_{project}$) and environmental effects (E) can be highlight in the tanle no.1. Its size it is estimated by a common system to the whole assembly (with +, - or zero), as follows:

- + positive influence
- 0 influence zero –
- negative influence

Assessment of quality index values

This assessment is based on:

- Quality index values (I_c) for each environmental factors;
- Worthiness note that corresponding of I_C values like in the Table 1.

Table 1.

Worthiness note	I_C value	Environmental effects
10	$I_c = 0$	Environmental is not affected by the developed activity.
9	$I_c = 0.0 \div 0.25$	Environmental is affected in admissible limits. Level 1. Positive effects.
8	$I_c = 0.25 \div 0.50$	Environmental is affected in admissible limits. Level 2. Positive effects.
7	$I_c = 0.50 \div 1.00$	Environmental is affected in admissible limits. Level 3. Positive effects.
6	$I_c = - 1.0$	Environmental is affected over admissible limits. Level 1. Negative effects
5	$I_c = - 1.0 \div - 0.5$	Environmental is affected over admissible limits. Level 2. Negative effects
4	$I_c = - 0.5 \div - 0{:}25$	Environmental is affected over admissible limits. Level 3. Negative effects
3	$I_c = -0.25 \div - 0.025$	- The medium is degraded, level 1. - The effects are harmful to long periods of exposure.
2	$I_c = - 0.025 \div - 0.0025$	The medium is degraded, level 2. - The effects are harmful to medium periods of exposure.
1	I_c = sub – 0.0025	The medium is degraded, level 3. - The effects are harmful to short periods of exposure

In the Figure 3 is shown how are polluted the environment factor by the worker in drilling for methane gas. It was accorded a worthiness notes for water (7), for air (9), for soil (10) and for noise (9).

There has been created a new quadrangle which overlays ideal rectangle (Fig. 3) Ideal rectangle has worthiness notes to water, air, soil and noises polluted 10.

As an indicator of environment is more polluted has a less worthiness note.

Global index of pollution is defined as the ratio between the surface of ideal rectangle and real quadrangle surface.

Depending on global index value of pollution, shall be determined how polluted is the work environment being studied.

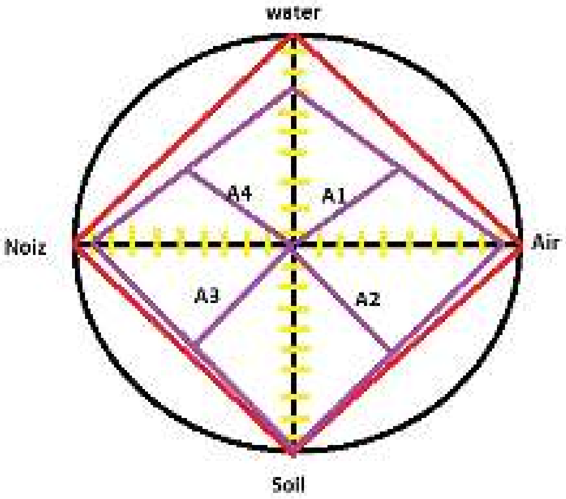

Fig. 3. *Quadrangle real which overlays ideal rectangle*

The worthiness notes according for Water = 7, for Air = 9, for Soil = 10 and for Noise = 9. In the next are calculate the value of surface A1, A2, A3, A4: A1 = 31.5 cm^2; A2 = 45 cm^2; A3 = 45 cm^2; A4 = 31.5 cm^2.

The surface of real quadrangle Sreal: S real = 153 cm^2.

The surface of ideal rectangle S ideal: S ideal = 10 x 10/2 = 50x4 = 200 cm^2.

Global polluted index is: Ic = Si/Sr = 1.3.

This value show that environment pollution is in admissible limits. Between water soil, air and noise we see that underground water is under suspicion to be polluted.

I_c = 1	- Environmental is not affected by human activity.
I_c = 1...2	- Environmental is affected in admissible limits.
I_c = 2...3	- Environmental is affected and existing a discomfort for life forms.
I_c = 3...4	- Environmental is affected and existing troubles for life forms.
I_c = 4...6	- Environmental is severe affected and existing multiple dangers for life forms.
I_c > 6	- The medium is degraded, unsuitable for life forms.

6. Conclusions and safety measures proposed

Risk factors	**Risk level**	**Measures proposed** **Nominating measure**	**Who is responsible**	**Remedy term**
1	**2**	**3**	**4**	**5**
F1 – Striking of The movement of pedestrian or and/or the movement of traffic accidents with motor vehicles for equipment transport.	3	Organizational measures: - Training the staff on the traffic on access roads inside the company - Will be made the training of the workers with regulations on the Road Code.	Leader workplace	Immediately and permanently

Flames - fire hazard.	3	Organizational measures: - Regularly check fire means within the company (fire extinguishers, hydrants) - OG.712/2005.	Leader workplace	Immediately and permanently
Electrocution touch voltages step indirect or appearance.	3	Organizational measures: - Permanently Check the electrical wiring and announcement in case of damage. - Making PRAM measurements in power switchboards.	Leader workplace	Immediately and permanently
Natural disasters - lightning strikes, hail, blizzards, collapsing trees.	3	Organizational measures: - Training of staff in accordance with Law 481/2004.	Leader workplace	Immediately and permanently
Mishandling of car during field displacement.	3	Organizational measures: - Staff training on traffic on the access roads within the company (access will be made on access roads marked on the right).	Leader workplace	Immediately and permanently
Failure of individual protective equipment (personal protective equipment, electrical means).	3	Technical measures: - Providing workers with personal protective equipment which is in accordance with art. 10, 16 (3) of GD 104/2006.	Leader workplace	Immediately and permanently

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DIMENSIONAL CHANGES IN SOME IRON-BASED POWDER METALLURGY ALLOYS

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ABSTRACT

The purpose of this paper is to present the dimensional changes in some iron-based (P/M) alloys. The specimens produced from atomized iron powder and alloyed powder with different sizes (< 45, 45-63, 63-100, 100-150, >150 µm) were subjected to compaction at 400 and 600 MPa. After compaction, the specimens were sintered at 1150 ℃ for 1 h. The density of green and sintered iron and iron-based alloys, the mechanical properties (hardness) and dimensional changes were evaluated.

KEYWORDS: powder metallurgy, sintering, density, dimensional changes

1. Introduction

Powder metallurgy (P/M) has rapidly increased in past years as a suitable alternative technology because of its low cost and the near-net-shape components.

The applications of powder metallurgy are continuously extended in different areas and included: components that are difficult to obtain by any other technology, such as molybdenum, tungsten or tungsten carbide, filters, porous bearings, magnetic components, connecting rods, camshafts, automotive clutch plates, and planetary gear carriers.

The main advantages of PM technology are: low unit cost, easy formability, near net shape components, components with high tolerance, use of 100% of raw materials [1-4].

Dimensional precision is an important factor in manufacturing of PM parts, especially for components with near-net-shape. The dimensional change of sintered compacts is influenced by many factors which affect the hardness of the produced part. The most important parameters are: chemical composition, particle size, powder density, sintering time and temperature, cooling rate and microstructure [5, 6]. The parameters like sintering temperature and time have effect in the specimen’s shrinkage. Other parameters like cooling rate have an important effect on the microstructural changes. Concerning the chemical composition of the powders, especially the alloying elements, has an important role in improving the mechanical properties of the sintered parts. In principle, the alloying elements have the same effect on the sintered steels as on conventional steels. In general, all alloying elements improve the hardenability. Molybdenum (Mo), one of the main pre-alloyed and highly effective elements used in powder metallurgy industry due to its relative small impact on compressibility has a good response in hardenability [7, 8]. Copper (Cu) is one of the widely used elements in P/M increasing the strength and hardness. The usual amounts of copper used as alloying element are 1.5-3 wt.%, after this percentage can causes swelling to iron. Copper is an advantageous alloying elements due to its melting point at 1083 °C, thus at the typical temperatures used to sinter ferrous alloys, Cu forms a liquid phase which promotes sintering and enhances the strength of the sintered part. During the melting of Cu particles, they are leaving from their original positions and are creating very small pores in their initial place, so called secondary porosity because the pores are much smaller than the larger primary pores [9-12].

Nickel (Ni), another usual alloying element, increases the sintered density. Nickel, during sintering is in solid state and is forming in the sintered microstructure the Ni-rich areas which have a positive influence on hardness and strength by providing a local ductility [13].

In this paper, the dimensional changes in some iron-based P/M alloys were studied.

2. Experimental details

2.1. Raw materials

The analyzed specimens in this research are represented by two types of metal powders obtained by water amortization with different particle sizes (< 45, 45-63, 63-100, 100-150, >150 µm):

- atomized pure iron (Fe) powder and
- atomized iron-based alloyed powder with Cu, Ni and Mo. This powder has wide application in automobile PM parts such as gears.

The chemical composition of the powders is shown in Table 1. Tables 2 presents the basic characteristics of elemental iron and alloyed powder, such as flow rate, apparent density and in Table 3 and 4 are represented the sieve size analysis of analyzed powders.

2.2. Mixing

The required mass of powders was weighed and blended with 1% zinc stearate (ZnSt) in a mixer device for 10 minutes at a constant speed (30 rpm) in order to achieve the homogenization of the powder mix. Zinc stearate is a lubricant and was added to ensure that the mixture was completely homogenous and to prior to add the extraction after compaction.

Table 1. *The chemical composition of analyzed powders*

Powder type	**C**	**Cu**	**Ni**	**Mo**
P_1	<0.01	0.10	0.05	0.05
P_2	<0.01	1.50	1.75	0.50

Table 2. *The physical properties of analyzed powders*

Powder type	**Apparent density, g/cm^3**	**Flow rate, s/50 g**
P_1	3.14	24.11
P_2	3.10	25.07

2.3. Compaction

The blended powders mass was then uniaxial compacted in a mold into cylindrical discs of 8 mm diameter and 6 mm height using a universal mechanical testing machine. The applied pressure was 400 and 600 MPa at the ambient temperature. The compaction process involves the flow of the powder particles past one another, the interaction between particles and with the mold walls. Also, a deformation of the particles it occurs. An increased in the applied pressure will conduct at an increased in density of the powder compact while the porosity decreased.

2.4. Sintering

After compacting, the green samples were subjected to sintering. Sintering of all samples was carried out in a laboratory furnace. The sintering cycle applied to the samples involves heating at temperature approximately of 1,150 °C and then holding at that temperature for 1h and then air-cooled to room temperature.

2.5. Density measurement

The density of all samples was measured. The green and sintered densities of the samples were determined from weight and dimensional measurements, which were accurate to within ± 0.01 g and ± 0.001 mm, respectively (Table 5).

