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ARCHAOMETALLURGY AND ITS IMPORTANCE IN THE RESEARCH OF THE PREROMAN DACIA MILITARY EQUIPMENT IN THE 1st B.C. – 1st A.C. CENTURIES

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ABSTRACT

Although it appeared in Romania 50 years ago, archaeometallurgy is still treated as a new discipline, despite the fact that it was understood from the beginning that this science, by its methods and by the correct interpretation of the results obtained as a result of modern techniques of characterization of materials generally leads to the obtaining of data that are particularly important for understanding the past. The present study aims to investigate the evolution and the stage in which this field is in terms of modern techniques of characterization of the materials applied to the military equipment of the classical Geto-Dacian period.

KEYWORDS: Dacian armament, archaeometallurgy, characterization of materials

1. Introduction

The present study considers the science of archaeometallurgy and its importance in the research of military equipment from the century I a. Chr. - I p. Chr. in the geographical area of Dacia before the Romans, which today corresponds to the territorial limits of Romania.

The emergence of archaeometallurgy more than a century ago has led to obtaining interesting and complementary data in archaeological research and implicitly in understanding historical realities. Today the contribution of this science, as we will show in the following, has led to the creation of an interdisciplinary connection without which archeology can no longer function in a professional manner.

The analysis of the various artefacts is made especially in the last years due to the emergence of the latest generation equipment, based on archaeometallurgy, with the mention that the latter is only a segment of a much wider interdisciplinary science called archaeometry.

Despite the fact that people have started to discuss more and more about this modern science (which uses natural sciences such as mathematics, physics, chemistry, biology or geology to support archeology or art history), this emerged at the end of the 19th century becoming a self-contained science in the 1950s [1], with the mention that after obtaining

spectacular results from the initial period, the taking over of the techniques of characterization from physics continued with the more refined methods of characterization from chemistry, respectively physics and the mechanics of artifacts properties [2].

Although in Romania one carried out metallographic studies at the end of the 19th century, archaeometry was born after 1970 and culminated in the establishment of the National Society of Archaeometry [1] in 2011.

In order to obtain as much information as possible on the weapons in the Geto-Dacians, archaeometallurgy is used, which aims to describe the conditions of mining and at the same time to try to reconstruct the modified metallurgy processes [3]. In other words, archaeometallurgy studies the whole process, starting from the incipient stage of obtaining the material from the mining, respectively the separation of ores and until the processing of the respective ore by various methods (forging, casting, etc.).

Also, together with the research of metals, it also falls into the sphere of archaeometallurgy research and the investigation of the residues resulting from the production of the respective metals [4].

Of course, in order to obtain the expected information, archaeometallurgy uses various methods of geology, geochronology, sedimentology, mineralogy, petrography, crystallography, as well as

physics, chemistry and metallurgy, in this hazy method of keeping the attention so that it is not lost sight, obtaining the results from the historical and implicit point of view and bringing a new contribution to its writing [3].

Unfortunately, for various artifacts made of iron or bronze, as is the case with weapons or tools, if at the beginning of the 1980s a series of armament pieces were subjected to methods considered at the time to be the most modern (emission spectrometry and absorption spectrophotometry) [5], both archaeologists and physicists or chemists have lately shown interest in performing metallographic analyzes specific to archaeometallurgy, especially on objects belonging to treasures made of precious metals. For example, we mention the situation of the late Dacian Latene treasure from Bucharest-Herastrau on which X-ray fluorescence analyzes were performed [6].

The importance of archaeometallurgy and modern materials characterization techniques must be viewed with at least the same expectations as archaeological research regarding the discovery and interpretation of military equipment at the Geto-Dacians.

Considering the fact that besides a series of armament pieces from the Geto-Dacian world there is another series of related discoveries (metallurgy workshops, ore reduction furnaces, crucibles, slag pieces and even iron ingots) [7], especially since it was established that in the local workshops the craftsmen also used imported iron ingots [7], it is proved that performing the analyzes specific to archaeometallurgy is an indispensable technique in obtaining information. Frequently performing these analyzes would be able to elucidate at any given moment the entire unclear situation regarding the precise origin of an ore, respectively of weapons created from it. Of course, this is possible only to the extent that specialists (both from Romania and from neighboring countries, where two millennia ago the Dacian population lives) would understand that it is absolutely necessary to carry out specific analyzes and to create a common database.

It should also be noted that the current level of knowledge in archaeometallurgy and understanding of how iron inventory objects behave when they are brought to the surface by archaeologists may be much more important than even gaining information about the respective objects through modern methods of laboratory investigation. That statement is easily to be proved since, in archaeological research, the lack of specialized personnel with regard to iron objects leads to the situation where properly harvested or unprotected artifacts are destroyed during the sampling, or possibly in the conservation phase of restoration, as it was the case of a Geto-Dacian arrow from Cetățeni, Argeș County, which was destroyed in

the laboratory while it was in the cleaning solution [8].

Handling antique ferrous objects is not always easy. In many cases, they are discovered in a state of advanced degradation due to the physico-chemical interactions that the piece has suffered in contact with the soil, or due to the sudden entry (after the discovery of the object) in contact with oxygen and humidity, all the more so the iron does not need more than 0.05 seconds to enter the corrosion phase [9].

Despite the fact that many weapons were discovered in a so advanced corrosion state that they practically sprayed without leaving behind information that usually accompanies such artifacts, as it is the case with the *umbo* shield from Cetățeni [10], the latest metallographic analyzes having completely saved such situations.

Cases of this kind in which the parts can be completely corroded, today provide valuable information that is preserved between the corrosion layers whose products have replaced the existing metal structures before corrosion [11].

Approaching research with the help of archaeometallurgy and implicitly of modern laboratory techniques can lead to clarification of some aspects down to the smallest details. For example, for more than half a century, certain stages during the forging, including the direction of the hammering force of the hammer used on the material, were found by observing the dark colored stripes showing the maximum concavity where the force to hit it exerts its maximum effect [12].

At the same time, archaeometallurgy can be the answer to those detailed analyzes (other than the archaeological research they have to complete), which archaeologists look for in order to obtain answers regarding the local or external techniques that were used in the workshops when creating various artifacts [13].

Also, if at the beginning of the twentieth century the examination of objects was carried out by destructive methods that often meant destroying the samples, at present these analyzes involve extremely small samples to which non-destructive and non-invasive analyzes are added, which, through various methods, apart by the fact that they can date the objects, they can lead to the identification of false ones [14].

Due to the practical experience and the concrete problems faced by the researchers, archaeometallurgy begins to impose a true "practical guide" that both archaeologists and the personnel with tasks in conservation-restoration must acquire. Specifically, the artifacts (especially the metal ones) must be subjected to the cleaning process, but this excessively applied process as a result of improper restoration

techniques leads not only to the aesthetic deterioration of the object, but also and especially to the impossibility of characterizing the object by studying some essential micro-surfaces [15], which can generate the loss of vital information regarding the techniques used in creating the respective piece or other elementary data.

It should also be noted that, on the one hand, archaeological research for various reasons, but justified primarily by the lack of financial resources, is almost devoid of modern techniques of characterization of materials, and on the other hand, they are not properly turned to account by publication, even if they were carried out, as is the case with military equipment pieces found inside four mounds investigated in Cugir in 1979 and 1981. Although it is stated that besides a series of analyzes on bones, wood and radiocarbon dating were new spectral and microfluorescence analyzes were performed, it seems that the respective studies remained in the manuscript stage [16].

2. Military equipment and research methods

2.1. Study of weapons from Bulbuc locality, Ceru-Băcăini Commune, Alba County

During 2014, on the southern edge of the Bulbuc hamlet, a metal-detecting enthusiast discovered a number of 5 complexes representing possible Dacian burial arrangements, but the analyzes carried out did not identify any traces of burning or other elements that usually appear in the context of the funeral rituals although there is the possibility that they were cenotaphs [17].

In total, the detector would donate to the National Union Museum in Alba Iulia 5 *sica*-type curved daggers, 3 javelins, 5 lace-heads, a spearhead and 3 sheaves, generally the daggers and spears being ritually bent.

Based on the analogies with other *sica*-type daggers, but especially on the basis of the analogies related to the hooves, it supports the dating of the discoveries towards the 1st century BC.

It should be noted that the weapons, although they had been on the ground for a very long time, were discovered in a very good physical condition that could be considered atypical, in this case the magnetite layer (Fe_3O_4) being preserved very well even if under it, the corrosion affected the metal core, which led to the maintenance of the functional and decorative elements on the blades and handles of daggers [18].

A particularly interesting aspect only valid for the spearhead and two of the lances is the fact that on

these was observed a red-cherry patina that can be attributed to ferric oxide (Fe_2O_3), hematite [18]. This situation is most likely explained by analogy with other types of ferrous materials found at Sarmizegetusa where on a series of iron spikes and targets containing the same red-cherry patina were performed in 1981, respectively 1995 emission spectroscopy analyzes, respectively emission fluorescence, the results of both analyzes being interpreted in the sense that the respective patina represented a primitive enamel used with the role of protecting against corrosion [19]. The analyzes performed by the engineer Gheorghe Topan, the head of the research laboratory at the Armatura factory in Cluj-Napoca and presented in Table 1 determined the chemical elements of an iron pyron provided with glaze (enamel), the chemical composition being expressed in % by weight.

Table 1. Iron pyron with glaze analysis bulletin (enamel) [19]

Elements	Concentration %	
	Polished face (metal)	Unpolished face (glaze)
Fe	Basic Element	Basic Element
C	0.03	-
Si	0.15	2
Al	-	2...3
K	≤ 0.01	0.1...0.6
Ca	≤ 0.01	0.2...0.8
P	≈ 0.05	0.04
Mn	0.04	0.15
Mg	< 0.01	-
Ti	0.01	0.04
V	< 0.004	0.03
Cr	0.02	0.02
Ni	0.03	< 0.01
Cu	0.03	0.04
Sn	0.07	< 0.01
W	0.03	-
Pb	0.02	-
Bi	0.01	-
Mo	< 0.05	0.02
Sb	0.05	-

Considering the excellent state of conservation of the weapons located on the ground, to clarify the whole situation, from the respective pits were collected several soil samples, two of them were analyzed to obtain data on the chemical composition and pH [18], both these and a series of metallographic analyzes being performed at the Research Institute for analytical instrumentation Cluj-Napoca [17].

The results of the soil samples S1 and S2 obtained by the destructive spectrometry method, the

inductive coupled plasma atomic emission spectrometry (ICP-AS) detailed in Table 2, respectively the inductive coupled plasma mass spectrometry (ICP-MS) in Table 3 are presented as follows:

Table 2. Experimental results obtained by the ICP-AS method [18]

Elem. determ.	S-1 mg/kg	S-2 mg/kg
Fe	28693	29540
Ni	31.4	32.4
Cr	26.4	26.3
Co	7.23	7.3
Cu	47.1	48.7
Zn	134	136
Pb	20.5	15.9
Na	-	111
Mg	<4860	5063
K	3427	3500
Ca	31167	37667
Mn	944	1020
Ba	162	172
Al	21037	22193
I	0.31	0.17
Cs	0.53	0.17
La	7.53	5.4

Determination of soil pH according to Table 4 was carried out by instrumental method of serial pH measurement in a 1:5 (V/V) dilute suspension of soil in water (pH in H₂O), in potassium chloride solution concentration 1 mol/L (pH in KCl water) [18].

Based on the soil analyzes, it was found that the very good state of preservation of the military equipment was due not only to the quality of the metal, but especially to the pH of the soil, whose alkaline value allowed the formation of oxide layers with a protective role. Also, the large amounts of calcium carbonates (present due to the decomposition of calcareous rocks in the soil) led to the formation of a protective layer that slowed down the corrosion, this being done randomly depending on the contact of the weapons and the position of the carbonates in the soil, the areas. of the respective contact having a black patina (magnetite) [18].

For the analysis of the composition was chosen the spearhead from Fig. 1, this one presenting the glove tube with perforation, for fixing the nail found detached from the blade with median rib.



Fig. 1. Spearhead, inventory nr. 4723 [17]

A sample of 0.5 g was taken from the spearhead, which was chosen from the sleeve, indicating that, unfortunately, a strongly corroded area was chosen, which certainly affected the analysis result.

Table 3. Experimental results obtained by destructive methods with ICP-MS [18]

Determ. elem.	S-1 mg/kg	S-2 mg/kg
Li	16.4	6.3
Be	0.61	0.22
Sc	1.6	1.3
V	19.6	12.7
Ga	2.7	1.9
As	21.9	12.3
Rb	11.9	9.1
Sr	11.8	8.7
Y	5.5	3.7
Zr	3.9	2.6
Nb	0.35	0.20
Mo	0.29	0.14
Cd	0.25	0.14
Sn	0.53	0.34
I	0.31	0.17
Cs	0.53	0.40
La	7.5	5.4

Table 4. PH values corresponding to the soil matrix [18]

Nr. crt.	Soil sample code	Quantity / volume of distilled water	pH	Temperature	Unit
1	S-1(985)	10.17 g/50 mL	7.90	20.1 °C	pH units
2	S-2(986)	10.16 g/50 mL	7.99	20.2 °C	pH units

The respective sample was subjected to destructive analysis of inductive coupled plasma atomic emission spectrometry (ICP-AES), oxygen

carbon technology (TOC) respectively, according to Table 5.