Table 3. *Sieve analysis of iron powder*

Sieve size (µ)	+150	+100	+63	+45	-45
Weight retained (%)	2.78	17.73	27.01	20.19	32.22
Cumulative weight retained (%)	2.78	20.51	47.52	67.71	99.93

Table 4. *Sieve analysis of iron-based alloyed powder*

Sieve size (µ)	+150	+100	+63	+45	-45
Weight retained (%)	3.72	20.88	30.54	20.80	23.82
Cumulative weight retained (%)	3.72	24.60	55.14	75.94	99.76

2.6. Mechanical tests

The hardness measurements were made using a Vickers hardness tester with a load of 5 kg and a time of 30 s. All the mechanical tests were done at ambient temperature and the test results were the average of three experiments.

3. Results and discussion

3.1. Microstructure analysis

The sintered specimens were analyzed according to their microstructure using an optical microscope (Olympus BX 50M).

In Fig. 1 are represented the optical microscope images for the sintered samples. From the image analysis of the specimen’s porosity, it can conclude that the sample P_1 has a higher porosity compared with sample P_2, in accordance with a lower density and mechanical properties values. Porosity in sintered P/M alloys had a negative effect because it may conduct to areas of stress concentration or stress raisers, affecting the mechanical properties by cracks propagation. Even after sintering, it is very difficult to obtain a component without a certain percent of porosity, excepting the situation when the porosity is deliberately desired into the component to satisfy the imposed requirements, such as filters and bearings. The alloying elements are dissolved in the base metal, leading to the formation of various microstructures and increasing the materials resistance. The influence of alloying elements on the sintered steels is having the same effects as on the conventional steels but not all elements commonly alloyed with conventional steels can be used on the sintered steels.

3.2. Green and sintered density

The conventional compaction and the sintering were used to obtain the sintered densities between 6.81 g/cm^3 and 7.10 g/cm^3. As expected, green and sintered density increase with an increase in the compaction pressure (Table 5).

3.3. Mechanical results

In Table 6 is presented the Vickers hardness of the green and sintered specimens. The highest value of micro hardness was achieved for specimen P_2 due to the presence of alloying element Ni which will form the so call Ni-rich areas, who had a positive influence on hardness and strength of the sintered materials. Also, by pressing with a compaction pressure of 600 MPa is ensuring an optimal compaction of the samples. In Table 7 is presented the dimensional change of samples in the green state, pressed at 400 and 600 MPa and in the sintered state.

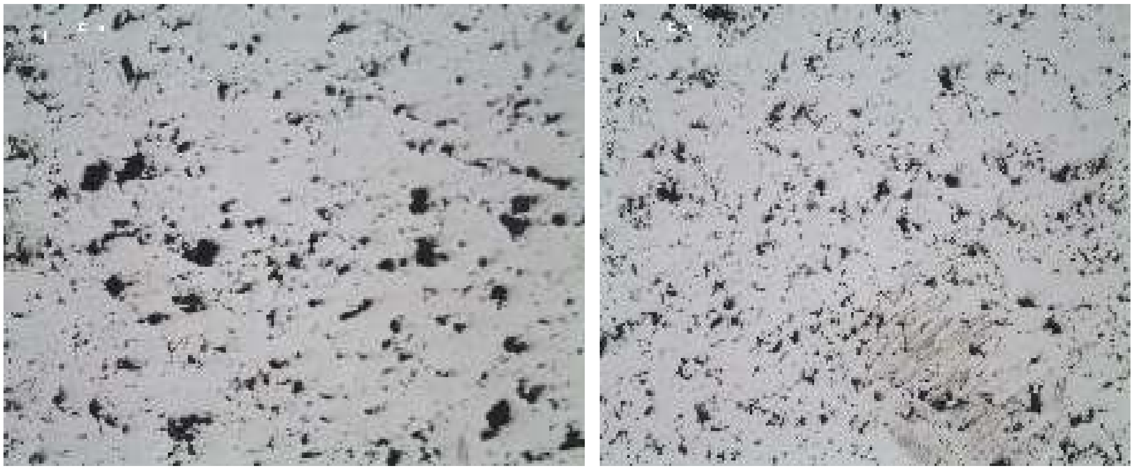

Fig. 1. *Optical image analysis for the sintered specimens: a) P_1, b) P_2*

Table 5. *Green and sintered density of analyzed alloys*

Powder type	**Pressure applied, MPa**	**Green density, (g/cm^3) – ρg**	**Sintered density, (g/cm^3) - ρs**
P_1	400 MPa	6.71	6.81
	600 MPa	6.93	6.98
P_2	400 MPa	6.78	6.83
	600 MPa	6.97	7.10

Table 6. *Vickers hardness in green and sintered state of analyzed alloys*

Powder type	Pressure applied, MPa	Vickers hardness, HV_5, (MPa) in green state	Vickers hardness, HV_5, (MPa) in sintered state
P_1	400 MPa	790	910
	600 MPa	870	1050
P_2	400 MPa	830	990
	600 MPa	960	1130

Table 7. *Dimensional changes of analyzed samples*

Powder type	Pressure applied, MPa	Dimensional change (%)
P_1	400 MPa	-0.06
	600 MPa	-0.03
P_2	400 MPa	-0.05
	600 MPa	-0.02

The dimensions of the pressed and sintered samples were measured with a micrometer with digital display. The dimensional change (ΔLDG) in % was determined using the following relation:

$$\Delta LDG = [(LS - LP) / LP] \times 100\%$$

where: LS is the length of sintered sample and LP is the length of pressed sample.

The dimensional change analysis that is presented in Table 7 indicated that the sample P_2 have a smaller dimensional change from die size as compared to the pure iron base P_1. The powder type and pressure applied are the major contributors to the final dimensional change values that were observed in this case. In powder metallurgy, it is important that the dimensional changes of the structural parts during sintering are as small as possible.

4. Conclusions

- The addition of alloying elements to the base materials is observed to improve the density.

- By pressing with a compaction pressure of 600 MPa is ensure an optimal compaction of the samples.

- The alloyed sample with Cu, Ni and Mo, P_2 can improve mechanical properties of sintered P/M alloys.

- The alloy compositions of the sintered steels for structural parts have to be carefully chosen not only with respect to the desire strength, but also with respect to the dimensional stability during sintering.

- The alloying elements distribution in the green compact can play a large role on the dimensional stability of a sintered part. As can be seen, the sample P_2 (pressed at 600 MPa) is having a dimensional stability higher compared with sample P_1.

- The shrinkage after sintering is the highest for the unalloyed sample P_1 -0.006% at 400 MPa and -0.03% at 600 MPa.

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ELECTRICAL PROPERTIES OF ULTRA-SONICATED EPOXY RESIN

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ABSTRACT

As ultra-sonication is a mostly used method to disperse the particles into the polymer matrix, the aim of this study is to point out the effect of epoxy's exposure to ultra-sounds over the electrical properties, especially the electrical conductivity. As the epoxy resins are insulators, the method is based on the determination of electrical conductivity via the measurement of electrical insulation resistance. The polymer solution was exposed for 45 minutes to ultra-sounds produced by one, two, three and four generators at different values of ultra-sounds frequency.

KEYWORDS: *electrical properties, ultra-sonicated, epoxy resin*

1. Introduction

The rapid spread of polymeric materials to new markets requires not only innovation in technological processes but equally the up-grade of the existing polymer processing technologies that allow them to expand into new areas of social life [1]. In recent years, considerable efforts have been made to improve the quality and reliability of thermosetting polymer materials [2, 3]. Thermosetting materials obtaining methods have the following advantages: easy processing in the initial stage because the resin systems are in the liquid phase, fibers or particles thermoset moistening is very easy, so that gaps, porosity and dry areas in composites are avoided, and affordable price of the required processing systems [4]. Epoxy resins have high mechanical strength, resistance to solvents, to heat, to moisture and show a very high internal cohesive force [5-7]. Strengthened, they have a good dimensional stability and outstanding electrical characteristics [8, 9]. The determination of electrical resistivity is recommended as a control measure for temperature processing and to establish the compliance with the specifications of particular strength where needed. Improved mechanical properties of conducting polymers increase their potential commercial applications. One of the immediate applications of conducting polymers is electrostatic and electromagnetic protection [10]. Although the search for new polymers with improved properties continues to attract great research interest, the economic drivers in the polymer industry demand the continual improvement of existing materials. This has led to a large effort aimed at modifying the existing polymers [11]. The number of papers describing electrical and other properties of nano-composites is increasing rapidly. The main results are summarized in recently published reviews [12-14]. The propagation of ultra-sonic waves in polymers depends on their viscoelastic behavior and density, resulting in polymers significantly affected by phase transitions occurring when changing temperature and pressure or during chemical reactions [15, 16]. Ultra-sound treatment is a way to improve the polymer material qualities, in particular during components matching phase of a composite and the formation of its structure, i.e. while the mixture is passing to its gel phase [17]. Under the action of ultra-sound, there is a change in homogenization, viscosity, relaxation time, and strengthening [18]. During formation, thermo-setting polymer resins undergo changes in their physical characteristics from a viscous liquid to a gel and finally to a hardened solid [19]. Therefore, in the present paper we intend to analyse the electrical conductivity of polymer materials exposed to ultra-sounds during the gelling phase.

2. Experimental

Four air-generators were used as ultra-sounds sources. The use of this type of generators had required a difficult work to identify their possible frequencies by maneuvering parts 4, 5, 7 and 8 in Fig. 1, together with fine variations of air pressure. In the end, four frequency values were found common for all the generators, namely 24 kHz, 26 kHz, 30k Hz and 42 kHz.

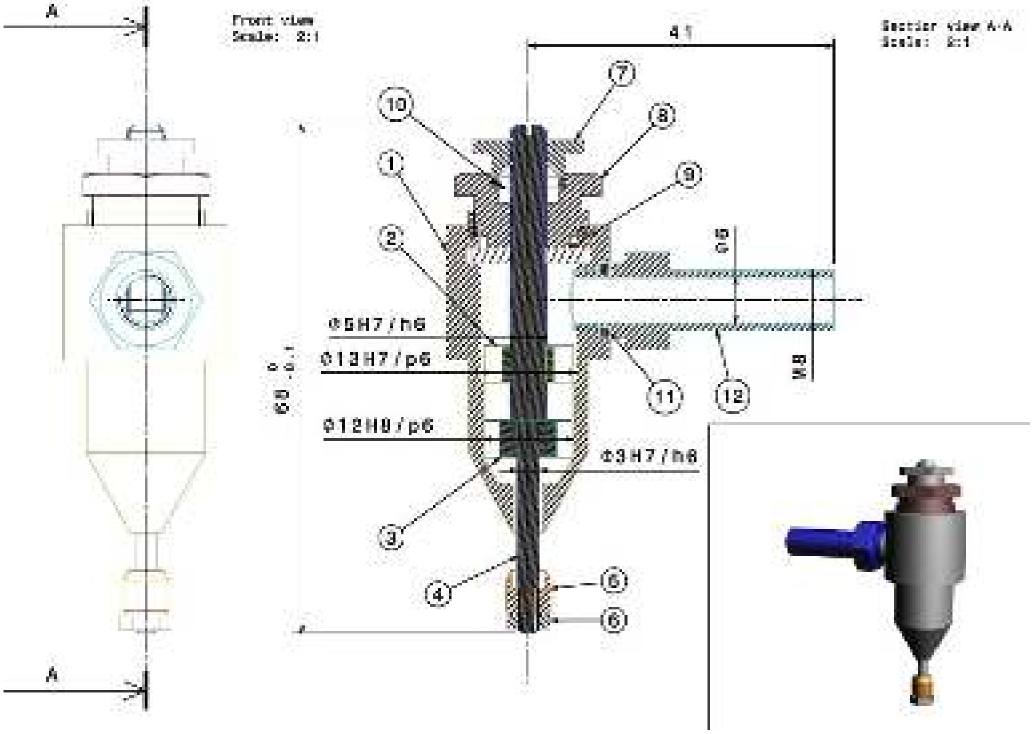

Fig. 1. *Ultra-sound source: 1 - nozzle; 2, 3 - cross sleeves; 4 - rod; 5 - resonator; 6 - screw nut; 7 - locknut; 8 - cover; 9, 11 - washers; 10 - gasket; 12 - nozzle*

It was possible to set the configuration (Fig. 2) which allows for samples exposure to the ultra-sounds generated by one, two, three or four air generators. In fact, using the same frequency for all the generators, the energy of the exposure is a multiple of the energy of one generator. The pre-polymer solution was poured into cylindrical molds and exposed for 45 minutes to ultra-sounds.

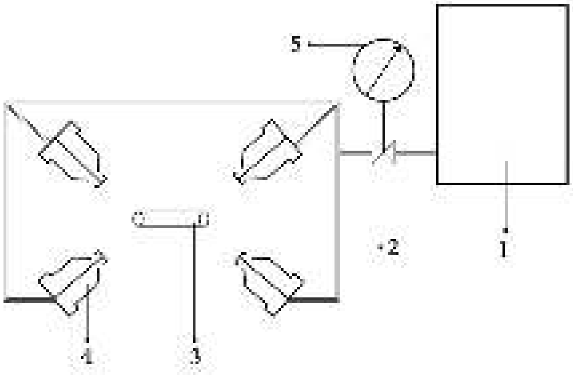

Fig. 2. *Configuration of ultra-sound sources: 1 - air compressor; 2 - supply hose; 3 - test sample; 4 - ultra-sound source; 5 - pressure gauge*

Noise measurements were performed according to Standard noise emission SR EN ISO 3744/2009. The molds were placed at 1 m distance from each ultra-sound air generator (Fig. 3) [20]. Generators calibration was performed using an UltraMic 200k model microphone with Sea Wave software (Fig. 4).

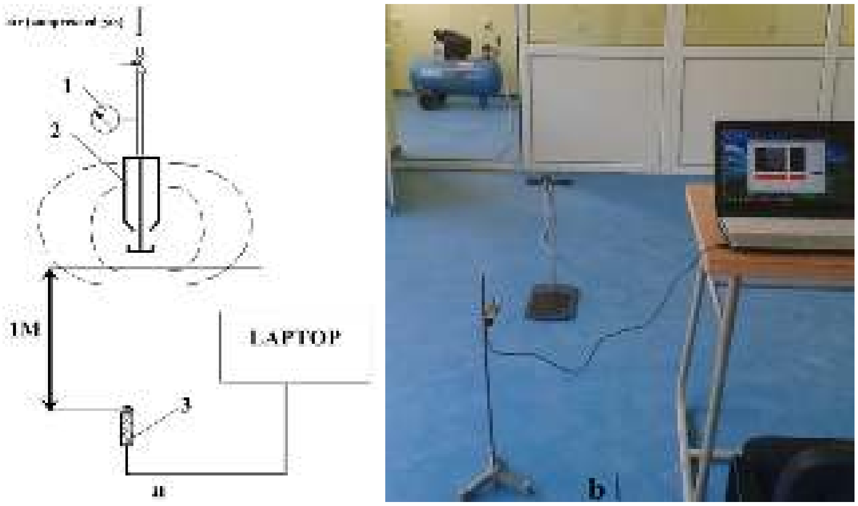

Fig. 3. *Acoustic measurements: a - scheme; b - picture; 1 - pressure gauge; 2 - experimental ultra-sound generator; 3 - microphone*

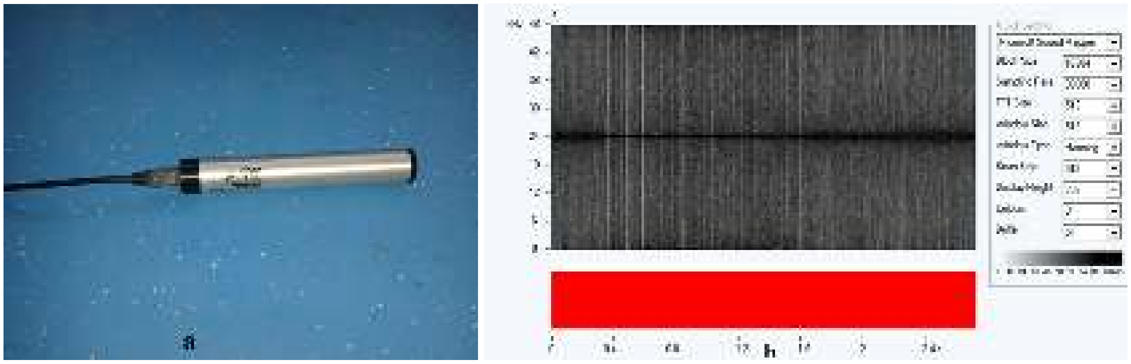

Fig. 4. *a - Ultramic 200 k microphone; b - ultra-sound generator calibration at 24 kHz*

Due to the energy carried by ultra-sounds, it is possible to appear some changes in the polymer structure. These changes could be observable in the final properties of the polymer. This study is oriented towards the identification of some changes in polymer electric conductivity. As any polymer is an electric insulator, the electric conductivity was evaluated via electric insulation resistance measurement using an insulation analyzer (Terra Ohm Meter) (Fig. 5).

Fig. 5. *Electric insulation resistance measurements*

3. Results

The electrical conductivity of the analyzed samples was evaluated on the basis of the well-known formula:

$$\sigma=\rho^{-1} \qquad (1)$$

where: ρ is the electrical resistivity derived from the measured electric insulation resistance R as:

$$\rho=RSl^{-1} \qquad (2)$$

where: S is a cross-section area of the sample and l is its length.

The electrical conductivity of epoxy resin is plotted as a function of the generators number (as the frequency is the same for all the generators which means that the electrical conductivity is plotted as a function of ultra-sonic energy) and at different values of frequency (cs-control sample, 1G - ultra-sonicated epoxy resin with one generator, 2G - ultra-sonicated epoxy resin with two generators, 3G - ultra-sonicated epoxy resin with three generators and 4G - ultra-sonicated epoxy resin with four generators).

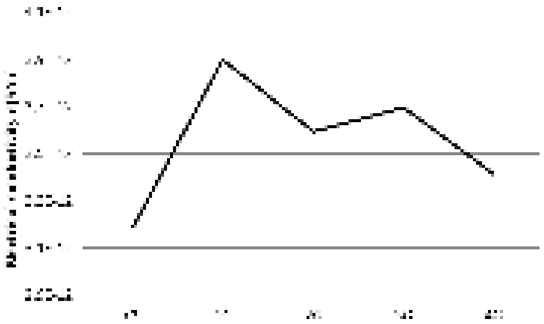

Fig. 6. *Electrical conductivity of 24 kHz ultra-sonicated epoxy*

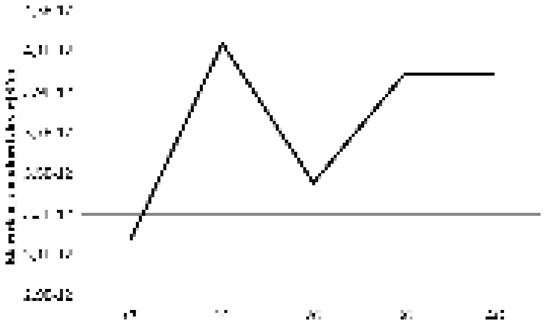

Fig. 7. *Electrical conductivity of 26 kHz ultra-sonicated epoxy*

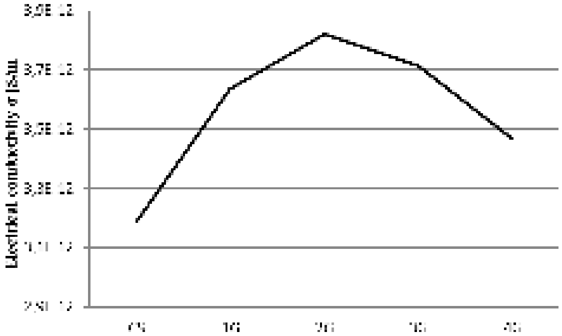

Fig. *8. Electrical conductivity of 30 kHz ultra-sonicated epoxy*

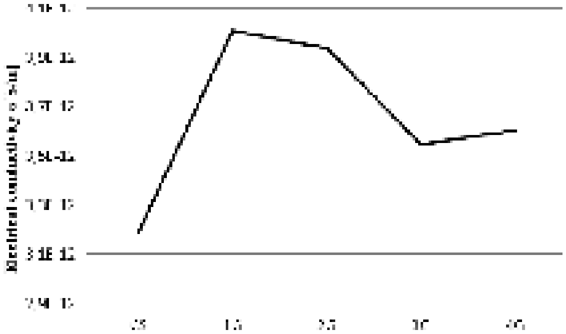

Fig. 9. *Electrical conductivity of 42 kHz ultra-sonicated epoxy*

The results, as it can easily be noticed in the four graphs above (Fig. 6-9), show that practically the electrical conductivity of the polymer depends neither on the frequency of ultra-sounds nor on the total energy of ultra-sounds. That means that from the electrical point of view, the ultra-sound exposure of epoxy resin does not change its electrical properties. From the electrical properties point of view, the use of ultra-sounds to disperse fillers into the polymer matrix is an advantageous method since the ultra-sound exposure does not change the basic electric properties of the polymer. Small variations of the evaluated parameter could be associated with gaseous intrusions or small changes of polymer induced by the environmental conditions (temperature, humidity, atmospheric pressure) that are, at this moment, uncontrollable.