Table 5. Chemical analysis of the spearhead [18]

Element	Mg/kg	Element	Mg/kg	Element	Mg/kg	Element	Mg/kg	Element	Mg/kg
Li	1.7	Zn	107	Ru	<0.3 2	Nd	<0.3 2	Ta	<0.3 2
Na	486.4	Pb	74.6	Rh	<0.3 2	Sm	<0.3 2	W	<0.3 2
Mg	139.4	Ga	1.04	Pd	<0.3 2	Eu	<0.3 2	Re	<0.3 2
Al	281	Ge	0.45	Ag	2.18	Gd	<0.3 2	Pt	<0.3 2
K	3534	As	20	Sn	6.82	Tb	<0.3 2	Au	<0.3 2
Sc	0.74	Br	2.2	Sb	24.4	Dy	<0.3 2	Hg	<0.3 2
V	18.35	Rb	0.43	I	<0.3 2	Ho	<0.3 2		
Cr	496.1	Sr	6.88	Cs	<0.3 2	Er	<0.3 2		
Mn	126.5	Y	0.4	Ba	17.48	Tm	<0.3 2		
Co	18.3	Zr	0.52	La	0.93	Yb	<0.3 2		
Ni	68.1	Nb	0.53	Ce	0.42	Lu	<0.3 2		
Cu	90.8	Mo	4.28	Pr	<0.3 2	Hf	<0.3 2		

The percentage of 0.80% carbon shows both the long heat treatment and the stopping of this treatment before the weapon becomes brittle, which resulted in obtaining a piece with an optimal ratio between resistance and elasticity [18].

2.2. The study of weapons from the Boeriu Collection, the National History Museum of Romania

Without knowing the place of discovery and without questioning the area of the Geto-Dacians' residence, in the years 2009-2010, Adrian Boeriu donated to the National History Museum of Romania two *sica*-type curved daggers, which he declared he had purchased from London [20].

Of the two daggers, the one with inventory number 334523, represented in Figure 2, had the chance to be analyzed from a metallographic point of view.

This fact was achieved within the project - *Studies of archaeometallurgy on the Dacian Gold and Silver using high-performance X-ray spectrometry methods* [21].



Fig. 2. *Sica*-dagger inv. 334523 [29]

X-ray fluorescence spectrometry (XRF) was performed including X-MET 3000TX portable spectrometer (with detector: Peltier cooled silicon diode, Window detector: Kapton, X-ray tube: RH anode, maximum voltage 30 KV, size spot: 6 mm x5 mm, determination of elements: from potassium to uranium, energy resolution: < 275 eV for K α -Mn). The XRF spectrum is shown in Figure 3.

From the investigations carried out it was found that a series of traces detailed in Fig. 4 that were observed on the blade were composed of a brass alloy remaining from the composition of the teak, a very

important aspect that led to the dating of the dagger in the 1st century a. Chr. Since these alloys appear after the time of Augustus [22].

2.3. Studying the evidence in Cugir locality, Alba County

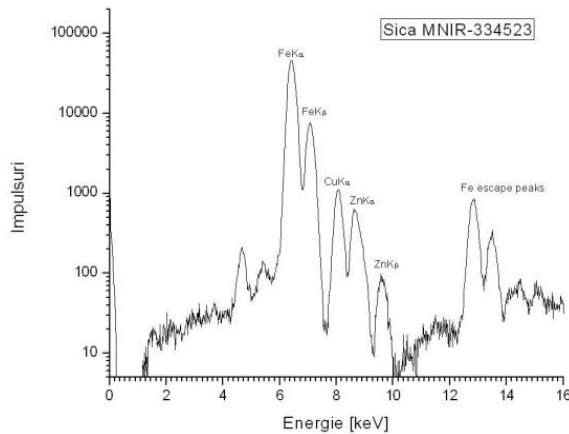


Fig. 3. XRF spectrum [21]



Fig. 4. Upper part with possible brass area from molten sheath [21]

During the excavations in 1979, on the S-V slope of the hill called "Cetate" near the town of Cugir, on which the Dacian fortress Singidava was identified, a number of four tombs containing incineration graves were discovered, the tumulus no. 2 revealing the surprise of the existence within it of a princely tomb [23].

The excavations continued in 1980 by Ioan Horațiu Crișan and Florin Mededeț showed that the four mounds were located in the immediate vicinity of the fortified enclosure, just next to the access road to the Dacian fortress [24].

Basically, the archaeological excavation of the mound with the number 2 revealed that the incineration of the warrior's body equipped with armor from chapels, helmets, Celtic type sword (whose sheath joined with the blade due to the strong burning from the tree), spear, shield with border and *umbo*, the plywood of a bow and a dagger of the *sica* type (all this set being made of iron) was made together with a number of 3 horses (about 100 kg of calcined bones of human and animal origin were harvested), the human body being burned in a ceremonial chariot right at the place where the mound [25] was erected.

Along with these weapons, in the tomb dated in the first half of the century I A.C., besides pieces of gold and silver jewelry from the warrior's clothing, but also from the harness that adorned the horses, one discovered numerous pieces from the chariot, harnesses, hooves, etc. from which samples were collected to establish the material from which they were made [26]. Their analysis is presented in Table 6.

Table 6. Cugir tomb analysis bulletin, raw material samples [19]

Sample nr.				Cu
0	1	2	3	4
I	The bandage of the wheels of the carriage	Steel	Metallography	
II	Bronze element of the carriage (or harness piece)	Bronze	Gravimetric + spectral	91.30
III	Metallic clothing accessory	Silver alloy	- -	4.21
IV	Granule from melting and agglomeration of metal parts (jewelry or clothing)	Silver	- -	0.72
V	Fragment of metal part from the carriage	Bronze	- -	73.70
VI	Rods for fixing the sides of the carriage	Bronze	- -	91.46
VII	Carriage ring	Bronze	- -	78.25
VIII	Bronze vessel (situla)	Bronze	- -	87.72

After establishing the alloy from which the flakes subjected to the analysis were made, one wanted to determine the chemical composition. The result of this analysis according to Table 7 showed that apart from the bronze pieces they contained besides copper and Sn, Pb, Ag, Al, Fe, Si, Mg, P and

Au, and the fact that they were subjected to a final heating on the 850 °C funeral pile, which was followed by a slow cooling due to the preservation of some combinations of chemical elements [19].