4. Conclusions

The paper presents the electrical properties of ultra-sonicated EPIPHEN epoxy resin cylindrical samples treated by different numbers of ultra-sonic air-jet generators for 45 minutes at different frequencies. Based on the above presented results, the use of air-jet generators treatment during epoxy resin curing was implemented. This investigation was focused on the possibility to eliminate the physical contact between the ultra-sonic device and the resin. This study has to be followed by others regarding the mechanical properties (tensile, compression, bending), tribological properties and thermal properties to completely characterize the effect of ultra-sound exposure of epoxy resin as intended matrix for some reinforced or filled composites. Since the modifications induced by ultra-sonic exposure on the electrical properties of polymer are negligible, the presented method can be used in a double way – first to disperse the particles of a potential filler or additive, and second to avoid the gaseous intrusions determined by the chemical reactions developed during the forming process.

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DETAILED MICROCONTROLLER ARCHITECTURE BASED ON A HARDWARE SCHEDULER ENGINE AND INDEPENDENT PIPELINE REGISTERS

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ABSTRACT

In the world of real time operating systems, task switching, communication between threads and synchronization are implemented in software. Some of the mechanisms used may introduce big latencies in task recurrence, task jitter. This kind of problem, which is sporadic, may lead to system failure for safety-critical areas. This issue may occur in the real time systems that have really fast response time as requirements. For this particular example, the tasks are succeeding very fast, resulting in a lot of overhead because of the time spent in task switch. Our research has led us to the conclusion that a microcontroller architecture, based on a static hardware Scheduler and independent Pipeline Registers, will be capable of executing multiple tasks with approximately no delay between every task switch (5 machine cycles). The nMPRA (n Multi-Purpose Register Architecture) architecture, which consists of 2 sets of registers: local such as coprocessor 2 and global such as a peripheral on the slow bus, offers support for preemptive real time operating systems. Both architectures, nMPRA and nHSE (n Hardware Scheduler Engine), complement each other and take the real time operating system programming to a whole new level.

KEYWORDS: real time system, static hardware scheduler, microcontroller, pipeline processor

1. Introduction

The real time properties of an embedded system lie in the implementation of the operating system, task synchronization and communication between threads. The RTOS (real time operating systems), used, in a real fast system must be small, in order to have less overhead caused by the operating system for a fast code execution.

Currently, the real time operating system from the safety critical areas will not use a small operating system because a powerful microcontroller can be chosen in order to supplement the power needed for event serving. In article [1] a CPU architecture is described (central processing unit), that provides hardware support for real time systems and very good related work. This new architecture is composed of 2 different architectures:

nMPRA (multiple pipeline registers architecture for n tasks): provides support for hardware synchronization between tasks and peripherals.

nHSE (hardware scheduler engine for n tasks): provides support for static and dynamic hardware scheduler for n tasks.

The combined architectures contribute to monitor resources and very fast events and they interrupt handling.

In [2] a MIPS processor was implemented in order to be modified for the new architecture. The MIPS architecture did not provide support for Coprocessor0 (COP0) or all the instructions that a MIPS32 processor can support. The only supported programming language was an assembler language, which was parsed by a tool chain written by us.

In article [1] the author points out that the Scheduler and the nHSE architecture can be included into a coprocessor or into the on-die implementation. The scheduler was implemented in the second manner while the nHSE architecture was implemented as a Coprocessor 2 (COP2) for the MIPS32 architecture.

First, in order to implement the Coprocessor 2, it was necessary to meet the following requirements:

A very tested functional MIPS32 architecture.

Support for coprocessor.

Support for a gcc (a compiler system produced by the GNU Project supporting various programming languages) tool chain and a high level programming language, which was considered as the most important part.

The project [3] which was thoroughly tested was used as a baseline for the new architecture. The project was created by Grant Ayers and funded by the eXtensible Utah Multicore (XUM) project at the University of Utah between 2010-2012.

The details of the classical 5-stage pipeline MIPS32 Release 1 architecture are:

- Harvard architecture with separate instruction and data ports.
- Full forwarding and hazard detection
- MIPS32 instruction set, including:
    - Atomic load linked.
    - Atomic store conditional.
    - Unaligned load and store.
- Complete Coprocessor 0 that allows ISA-compliant interrupts exceptions and user / kernel modes.

2. Detailed architecture of the microcontroller

The main differences between the processor located at [2] and the one implemented in [3] are the presence of the COP 0, support for all MIPS32 instructions, including the assembler instructions for COP 0 and the use of only one clock signal for the entire processor.

The MIPS32 Release 1 architecture is a project developed in Verilog using the Ide Xilinx ISE Design Suite 14.2, which was modified in order to support the architecture described in [1]. A multiplexer / demultimexer was introduced to manage the resources RAM, ROM, ALU, Control and Coprocessor 0, which are shared between the 5 threads and the static dual priority Scheduler (Figure 1).

The MIPS32 architecture is special because it left room for further implementations of new hardware modules. The MIPS32 architecture defines 4 coprocessors [4]:

- Coprocessor 0 (COP0): already implemented and supporting exceptions and virtual memory system.
- Coprocessor 1 (COP1): reserved for floating point custom implementation.
- Coprocessor 2 (COP2): available for user defined implementation.
- Coprocessor 3 (COP3): reserved for floating point module in Release 1 implementation of the MIPS64 architecture and for all Release 2 implementations of the architecture.

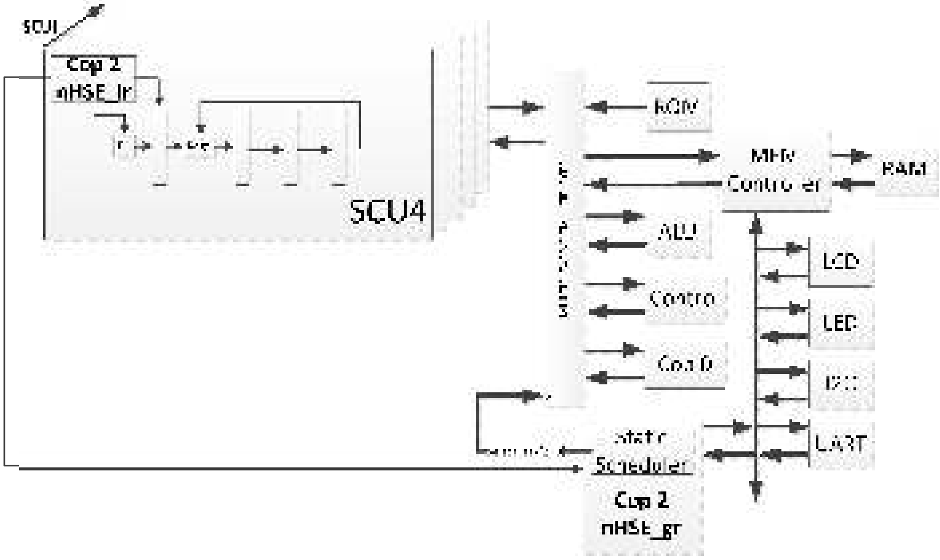

Fig. 1. *Controller with nHSE and nMPRA architecture*

The gcc tool chain also provides support for low level and high level programing language for the processor and assures us that we can use the 4 coprocessor in our implementation. The nHSE and nMPRA architecture will be tested using gcc, which is a widely used tool chain. In this way, we can create a benchmark between the old processor and the new architecture, using the same tool chain and programing language.

The nMPRA architecture was implemented to be COP2 compliant in order to benefit from the gcc tool chain. In Figure 1 is described, at a macro level, the cohesion between the nMPRA and nHSE architecture. SCPU0 (semi processor 0) will configure the Scheduler, which is a part of nHSE, to supervise the correct execution of the hardware tasks, because it has the highest priority and is the only hardware task that is allowed to configure the hardware Scheduler.

The nMPRA architecture contains:

- independent pipeline registers.
- a multiplexer and demultiplexer that share the resources that were not multiplicity.
- Local registers used for inter task synchronization.

The custom microcontroller can run 5 different tasks (5 ***SCPUi***) independently without the need of the nMPRA architecture. In this manner, the system can be considered as equivalent to the microcontroller with RTOS.

The nHSE architecture complements the nMPRA by adding an important part of an RTOS event, interrupts handling and inter task communication.

As described in article [1], the internal organization of the logic is divided into 2 different segments:

- The local segment consists of local registers that are visible only in the ***SCPUi*** (***nHSE_lr*** in Figure 1) and are located after the pipeline register ***Instruction Decode*** (***ID***). In this particular case, the access time to registers from ***nHSE_lr*** will be of 2 machine cycles because one machine cycle will be used to extract the instruction from ROM memory and the other machine cycle to decode and execute the COP2 instruction.
- The global segment consists of global registers from the external bus (***nHSE_gr*** in Figure 1). In this case, the access time will be of 5 machine cycles for our architecture because 4 steps will be driven through the pipeline registers until ***Memory Access*** (M) is reached and 1 machine cycle will be used to write or read from the ***nHSE_gr*** peripheral.

As a consequence of this architecture, the access to the local segment is faster than the access to the global segment.

The interaction between the static Scheduler and the nHSE resources is very tight, therefore the algorithm of the Scheduler, detailed in [2], was improved in order to support the most powerful instruction, wait (detailed in [1]). The nHSE_lr (Figure 2 a)) module will use TaskNeedReset wire to signal the Scheduler that the SCPUi must be reset because the watch-dog (register mrDEVi detailed in Chapter IV) has expired, and TaskDeepSleep to signal the Scheduler that the task is not blocked, but is only waiting for an external or internal event, in order not to be promoted to long task queue (***LTQ*** in [2]).

In order to have a better understanding of the Scheduler function, detailed in [2] and modified in Figure 3, we are going to repeat some relevant information.

Each ***SCPUi*** can belong to one of the following classes:

The class of active tasks (**AQ**) that are scheduled based on priorities in the Running State (***RS***) of the Scheduler.

The class of interrupted tasks (***ITQ***) that are scheduled based in priorities, only in the ***Idle State*** (***IS***) of the Scheduler.

The class of long execution tasks (***LTQ***) that are scheduled based on a ***Round Robin*** (***RR***) algorithm only in the Idle State (***IS***) of the Scheduler.

The wait instruction allows for the synchronization with several events that are located into the ***crTRi*** (Table 1) and ***crEVi*** registers, without the need of the software intervention.