Table 7. Bulletin of the Cugir tomb analysis, chemical elements and sample components [19]

Content in chemical elements %												
Ag	Sn	Pb	Al	Fe	Si	Mg	Mn	P	Au	Bi	Ni	C
5	6	7	8	9	10	11	12	13	14	15	16	17
				≈0.90								≈0.05
≈0.1	5.50	1.86	0.1... 0.5	≈0.1	≈1	≈5.10 ⁻²	10 ⁻³ ... 5.10 ⁻³	0.5...1.0	≈10 ⁻³	≈10 ⁻²	5.10 ⁻³ ... 10 ⁻²	
92.0	0.5... 1.0	≈1	≈0.1	≈0.1	0.5...1	10 ⁻² ...5.10 ⁻²	≈10 ⁻³ ...	5.10 ⁻²	≈0.1	0.5... 1.0	5.10 ⁻³	
84.61	13.94	0.1... 0.5	10 ⁻³ ... 5.10 ⁻³	10 ⁻² ... 5.10 ⁻²	10.5... 1	≈5.10 ⁻²	10 ⁻³ ... 5.10 ⁻³	≤5.10 ⁻²	≈1	≈1	≤5.10 ⁻³	
2.78	6.55	0.1... 0.5	5.10 ⁻² ...10 ⁻¹	0.1... 0.5	10.5... 1	10 ⁻³ ... 5.10 ⁻²	10 ⁻³ ... 5.10 ⁻³	5.10 ⁻² ... 10 ⁻¹	≈5.10 ⁻³	5.10 ⁻³ ... 10 ⁻²	5.10 ⁻² ... 10 ⁻¹	
0.1... 0.5	0.52	≈0.1	≤10 ⁻³	0.1... 0.5	10 ⁻² ... 5.10	5.10 ⁻³	≤10 ⁻³	≤5.10 ⁻²	<10 ⁻³	<10 ⁻³	≈10 ⁻²	
≈0.1	6.90	1.55	5.10 ⁻² ... 10 ⁻¹	0.1... 0.5	0.5...1	10 ⁻² ... 5.10 ⁻²	10 ⁻³ ... 5.10 ⁻³	5.10 ⁻² ... 10 ⁻¹	≤10 ⁻³	0.1... 0.5	≈10 ⁻²	
≈0.1	7.60	≈0.1	10 ⁻² ... 5.10 ⁻²	0.1... 0.5	0.1... 0.5	10 ⁻² ... 5.10 ⁻²	≤10 ⁻³	≈0.1	≤10 ⁻³	<10 ⁻³	≈10 ⁻²	

2.4. Studying the evidence in Orodel place, Dolj County

In 1917, on the right side of Orodel Valley, in the area of the old church and the cemetery, a cremation tomb was discovered (although no traces of the cremation were found, the patina of the weapons proved that they were passed through the fire) at that time, a Celtic sword, jagged, a spearhead and a *sica*-type dagger [27], detailed in Fig. 5.



Fig. 5. Sica dagger from Orodel place [29]

Quite rightly, the respective *sica* due to the accidental discovery and without a clear context was challenged as to whether it belonged to the same eventual grave in which the other weapons were discovered [28], especially since it is a weapon specific to the Geto-Dacian population.



Fig. 6. Sica blade detail with copper-lead alloy ornaments, possibly from the sheath [21]

2.5. Studying the evidence in place. Piatra Roșie, Lunca Village, Hunedoara County

A spectacular warehouse of Dacian pieces that included besides several dozen tools, some three pieces of military equipment consisting of a spearhead and two lance-heads, shown in fig. 8, one of which was unfinished, being processed, was donated to the museum of the Castle of Corvinești approximately between the years 1995-1996 by an unknown person, without knowing the context of the discovery, but only that it took place in the proximity of the fortress Piatra Roșie [30].

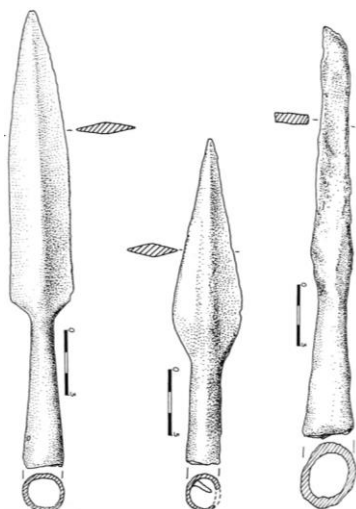


Fig. 7. lance-head, spearhead, unfinished lance-head [30]

On the respective pieces, in the laboratories of the Iron and Steel company Hunedoara, later turned into Mittal Steel, chemical analyzes were performed with the help of a spectral analyzer, respectively metallographic ones carried out under a microscope [30], which revealed, in addition to a series of characteristics related to the metallurgical processes to which they have been subject to the respective objects also the chemical elements in their composition according to Table 8.

Regarding the component parts of the warehouse, based on their characteristics, but also on the basis of analogies with different pieces from the Dacian environment, the authors of the study proposed as a chronological landmark the period between the years 101-105 p. Chr. [30].

Table 8. Chemical elements in the composition of the armament pieces, Piatra Roşie [30]

Nr. sample	%	C	Mn	Si	S	P	Cr	Ni	Cu	Al
8	Spear head	0.41	0.01	0.03	0.018	0.100	<0.01	<0.01	<0.01	0.009
12	Spear head	0.21	-	-	-	0.012	-	-	0.03	0.005

2.6. Weapons study in Rastu Commune, Dolj County

In the respective locality, in Griful Şifarului point, systematic archaeological investigations were carried out in 1950, which led, among others, to the discovery of cremation graves and pieces of military equipment consisting of *sica*-type knives, lances and sheaf fragments [31].

The respective pieces currently owned by the National Museum of History of Romania were classified in the 2nd-1st centuries BC, following analogies from Oltenia, Histria or northern Bulgaria [32].

Of the total weapons discovered, only two of the *sica*-type daggers were investigated. The microstructure analyzes performed on the *sica* with inventory number III 5962 from Fig. 8 (left), reveals that the weapon had been ritually bent with its burial, although it had probably been tempered, this being subjected to a warming above the critical point after which the descent took place [32].

Regarding the other weapon with inventory number III 5963 from Fig. 8 (right), it was subjected to a metallographic analysis that revealed that it was made of 0.7-0.8% carbon steel, was uncoated and had been made by forging [32].

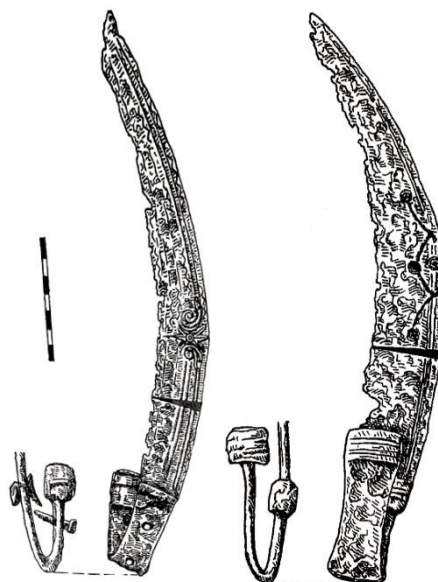


Fig. 8. *Sica* inv. 5962 (left) and *Sica* inv. 5963 (right) [32]

As with the other curved dagger, it was also found that it must have been initially hardened, especially due to its functionality, and the heating above the critical transformation point that led to the decay was accounted for by the ritual burning of at

the funeral parade, an explanation that is perfectly logical.

3. Conclusions and perspectives

As for the answers offered by the archaeometallurgy, they come as a result of the requests received from archaeologists as a rule, specifying that these analyzes are performed according to the questions to which the archaeologists expect answers, and the methods of characterization of the materials are influenced by the existing facilities.

At the same time, the remaining scraps from the metallurgical process, respectively the slag, should be treated with the same importance as the finished parts under analysis. The detailed study of these slags can bring a number of relevant data including the metallurgical processes through which the slag has passed.

In the situation of these remains, one must understand that only scientific research can link the piece of slag to the piece of metal that was created [4].

The stake of the proper research of these slags is a special one. Practically, the careful archaeological research in the workshop areas, respectively of the ore reduction furnaces, followed by the collection and transmission to the laboratory of these remains can finally lead to the clarification of the eternal disputes in the specialized bibliography regarding the local origin or the origin of the import of certain military equipment.

In general, it should be borne in mind that the process of physical-chemical characterization of some archaeological finds led to the knowledge of technologies and materials used in the past and at the same time contributed to obtaining new information on trade, human migration, as well as the penetration of various cultures, which led to data that can be used in dating objects [14].

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RESEARCH REGARDING THE PARTIAL REPLACEMENT OF AGGREGATES IN CONCRETE WITH A BY-PRODUCT OF STEEL INDUSTRY

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ABSTRACT

A continuous increase in demand for natural resources, in a high proportion for the construction sector, creates the necessity to search for alternatives. This work is intended to do so and the aim is the replacement of natural aggregates in some concrete samples with a metallurgical industry by-product. The replacement was gradual and only for one type of the three dimensions utilized. The results of the many tests conducted revealed the possibility of natural aggregate replacement in some extent, keeping the resulted properties of samples within the limits of the standards.

KEYWORDS: cement; concrete; aggregate; steel slag; compressive strength

1. Introduction

In the last decades, different materials were used in concrete composition in order to utilize some industrial wastes or for reutilization of aggregates from demolitions. In the concrete composition, the aggregate represents an important share (at least 75% from the concrete volume) and an important influence towards concrete properties. Although, at first, the aggregate was considered as an inert material, dispersed in the cement paste, today, the conception regarding the aggregate role in concrete is changed being regarded as a material linked in a cohesive whole through cement stone. The physical, thermic and sometimes the chemical properties of aggregates influence the concrete performances. Aggregate costs are much lower compared to the cement and thus, it is indicated for aggregate to be used as much as possible [1].

Different types of materials can work together with concrete or can participate in its structure, like industrial by-products or different wastes. Numerous studies were mainly focused on replacing the cement with different quantities of fly ash, slag or ultrafine silica [2]. Replacing the aggregate with industrial by-products remained secondary since the price of this concrete component is lower.

In the first stage, aggregate replacement was done using metallurgical slags, in different compositions, for civil and hydrotechnical constructions or for roads. First tests, using these

aggregate replacements satisfied mechanical strength imposed by the natural aggregate concretes yet it is necessary to deepen the studies on concrete types, being required tests specific to each concrete type [2].

For construction concretes, replacement of natural aggregates with slag aggregates leads to higher concrete densities, recommending these concretes in foundations or massive constructions (hydrotechnical constructions for example) thus, other analyses are imposed: permeability and freezing-thaw resistance [3].

Linz-Donawitz (LD) slag is a type of industrial by-product that was used as partial replacement of aggregate in a former study [4], and promising results were obtained. The burden of the mentioned study was the weathering of the industrial by-product through the process named carbonation with the purpose to diminish the CaO content, responsible for slag swelling in prolonged contact with water. Different studies regarding mineral carbonation of LD slag also occurred [5-8], and the process, although rapid and efficient remains costly. The present study aimed using an already marketed material obtained from the same LD slag, namely LiDonit.

LiDonit utilisation may offer great economic and ecological benefits. This product, which is a trademark of the German industrial group ThyssenKrupp, through its DSU division [9], is successfully used for roads and railroads construction in Europa, being legally approved in different countries for these purposes. Although it has a greater

porosity than that of traditionally used natural aggregates, the LiDonit, with a special crystallin-mineralogical composition, can compete with the hardest rocks regarding their wear, impact and compression resistance. Obtained by slag crushing, the LiDonit granules are polyhedral in shape, with sharp edges and corners and roughened faces. Also, the density which is 20% higher and in appearance seems a defect, helps this material to increase its auto-compacting characteristic. All these features make this secondary product of the Linz-Donawitz process a material fit to be used especially in the construction of roads in all road layers [10].

The utilization of LiDonit in road construction is well documented [11] and already a success in many construction sites. This paper aims to present an alternative for the use of this material, namely as partial replacement of aggregate in concretes. Increasing the utilization of slag derived materials will drive the reduction of piled by-products from the steel industry and the impact to the environment along with it. In this regard, two concrete recipes were chosen, and five concentrations of natural aggregate-LiDonite mixtures for each type of the two concrete recipes. The final purpose was to demonstrate through relevant laboratory tests the optimal mixture of the LiDonit containing aggregate.

2. Materials and methods

2.1. Aggregates

The materials used as aggregates were divided in three sorts: 0/4 mm; 4/8 mm and 8/16 mm. The first two sorts used in this work were of natural provenience and since LiDonit is usually commercialised as coarse aggregate, in this study the replacement of natural aggregate was realised only for the 8/16 mm type sort (out of the three sorts considered). The grades of coarse aggregates must be

determined by using the dimensions of the sieves presented in SREN 12620+A1: 2008. Thus, the general characteristics of the granulosity is expressed as a percentage of mass transfer of the aggregate with the respective tolerances presented in SREN 12620+A1: 2008 [12].

LD slag is formed during steel production using a technique developed in Linz and Donawitz (both in Austria). LiDonit is produced by adding silicates and oxygen to the still liquid slag to prevent possible expansion and guarantee stability. Under quality monitoring regulations, its construction- and environment-related parameters are subjected to regular internal and external checks to guarantee a high-quality building material product [13].

2.2. Cements

Two types of binders were used in this study, namely the CEM II A-V/42,5R and CEM III A-42,5N-LH class cements. Both types were obtained by using industrial wastes in their content, CEM II A-V/42,5R type cement contains fly ash while CEM III/A 42,5 N-LH type cement contains granulated blast furnace slag, making the two concrete recipes used in this paper even more environmentally friendly. The selected binders are typically used in civil and industrial constructions, hydrotechnical constructions, roads, bridges *et al.* [14].

2.3. Obtaining concrete samples

The concrete samples were obtained by mixing cement, water, a superplasticizing additive and aggregates in fixed quantities except for water. Water quantity was varied so that the workability met the standards [14]. The variation of water to cement ratio can be observed in Figure 1 and is represented for each concrete recipe using the two types of binders.