Table 1. *crTRi (Control registers)*

31..	7	6	5	4	3	2	1	0
0..0	lr_run_sCPUi	lr_enSyni	lr_enMutexi	lr_enInti	lr_enD2i	lr_enD1i	lr_enWDi	lr_enTi
	rw	rw	rw	rw	rw	rw	rw	rw

lr_enTi: validates/inhibit generated timer event.

lr_enWDi: validates / inhibits the events generated by the watchdog.

lr_enD1i: validates / inhibits the events generated by deadline 1.

lr_enD2i: validates / inhibits the events generated by deadline 2.

lr_enInti: validates / inhibits the events generated by interrupts.

lr_enMutexi: validates / inhibits the events generated by mutex.

lr_enSyni: validates / inhibits the events generated by timing events.

lr_run_sCPUi: validates / inhibits the program execution SCPU.

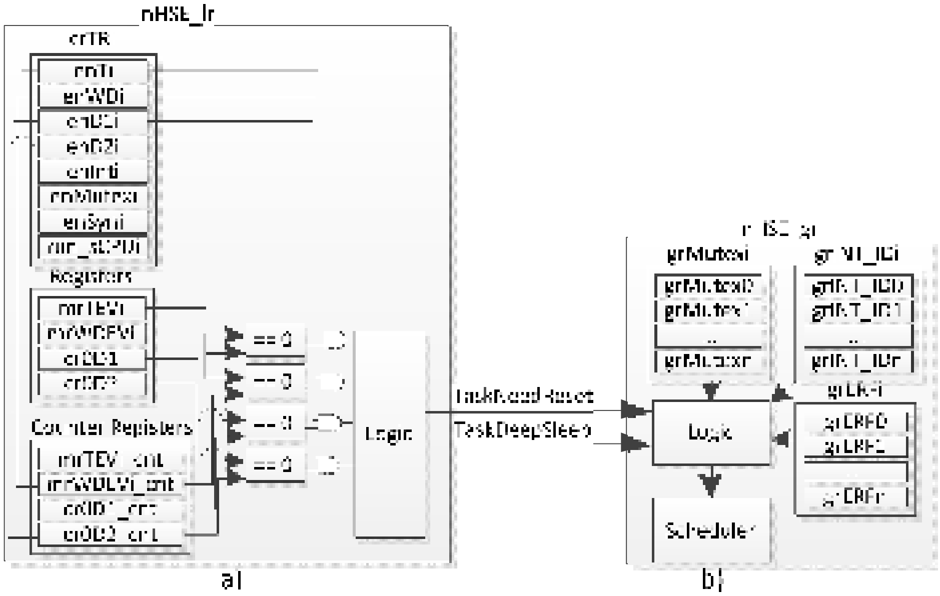

Fig. 2. *nHSE_lr and nHSE_gr internal architecture*

Table 2. *crEVi (Events Register)*

31..	7	6	5	4	3	2	1	0
..	lr_run_sCPUi	SynEvi	MutexEvi	IntEvi	D2EVi	D1EVi	WDEvi	TEvi
	rw	rw	rw	rw	rw	rw	rw	rw

TEvi: the event generated by the timer has occurred.

lr_enWDi: the event generated by the watchdog has occurred.

lr_enD1i: the event generated by deadline 1 has occurred.

lr_enD2i: the event generated by deadline 2 has occurred.

lr_enInti: the event generated by interrupts has occurred.

lr_enMutexi: the event generated by the mutex has occurred.

lr_enSyni: the event generated by timing events has occurred.

lr_run_sCPUi: the copy of the bit lr_run_sCPUi from register crTRi.

The current assembler instruction, which is decoded by ***nHSE_lr*** (Figure 2, a)) module, is relatively unique because one atomic instruction will stop the current ***SCPUi*** from execution, equivalent with entering a low power mode, and will alert the Scheduler not to promote the current task to ***LTQ*** through the wire ***TaskDeepSleep*** (Figure 2).

The static scheduler algorithm, reused from [2], modified and detailed in Figure 3, supports a self-sustaining state (***Waiting State*** from Figure 3) that my last as long as the task needs it. This feature assures us that the current modified architecture is not rigid; on the contrary, we could say that it can support a large number of tasks.

The Scheduler is incorporated into ***nHSE_gr*** (Figure 1) because it must have access to the global events, presented in ***Chapter IV***, in order to stop the active ***SCPUi*** and schedule the right ***SCPUi*** to serve the event or just schedule the correct ***SCPUi***.

The number of registers that are used for inter task synchronization, such as mutex or message passing, must be standardized in order to serve all the tasks. For example, the minimum number of registers for mutexes (***grMutexi***) and message passing (***grERFi***) must be equal to the number of tasks to the power of two. This allows us to use a mutex or send a message from one to all the others.

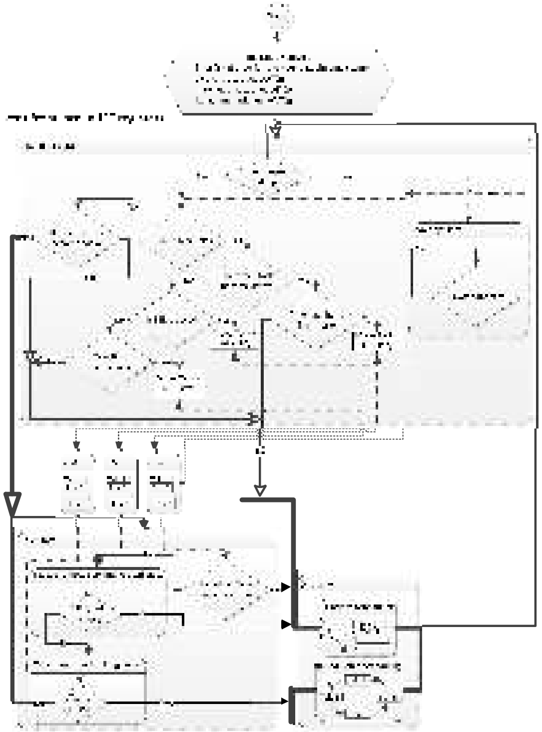

Fig. 3. *The flowchart of the scheduler with a dual priority algorithm*

3. Local events

The internal architecture of ***nHSE_lr*** block is described in Figure 2, a).

*Watch dog timer(***mrWDEVi***)*

If the watchdog is configured and the timer expires, the ***SCPUi*** will be reset. The timer of the watch dog will be reset each time the task has ended successfully.

*Alarms(**mrD1EVi**, **mrD2EVi**)*

Each ***SCPUi*** has 2 alarms that will signal, via ***lr_enD1i*** and ***lr_enD2i***, that the configured time has passed. The alarms may be used to find out how long the execution of the code lasted.

Every time the task begins again to execute the code, the local registers (Figure 2, a)) ***mrTEVi_cnt***, ***mrWDEVi_cnt***, ***cr0D1_cnt*** and ***cr0D2_cnt*** will be initialized with the values defined in the related registers. After the initialization process, the registers will start decrementing the defined values. When the counters are equal to 0, a flag will be set and further action will be taken, depending on each register functionality.

*Timers(**mrTEVi**)*

Can be used as a general purpose timer to wait for an event or just for synchronization with other tasks or events. The wait instruction can be used to generate a fixed recurrence of a task when an input is scanned periodically. Thus, the processor will consume less power.

4. Global events

The internal architecture of ***nHSE_gr*** block is described in Figure 2 b).

Mutexes

Table 3. *grMutexi (task ID for interrupt attached register)*

31	30..4	4	3	2	1	0
TaskID31	..	TaskID4	TaskID3	TaskID2	TaskID1	TaskID0
Mutexi	0	rw	rw	rw	rw	rw

TaskID = the task id that acquired the mutex.

Mutexi = 1 means the mutex is taken.

Acquire / release a mutex (Table 3): The operation is atomic (write to ***nHSE_gr***) because the data path of the processor is not used. Instead it is used a specific asm instruction from COP2 (Figure 2 a)) (***mtc2***). The ***nHSE_lr*** is going to decode the instruction and write the relevant data to ***nHSE_gr*** to acquire the mutex. A mutex can be released only by the task that acquired it.

Read the status of a mutex: the operation uses the data path of the SCPUi, because the MIPS architecture can perform only operations based on registers. Therefore, a value from RAM or peripheral must be stored in one of the 32 registers from SCPUi in order to be used in computation.

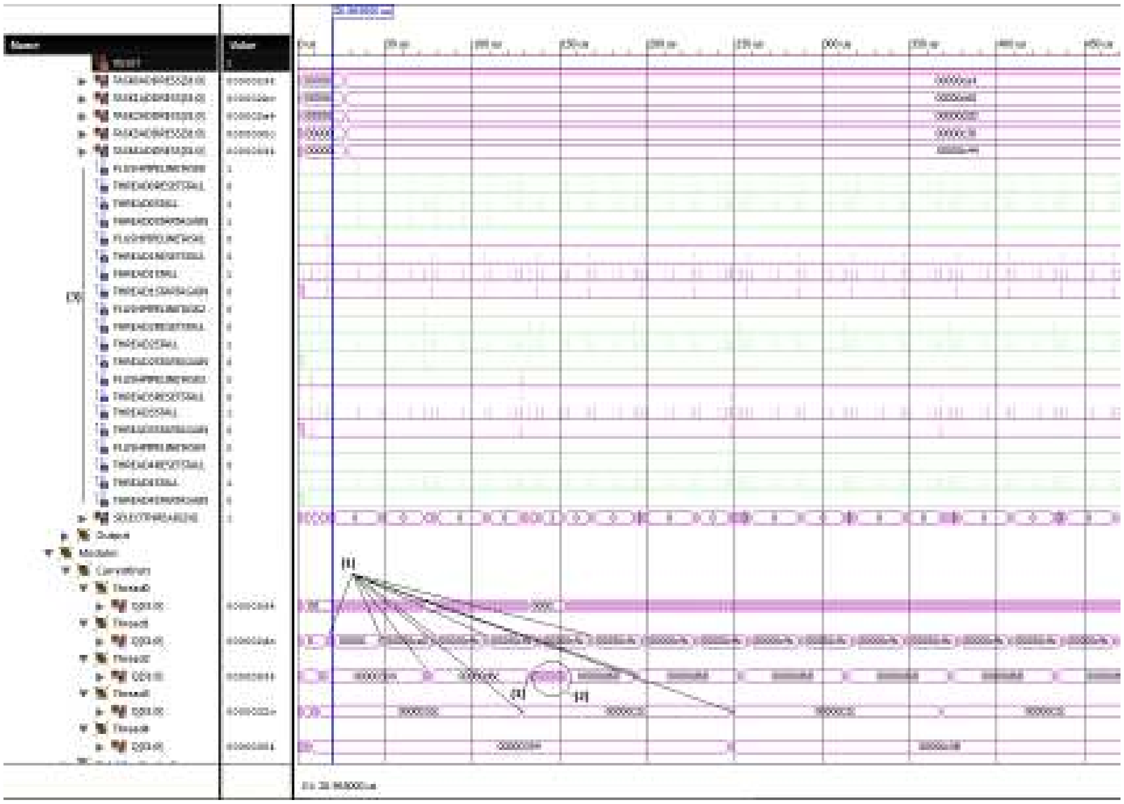

Fig. 4. *Scheduling waveform of 5 hardware tasks (capture from Xilinx ISE Simulator)*

Interrupts

Table 4. *grINT_Idi (Task ID for interrupt attach register)*

31	30..3	2	1	0
	…	TaskId 2	TaskId 1	TaskId0
0	0	rw	rw	rw

The register grINT_IDi selects the id of the SCPUi that will execute the interrupt routine code (Table 4). A simple explanation is that a SCPU4 can only execute the interrupt service routine of a GPIO (General Purpose Input Output) pin while the SCPU3 can only execute the interrupt service routine of an exception from the communication peripheral.