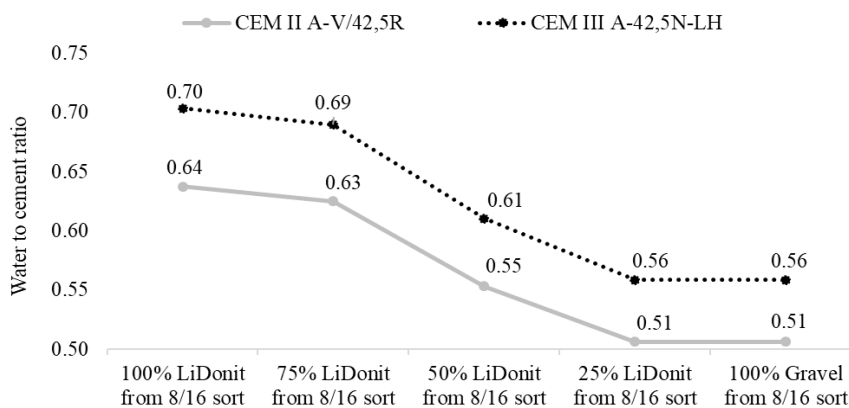


Fig. 1. Representation of water to cement ratio used for each concrete recipe

Figure 1 also presents the weight percentage of LiDonit used to replace gravel (the 8/16 mm aggregate sort). Thus, as it is observable in the figure, five different recipes for each type of cement were chosen as follows: 100%, 75%, 50% respectively 25% LiDonit out of the 8/16 mm sort and 100% gravel as 8/16 mm aggregate sort.

2.4. Testing procedures

Different types of tests were used to analyse the aggregate mixtures and then each concrete recipe. Aggregate mixtures were tested from the granulometry, shape coefficient and degree of wear point of view, while concrete samples were analysed,

before hardening, from the density and workability point of view. After hardening (curing), concrete samples were analysed regarding their compressive strength, impermeability and freezing-thaw resistance properties. All tests were conducted according to the existing norms [12, 14-41].

3. Results and discussions

Prior to concrete recipes formation, LiDonit containing aggregate mixtures were analysed and compared with all-natural aggregate mixtures using three above mentioned tests: granulometry, shape coefficient and degree of wear.

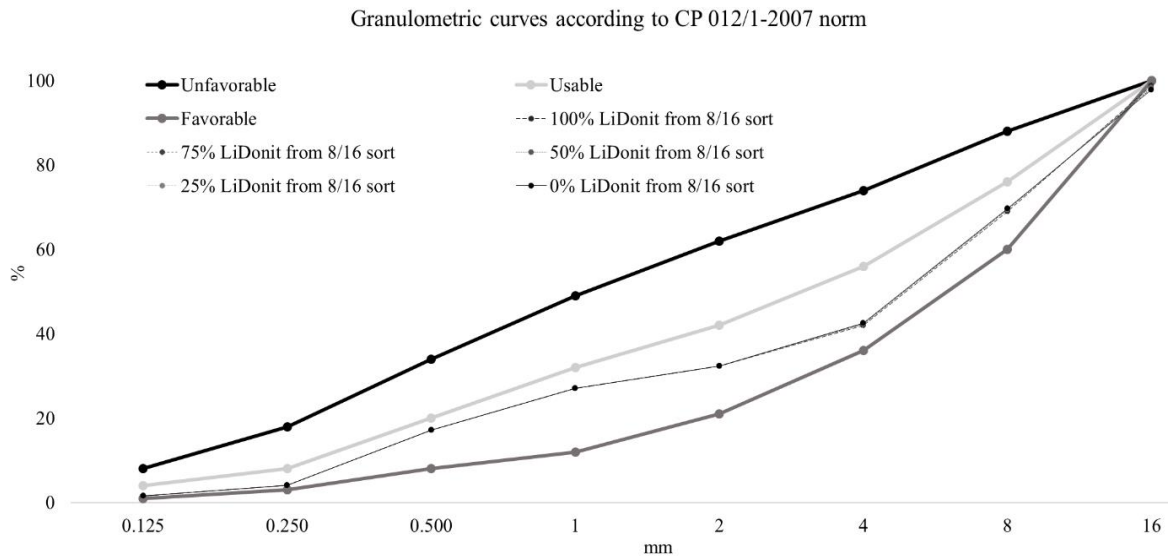


Fig. 2. Granulometric curves for all aggregate mixtures used in this study, compared to the unfavourable, usable and favourable limits, according to CP 012/1-2007 norm

From the first mentioned test results point of view, all mixtures, with small differences, are between usable and favourable curves, meaning that the granulometry of all aggregate mixtures is in accordance to the standards (Figure 2).

As for the shape coefficient results, Figure 3 presents the limit of this type of analysis set by the appropriate normative. The maximum for this test, namely 25%, was exceeded only by the LiDonit 8/16 mm sort, while for the 4/8 mm and 8/16 mm sorts the values were well below the admissible value. This test is important in order to determine mass of all plate and acicular granules from the analysed sample and the higher-than-admissible value for LiDonit 8/16 mm sort is not of great concern since the purpose of this work was to establish the optimal degree of natural aggregate replacement with this metallurgical

by-product. If replacing 50% of the natural 8/16 mm aggregate sort with LiDonit of the same granulometry, the average value for the shape coefficient test would still be under the maximal admissible value set by the utilized standard.

The last test involving the aggregates used in this study was the one regarding the wear degree, using a Los Angeles type machine. The test results (Figure 4) showed a good behaviour of the LiDonit 8/16 mm aggregate sort, compared to the same sort of the natural provenience material, both samples recording results under the maximum 30% established by the standard.

Thus, the results from three tests used for the aggregates proves the viability to use the LiDonit material as partial replacement of natural aggregate in some concrete recipes.