Events

Table 5. *grERFi (event global register)*

	Nj-1	..	0	nj-1	..	0	k-1	..	0
0/1	sIDnj-1	..	sID0	dIDnj-1	..	dID0	mess	..	mess0
event	Source task id			Destination source task			message		
rw	rw		rw	rw		rw	rw		rw

Event = 1 means the event is active.

The task will be awakened by the Scheduler when the ***wait*** assembler instruction is used and a message is received. The data path of the SCPUi will be used to access data from the register (Table 5).

5. Simulation

In Figure 4 (1) is visible the PC (Program Counter) of each ***SCPUi*** (***Modules\CurentInstr***), that whenever is changing the current of the ***PC***, the line will be changed. By looking at this pattern we can see that the hardware tasks are scheduled periodically at the same recurrence.

In Figure 4 (2) the ***SCPU2*** hardware task (***Modules\CurentInstr\Thread2\Q***) does not respect the pattern because it is executing more codes, for the first time, than the other ***SCPUi***. The code for all ***SCPUi*** was written in this manner on purpose, to show that the hardware tasks are scheduled regularly at the same recurrence. In Figure 4 (3), the hardware signals are used to perform a task switch of a ***SCPUi***. A more detailed explanation about the task switch is provided in [2]. The current response time of the nHSE architecture, using Verilog simulation is the following:

nHSE_lr – 1 machine cycle for internal handling, where the atomic instructions are executed in 2 machine cycles. One machine cycle to extract the instruction and another machine cycle to execute de instruction.

nHSE_gr – 1 machine cycle for internal handling.

Scheduler – 1 machine cycle to schedule a task (response time) and 5 machine cycles to perform a task switch. The process of a task switch is described in [2].

The above response time is obtained using simulation and can be different from the case where the design is synthetized, because it depends on the developer that is designing the RTL (register-transfer level).

The current proposed solution is completely simulated using ISE Design Suite 14.2 and ISE Simulator, proving that the functionality, proposed in [1], is working and can be implemented in hardware. A problem that must be handled in the future is that different authors have made some significant improvements, such as improved response to interruptions [5, 6] and events [7, 8]. Therefore, the nHSE features must be extended and new registers for configuration must be added.

6. Conclusions

In this paper we presented a possible implementation of the nHSE architecture as a MIPS coprocessor, Coprocessor2 (COP2). We outline, for the first time, the nHSE registers and some of their functionalities for the local registers (coprocessor 2) and global registers (such as the peripheral on the slow bus).

The solution has the great advantage of being able to take advantage of all gcc tool chain support, that can use a high level programming language to generate machine code for the modified MIPS processor architecture, was considered the most important part.

This new architecture has a response time for the nMPRA architecture of 3 machine cycles for the local registers (***nHSE_lr***), 1 machine cycle for global registers (***nHSE_gr***) and 6 machine cycles for the Scheduler in order to respond and make a task switch.

The solution has been implemented using Verilog, as a hardware description language, and ISE Simulator for simulation purpose.

We can say that the overall response time of this architecture is less than the execution of a load instruction.

Acknowledgement

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WATER-IN-DIESEL EMULSIONS AS ALTERNATIVE FUEL FOR DIESEL ENGINES. PART I: WATER-IN-DIESEL EMULSIONS. A LITERATURE REVIEW

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ABSTRACT

Although emulsions have found numerous and various applications in chemical, pharmaceutical and food industries, emulsions of water in diesel fuel are applicable alternative fuels for the existing diesel engines.

Water-in-diesel emulsion fuel can improve the combustion efficiency of a diesel engine and reduce harmful exhaust emission, especially nitrogen oxides and particulate matter.

In general, due to the lower heating values of water-in-diesel emulsion fuels, torque and power produced by diesel engines fueled with emulsified fuels are lower as compared to the neat diesel fuel.

The heterogeneous results regarding the use of water-in-diesel emulsions as fuel for diesel engines suggest that more experimental work for optimizing the emulsion formulation is recommended.

KEYWORDS: water-in-diesel emulsion, diesel engines, combustion, emissions

1. Introduction

The technique concerned with introducing water into the engine combustion chamber was proposed by Prof. B. Hopkinson in 1913, to make better internal cooling of the gas engine and to increase the engine output. Furthermore, the technique was developed to improve the thermal efficiency and reduce exhaust emissions, or used as safety fuel [1].

More and more attention is paid to diesel engines which can be used in transportation, industrial and agricultural applications due to their high efficiency and reliability [2].

The main pollutants produced from the exhaust of diesel engines are nitrogen oxides (NOx), particulate matter, black smoke, carbon monoxide and carbon dioxide. The presence of these pollutants in atmosphere will cause serious damage to the environment such as the greenhouse effect, acid rain, and the destruction of the ozone layer [3].

Water-in-diesel emulsion fuel (W/D) is a promising alternative fuel that could fulfill such requests in that it can improve the combustion efficiency of a diesel engine and reduce harmful exhaust emission, especially nitrogen oxides (NOx) and particulate matter (PM). Up to date, there have been many W/D emulsion fuel studies, especially regarding performance, emissions and micro-explosion phenomena [4].

Four major approaches for introducing water into the combustion zone have been reported in the literature [5]:

(i) Fumigating the water into the engine intake air;
(ii) Direct injection into the engine through separate injectors;
(iii) In-line mixing of water and fuel prior to injection (unstabilized emulsion);
(iv) Mixtures of stabilized emulsions treatable as a single-phase drop-in replacement fuel.

The intake manifold fumigation and direct water injection methods lead to an increase in the formation of hydrocarbon (HC) and emission of carbon monoxide (CO). Furthermore, as the water is introduced into the combustion chamber, it tends to be in direct contact with the fuel feed system and cylinder piston group, thus resulting in oil contamination and increasing wear. In addition, both methods require highly complex engine modification in order to integrate the water addition device into the engine. Thus, they require high additional cost [4].

Of all the methods proposed to introduce water into the combustion chamber, diesel oil emulsions appear to be the most appropriate, because they require no engine retrofitting [6].

The main reason for a stronger interest in incorporating water in diesel rather than in gasoline is that the high combustion temperature and the high pressure that exist in diesel engines are particularly suitable for the concept. This was found experimentally and verified by theory almost 30 years ago. The use of diesel emulsions has been shown to give several interesting effects, such as (i) reduced nitrogen oxides (NOx) emission and also lower soot and particulate contents in the exhaust, and (ii) improved combustion efficiency [7].

There is a special occurrence in W/D ignition called the micro-explosion phenomenon that intrigues researchers worldwide, as it is non-existent in other normal diesel combustion. It is a secondary atomization of the primary spray as a result of the rapid evaporation process of water that is initially contained in the oil drop, making the combustion more efficient [8].

All the reviewed studies on the preparation and use of water-in-diesel emulsions have been focused on different aspects of the effects of this fuel on the engine performance and emissions [9].

This paper presents a literature review of the current status of water-in-diesel emulsions and their influence as alternative fuel for diesel engines.

2. Water-in-diesel emulsion fuel

An emulsion is a blend of two or more liquids which are unblended in nature, one present in continuous phase and others in dispersed phase [10]. Emulsions consist of at least one immiscible liquid intimately dispersed in another under the form of droplets, whose diameters, in general, exceed 0.1 μm [11].

The emulsion is formed with the help of mechanical agitation together with the chemical additives called surfactants to keep the immiscible liquids mixed together, forming one solution. Generally, emulsions are divided into two types: oil-in-water emulsions (O/W) and water-in-oil emulsions (W/O) [4, 12].

2.1. Surfactants used in water-in-diesel emulsions

Surfactants or surface-active agents are amphipathic substances with lyophobic and lyophilic groups, making them capable of adsorbing, at the interfaces between liquids, solids and gases. They are capable of forming self-associated clusters, which normally lead to organized molecular assemblies / aggregates, monolayers, micelles, vesicles, liposomes and membranes. Apart from traditional applications such as detergents, emulsifiers, dispersants, wetting and flotation agents, they have tremendous and not yet fully appreciated potential for engineering functional interfaces and surface coatings [12].

The surfactants possess a polar or hydrophilic head, and a nonpolar or hydrophobic tail. The surfactant is incorporated to weaken the surface tension of the medium in which it dissolves. When it is placed in an oil-water mixture, the polar groups orient towards the water and the nonpolar group orients towards the oil as it lowers the interfacial tension between the oil and water phases. They are classified into cationic, anionic, amphoteric, and nonionic, based on the type of polar group of the surfactant [10, 13]. Figure 1 [14] shows the molecular structure of some surfactants such as Span 80, Tween 80, Span 85 and OP 10.

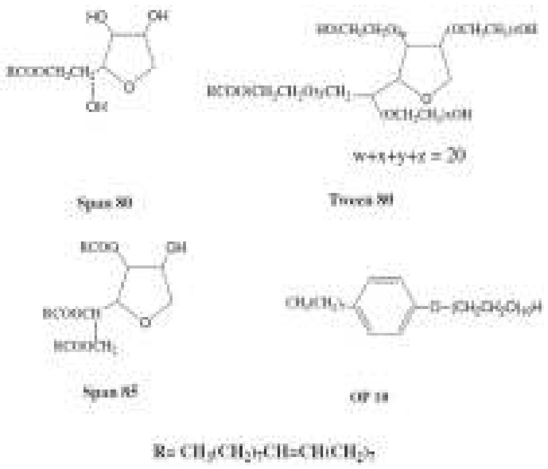


Fig. 1. *Molecular structure of Span 80, Tween 80, Span 85 and OP 10* [14]

A frequently used method for selecting surfactants as emulsifying agents is known as the HLB (hydrophilic–lipophilic balance) method. In this method, a number (0–40) indicative of emulsification behavior and related to the balance between the hydrophilic and hydrophobic portions of the molecule has been assigned to many commercial emulsifying agents [14].