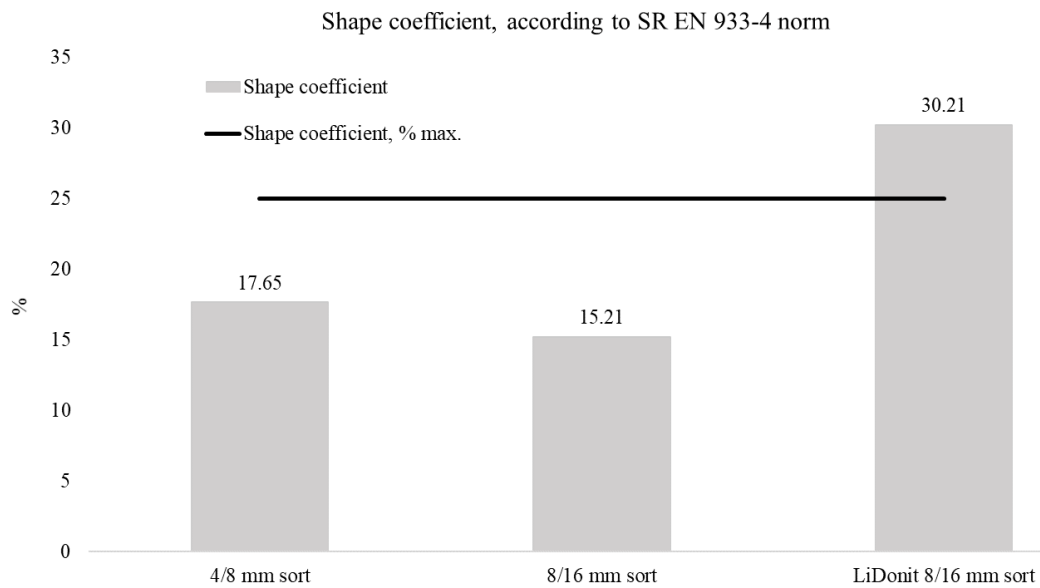


Fig. 3. Results of the shape coefficient test for 4/8 mm, 8/16 mm and LiDonit 8/16 mm sort, compared to the highest limit established through SR EN 933-4 norm

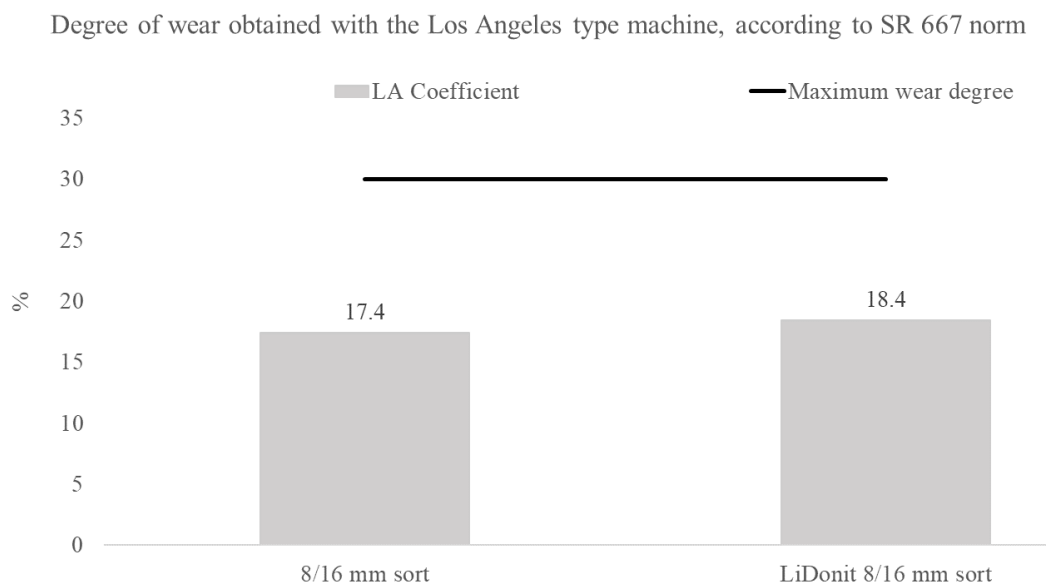


Fig. 4. Values from the wear degree of natural 8/16 mm and LiDonit 8/16 mm sorts obtained with the Los Angeles type machine and compared with the maximum admissible, according to the SR 667 norm

After mixing all components, before curing, the obtained samples were first tested from the workability and density point of view. Table 1 presents the results of workability test. Data for this type of test shows a variety of results depending on the LiDonit content. For samples obtained using the CEM II/A-V type cement, the values for workability increases with LiDonit content while for the samples obtained using the CEM III/A type cement, the values decrease with LiDonit content increase. LiDonit,

being a porous material, is expected to cause workability decrease if used in higher quantities thus, data for samples obtained using CEM III/A type cement was expected. However, the exceeding of 50-150 mm required minimum is considered acceptable and may be attributed to the human error during sample preparation. The workability test results indicate that an aggregate replacement with LiDonit might be feasible at least for the 25-50% of the 8/16 mm aggregate sort.

Table 1. Results from the workability test for all mixtures

CEM II/A-V	100% LiDonit from 8/16 sort	75% LiDonit from 8/16 sort	50% LiDonit from 8/16 sort	25% LiDonit from 8/16 sort	0% LiDonit from 8/16 sort	Minimum required [mm]
Workability [mm]	160	180	160	155	155	50-150
CEM III/A	100% LiDonit from 8/16 sort	75% LiDonit from 8/16 sort	50% LiDonit from 8/16 sort	25% LiDonit from 8/16 sort	0% LiDonit from 8/16 sort	Minimum required [mm]
Workability [mm]	120	135	145	155	150	50-150

As for the density measurements, presented in Table 2, for the same sample types as for the workability tests, results show a decrease in density for almost all samples with higher than 25 % LiDonit content out of the 8/16 mm aggregate sort. Although the values are small enough for the samples to be

considered acceptable, the obtained results indicate a certain increase in volume for the samples with higher LiDonit content. Again, as for the workability test, the indicated LiDonit content is also considered optimum between 25-50% out of the 8/16 mm aggregate sort, from the density point of view.

Table 2. Density test results for all mixtures

CEM II/A-V	100% LiDonit from 8/16 sort	75% LiDonit from 8/16 sort	50% LiDonit from 8/16 sort	25% LiDonit from 8/16 sort	0% LiDonit from 8/16 sort	Planned [kg/m ³]
Fresh concrete [kg/m ³]	2349	2337	2332	2327	2340	2413
Hardened concrete [kg/m ³]	2383	2361	2353	2326	2320	2400
Difference between fresh and hardened concrete [kg/m ³]	-34	-24	-21	1	20	13
CEM III/A	100% LiDonit from 8/16 sort	75% LiDonit from 8/16 sort	50% LiDonit from 8/16 sort	25% LiDonit from 8/16 sort	0% LiDonit from 8/16 sort	Planned [kg/m ³]
Fresh concrete [kg/m ³]	2379	2349	2379	2327	2380	2413
Hardened concrete [kg/m ³]	2400	2360	2352	2324	2340	2400
Difference between fresh and hardened concrete [kg/m ³]	-21	-11	27	3	40	13

Hardened samples of concrete, with various content of LiDonit replacing the aggregate, were tested for the compression strength (Figures 5 and 6), after 7 and 28 curing days. This test demonstrated that aggregate replacement with LiDonit may be feasible for concrete recipes using some type of cements. In this case, the samples obtained using CEM II/A-V type cement registered higher values of compression strength for all (after 7 or 28 curing days) LiDonit contents, compared with the samples obtained using CEM III/A type cement. Moreover,

for the samples obtained using the CEM III/A type cement, after 7 curing days, only the one with 25% of LiDonit as replacement for the 8/16 mm aggregate sort, obtained a compression strength value higher than the minimum required, while the other samples registered lower values. For the same type of concrete samples, after 28 curing days, all samples with LiDonit content registered values lower than the minimum required. On the other hand, for all samples obtained using CEM II/A-V type cement, the compression strength results were above the

minimum required with values decreasing with LiDonit content increase. The value for the compression strength test closest to the one of the LiDonit free sample was registered for the 25%

replacement of 8/16 mm aggregate sort, making this content the preferable one proposed for the samples using CEM II/A-V type cement.