This dimensionless scale ranges from 0–20 for non-ionic surfactants. A low HLB (<9) refers to a lipophilic surfactant (oil soluble) and a high HLB (>11) to a hydrophilic (water soluble) surfactant. Most ionic surfactants have HLB values greater than 20, for example, sodium dodecyl sulfate has an HLB of 40. Some examples of surfactant HLBs are given in Table 1. In general, water-in-oil (W/O) emulsifiers exhibit HLB values in the range 3-8, while oil-in-water (O/W) emulsifiers have HLB values of about

8–18. If the value is not known, then lab emulsification tests are required, using a series of emulsifying agents of known HLB values [15].

Emulsion is formed by mechanical agitation. The mechanical agitation can be generated by ultrasonic vibration machine, magnetic stirrer and centrifugal type mixer [13].

Table 1. *Approximate surfactant HLB values** [15]

Surfactant	HLB
Oleic acid	1
Sorbitan tristearate (SPAN 65)	2
Sorbitan monooleate (SPAN 80)	4
Diethylene glycol monolaureate	6
Sorbitan monolaurate (SPAN 20)	9
Glycerol monostearate	11
Polyoxyethylene (10) cetyl ether (BRIJ 56)	13
Polyoxyethylene sorbitan monooleate (TWEEN 80)	15
Sodium octadecanoate	18
Sodium dodecanoate	21
Sodium octanoate	23
Dioctyl sodium sulfosuccinate	32
Sodium heptadecyl sulfate	38
Sodium dodecyl sulfate	40
Sodium octyl sulfate	42

*SPAN, BRIJ and TWEEN are trademarks of ICI Americas Inc.

The surfactant works as a surface active agent that is a typical chemical additive to attract both immiscible liquids (water and oil) into forming one stable solution. The surfactant functions by reducing the surface tension of the water, by adsorbing at the liquid-gas interface. It also reduces the interfacial tension between oil and water by adsorbing at the liquid-liquid inter phase [4, 16].

The most common surfactants used in the water-in-diesel emulsion are sorbitan monooleate, which is called Span 80 [4, 13], and polyethylene glycol sorbitan monooleate mixture [13], polyoxyethylene nonylphenyl ether [4, 13, 16], called Span 80 and Tween 80 [4], polyethylene lycol sorbitan monooleate (polysorbate 80) and sorbitol sesquioleate (SSO) mixture, sorbitan monolaurate [13], gemini [12], octylphenoxy polyethoxy ethanol, called Triton X-100, dai-ichi kogyo seiyaku (solgen and noigen TDS-30) [4, 16], polysorbate 20 (commercially know as tween 20) [17], sorbitan trioleate (Span 85) andisooctylphenol poly(ethylene glycol) ether (OP 10) [14] and liquid soap or glycerin [4, 13]. The percentage of the surfactant being added in the mixture of the unblended fluids is generally between 0.1 and 2% [4].

2.2. Types of water-diesel emulsions

Emulsions are colloidal dispersions in which a liquid is dispersed in a continuous liquid phase of different composition. The dispersed phase is sometimes referred to as the internal (disperse) phase and the continuous phase as the external phase [15].

A system that consists of water droplets dispersed in an oil phase is called a water-in-oil or W/O emulsion (Figure 2, left [13]), and a system that consists of oil droplets dispersed in an aqueous phase is called an oil-in-water or O/W emulsion (Figure 2, right [13]) [4, 15].

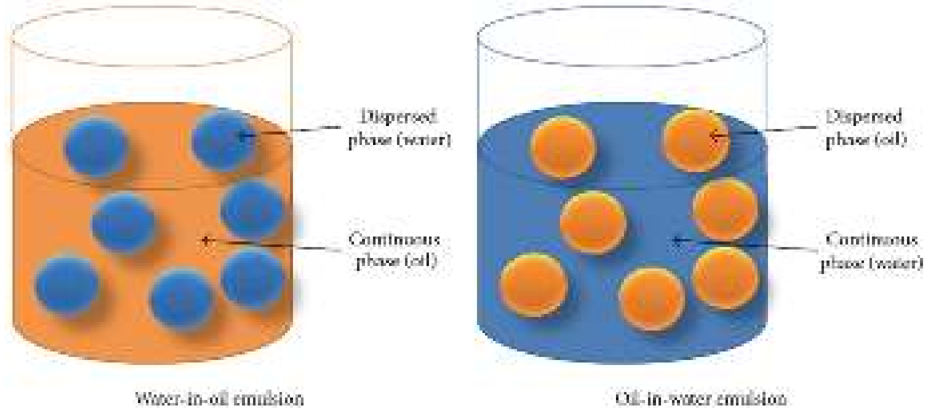


Fig. 2. *Concept of two-phase water-in-oil and oil-in-water emulsions* [13]

The O/W emulsion is not suitable to be an alternative fuel. This is due to the large amount of water that might come into direct contact with the cylinder-piston group and fuel feed system, which will result in failure of the fuel combustion. The W/O emulsion fuel is the most suitable and widely used as the alternative fuel for fueling compression ignition engines by researchers and experts [4]. The two-phase emulsion constitutes one continuous phase and one-dispersed phase liquids while the three-phase emulsion constitutes one continuous phase and two or more dispersed phase liquids [13].

Multiple emulsions consist of three phases: an inner and an outer phase separated by a dispersed phase [15]. In Figure 3 [13] are presented the three-phase emulsions or double emulsions which are denoted as: O/W/O (oil-in-water-in-oil) and W/O/W (water-in-oil-in-water) [15].

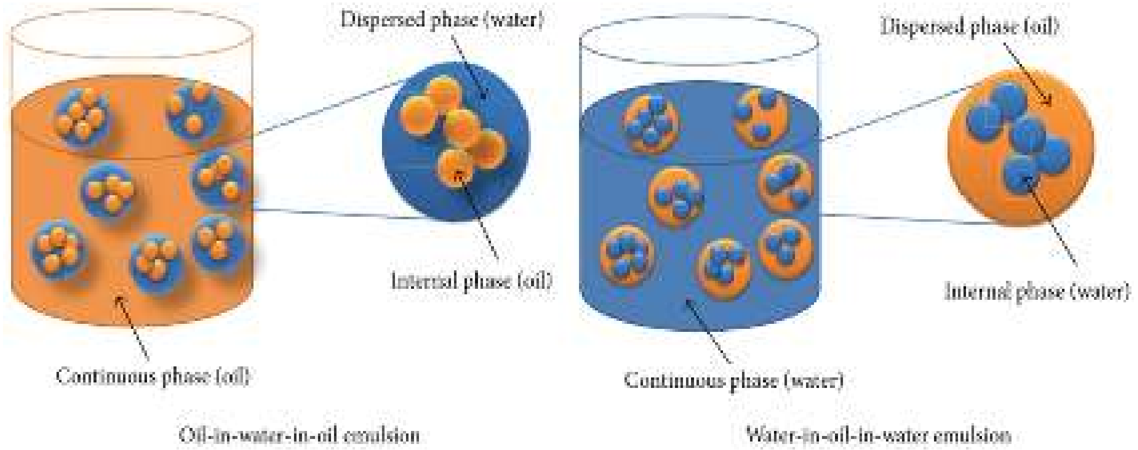


Fig. 3. *Concept of three-phase oil-in-water-in-oil and water-in-oil-in-water emulsions* [13]

Multiple emulsions are complex liquid multiphase systems. They are also called „emulsions of emulsions" because the dispersed phase of these emulsions consists of an emulsion itself. In water-in-oil-in-water (W/O/W) emulsions, water droplets are dispersed in an oil phase which itself forms drops in a continuous waterphase. This complex structure enables their use for different applications ranging from separation processes and encapsulation of specific molecules for cosmetic, pharmaceutical, agrochemical and food products to fat reduction in food [18].

Three-phase emulsions can be prepared by three techniques, namely, phase inversion, mechanical agitation, and two-stage emulsion. A two stage emulsification technique has been used for the preparation of three-phase oil-in-water-in-oil emulsion by many researchers. This technique, which is the most common technique in three-phase emulsions, uses both lipophilic and hydrophilic types of surfactants. First, a two-phase oil-in-water emulsion is prepared by using a hydrophilic type surfactant and a mechanical homogenizer machine. A lipophilic type of surfactant is then used to further emulsify the two-phase oil-in-water emulsion in oil and form three-phase oil-in-water-in-oil emulsion [13].

Nano-emulsions consist of very small emulsion droplets, commonly oil droplets in water, exhibiting sizes lower than 300 nm.

Like conventional emulsions (with sizes > μm), nano-emulsions are, from a thermodynamic point of view, in a non-equilibrium state [19].

The confusion between nano-emulsions and micro-emulsions is, in fact, as much a result of their formulation processes as of their structural (macroscopical and molecular) aspects, both being to some extent very close. Nano-emulsions are only formed if surfactants are first mixed with the oily phase. If they are first mixed with water before adding the oily phase, only a "macroscopic" emulsion will be generated. Micro-emulsions, on the other hand, will be strictly identical whatever the order in which the compounds are mixed (after equilibration time) [19].

Microemulsion based fuel formulations date back to 1976 when Gillberg and Friberg published a paper on the use of water-in-diesel micro-emulsions as fuel [4, 7]. In Figure 4 [7] are shown the characteristic differences between emulsions and micro-emulsions.

The size of the drops in an emulsion are in the range of 1-10 μm, while in a micro-emulsion they are much smaller, e.g. 5-20 nm [20].

Micro-emulsions are thermodynamically stable, while emulsions are thermodynamically unstable and will separate into two phases in due time, although this separation can be delayed by a careful choice of surfactants and polymers [20].

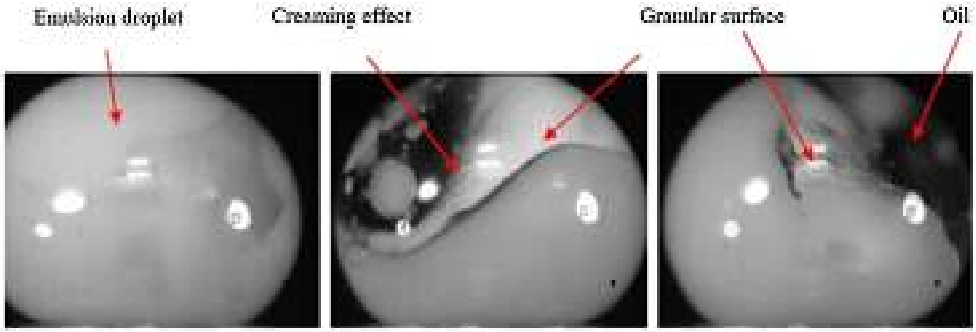
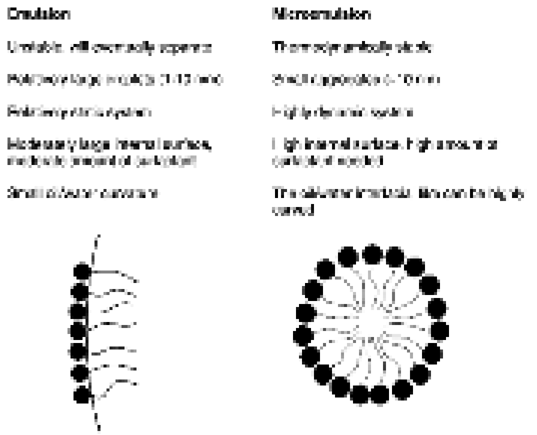


Fig. 5. Sequence of creaming process [4]



Emulsion	Microemulsion
Unstable, will eventually separate	Thermodynamically stable
Relatively large droplets (1-10 [illegible])	Small aggregates (~10 nm)
Relatively static system	Highly dynamic system
Moderately large internal surface, moderate amount of surfactant	High internal surface, high amount of surfactant needed
Small [illegible] curvature	The surfactant interfacial film can be highly curved

Fig. 4. Characteristic differences between emulsions and microemulsions [7]

The thermodynamic stability of the micro-emulsion does not compensate for the drawback of the much higher loading of surfactants needed in a micro-emulsion formulation compared to an emulsion formulation. The microemulsion route is probably too costly for a very large scale application, such as fuels for vehicles [7].

2.3. Emulsion fuel stability

The stability of the diesel emulsion is affected mainly by the emulsification technique, emulsification duration, volume fraction of water (dispersed phase), viscosity of the continuous phase (diesel oil), stirring speed (or ultrasonic frequency) and concentration of surfactants (it is the most important factor) [13].

If the emulsion is destabilized during the engine running time, the probability of the engine failure to operate is high. It may damage the parts inside the engine [4].

In paper [21] it has been demonstrated that the stability of the emulsion fuel is tested under various environmental temperatures for 1 year, and no significant separation is noticed. It is better than normal emulsion fuel which can only maintain the state for up to 3 months.

The destabilization process of W/D emulsion fuel will occur after it goes through several phenomena: creaming, aggregation and coalescence. For the case of the W/D emulsion fuel, the internal phase, which is the water, will sink to the bottom. Figure 5 shows the sequence of the creaming phenomena. The aggregation process is where the droplets in the internal phase attract each other [4].

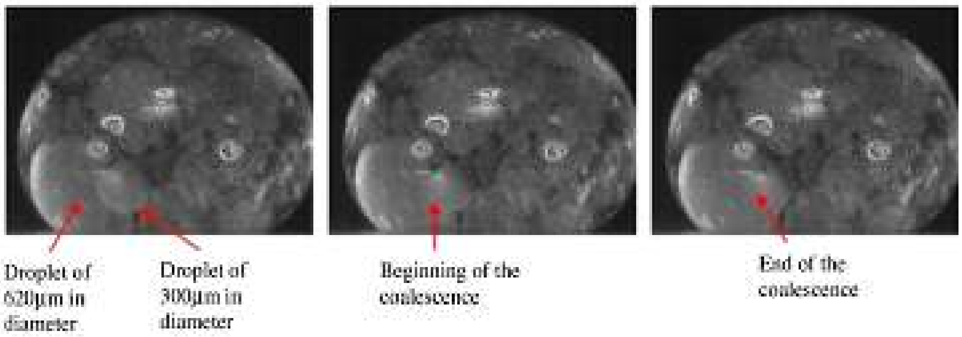


Fig. 6. Sequence of coalescence process [4]

The sequence of the coalescence process is presented in Figure 6. All of these processes will continually destabilize the emulsion until the water and the diesel fuel are fully separated. In addition, the W/D emulsion fuel separation can be initiated by these following cases [4]:

- low speed environment (the phases after a long period will be separated by the gravity effect),
- increase in temperature (lower viscosity),
- external electric field,
- high shear stress in the emulsion,
- the addition of a chemical that influences the emulsifier or liquids, and
- the addition of a diluting liquid.

A colloidal dispersion can be kinetically stable with respect to coalescence, but unstable with respect to aggregation. Or, a system could be kinetically stable with respect to aggregation but unstable with respect to sedimentation. In summary, although lyophobic colloids are thermodynamically unstable, they may be relatively stable in a kinetic sense, and it is crucial that stability be understood in terms of a clearly defined process [15].

2.4. Emulsion fuel viscosity

In general, water-fuel emulsions exhibit greater viscosity than pure liquid fuels, and both water content and size of the droplets dispersed in the emulsion significantly influence its viscosity (Figure 7 [22]) [23].

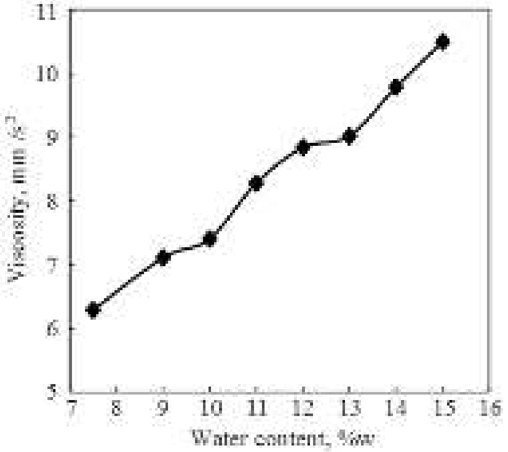


Fig. 7. *Effect of the water content on the viscosity of a micro-emulsion diesel oil* [22]

Ochoterena et al. [20] present an experiment where they compared the performance of EUD (European ultra-low sulphur diesel), water-in-diesel emulsion (88% diesel, 10% water and 2% additives) and micro-emulsion (80%, 10% water and 10% additives). They found that the viscosity of the water-containing fuels is higher than the viscosity of EUD as displayed in Figure 8, but the surface tension of the emulsion fuel across the studied temperature range was similar to that of the regular diesel.

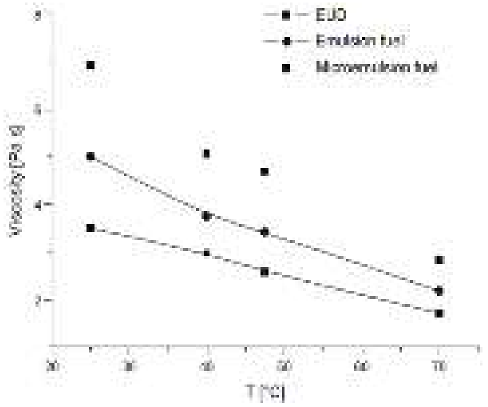


Fig. 8. *Viscosity of the three fuels vs. temperature from 25 to 70 °C, showing the higher viscosity of the water-containing fuels* [20]

The size distribution also has an important influence on the viscosity. For electrostatically or sterically interacting species, the dispersion viscosity will be higher, for a given mass or volume concentration when the species are smaller. The viscosity of all dispersions will tend to be higher when the dispersed species sizes are relatively homogeneous, that is, when the particle size distribution is narrow rather than wide [15].

In Figure 9 from [24], the viscosity of diesel fuel emulsion increases with water content up to the value of 43 centi-poise at 15% water, due to more complex micellar structures formed and it shows the water in oil (O/W) phase at this condition.

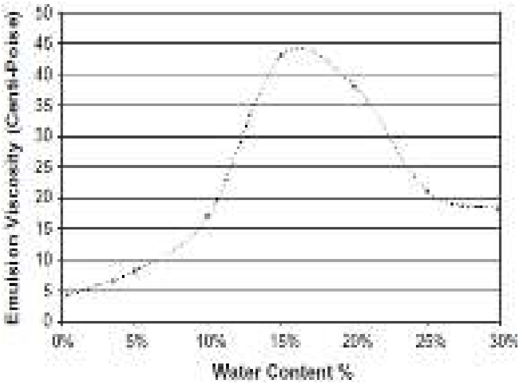


Fig. 9. *Viscosity of emulsion diesel fuel versus water content* [24]

Further addition of water changes the phase to the oil in water (W/O) and leads to the decrease of the viscosity. Therefore, increasing the viscosity of emulsified fuel tends to advance injection timing in some injection systems.

3. Conclusions

The technique concerned with introducing water into the engine combustion chamber was proposed by Prof. B. Hopkinson in 1913.

The main pollutants produced from the exhaust of diesel engines are nitrogen oxides (NOx), particulate matter, black smoke, carbon monoxide and carbon dioxide.

Water-in-diesel emulsion fuel (W/D) is a promising alternative fuel that could fulfill such requests in that it can improve the combustion efficiency of a diesel engine and reduce harmful exhaust emission, especially nitrogen oxides (NOx) and particulate matter (PM).

Of all the methods proposed to introduce water into the combustion chamber, diesel oil emulsions appear to be the most appropriate, because they require no engine retrofitting.

The emulsion is formed with the help of mechanical agitation together with the chemical additives called surfactant to keep the immiscible liquids mixed together, forming one solution. Generally, emulsions are divided into two types: oil-in-water emulsions (O/W) and water-in-oil emulsions (W/O). Multiple emulsions are complex liquid multi-phase systems.

Surfactants or surface-active agents are amphipathic substances with lyophobic and lyophilic groups, making them capable of adsorbing solids and gases at the interfaces between liquids.

A frequently used method for selection of surfactants as emulsifying agents is known as the HLB (hydrophilic–lipophilic balance) method.

The stability of the diesel emulsion is affected mainly by the emulsification technique, emulsification duration, volume fraction of water, viscosity of the continuous phase, stirring speed and concentration of surfactants.

In general, water-fuel emulsions exhibit greater viscosity than pure liquid fuels, and both water content and size of the droplets dispersed in the emulsion significantly influence their viscosity.

With the advantage of energy saving and less environmental pollution for W/D emulsion, together with the newly developed emulsion fuel making device, it will provide a great contribution to the industries, and, at the same time, reduce the consumption of energy and ensure less pollution to the environment.

The obstacles that slow down the commercialization of emulsion fuel are the high production cost involved and the fuel stability issues. In order to eliminate the barriers to the commercialization of W/D emulsion fuel, simplification and optimization of the fuel production device can be investigated.

Some characteristics, such as water percentage, dispersed droplet size and viscosity depending on the engine working conditions, such as engine load and speed would be an interesting research area that can be explored fundamentally and practically in the near future.

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