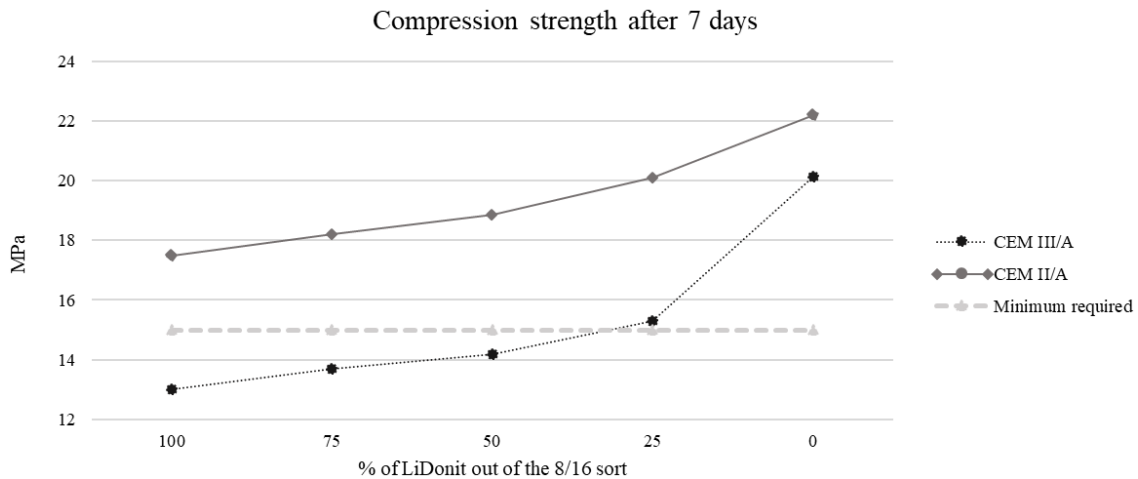


Fig. 5. Compressive strength test for all mixtures after 7 days curing

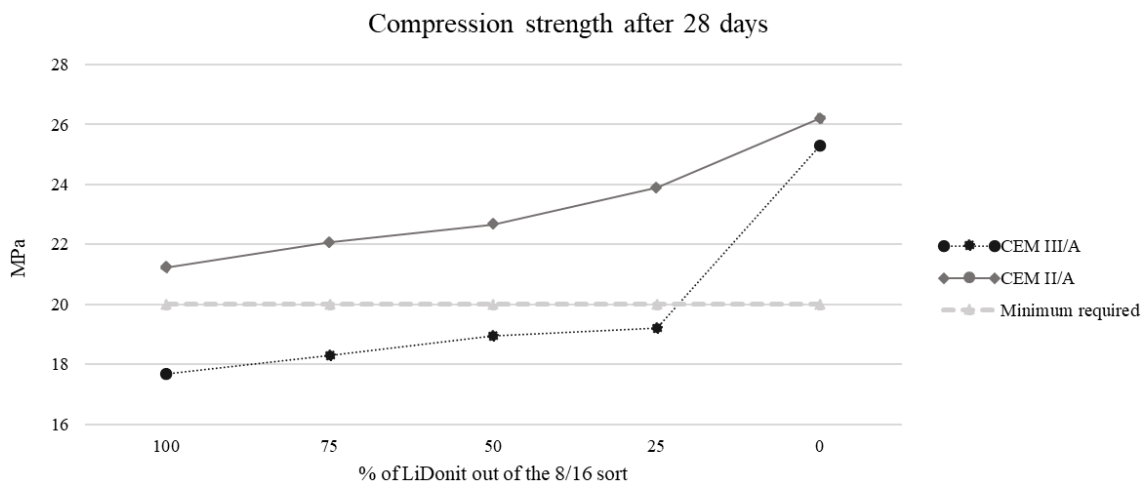


Fig. 6. Compressive strength test for all mixtures after 28 days curing

Further tests were performed to observe the possibility of LiDonit utilization as aggregate replacer namely impermeability and freezing-thaw resistance tests. Results of these tests are presented in Tables 3-5. The samples used for these tests were obtained using only the CEM II/A-V type cement, since samples using this type of binder behaved within standard limits for all earlier tests. As for the LiDonit content, for these two last tests, only a 100% LiDonit replacement of 8/16 mm aggregate sort and a 100% gravel out of the 8/16 mm aggregate sort were used. Again, for both later tests, blocks of 150x150x150 mm samples were used. Regarding the impermeability test, results showed a higher water penetration for the LiDonit containing samples (an

average of 38 mm compared to an average of 21 mm) yet well within the admissible limit of 100 mm. Therefore, one can only extrapolate, and will certainly obtain a smaller value for the samples containing 25% LiDonit content out of the 8/16 mm aggregate sort, which was stated to be the preferred case for the concrete using CEM II/A-V type cement.

From the last test performed we retrieved different types of data (initial/final mass, initial/final dimensions, compressive force, section surface, initial/final density, compression strength, observed and expected loss in resistance) from which we can observe small differences between the two samples analysed. The most important values from this test are considered to be the ones from the observed and

expected loss in resistance. As expected, this loss in resistance is infimal for the samples containing 100% gravel out of the 8/16 mm aggregate sort. Also, a small difference (3.90% for LiDonit containing sample, compared to 2.20% for gravel containing

sample) and well below the maximum accepted value (25%), was obtained for the LiDonit containing sample. Once again, one can only extrapolate a loss in resistance value for a sample with less LiDonit content.

Table 3. Impermeability test results for the most relevant concrete mixtures

CEM II/A-V		Sample 1	Sample 2	Sample 3
100% LiDonit 8/16 mm sort	Sample dimensions [mm]	150x150x150	150x150x150	150x150x150
	Limit of depth penetration [mm]	100	100	100
	Depth penetration of water in sample [mm]	35	38	41
	Average of water penetration in samples [mm]	38		
100% Gravel 8/16 mm sort	Sample dimensions [mm]	150x150x150	150x150x150	150x150x150
	Limit of depth penetration [mm]	100	100	100
	Depth penetration of water in sample [mm]	25	21	17
	Average of water penetration in samples [mm]	21		

Table 4. Results from the freezing-thaw resistance test (50 cycles) for the sample of concrete containing 100% LiDonit from 8/16 mm sort and CEM II A-V 42,5R type cement

	Witness sample 100% LiDonit		Sample used in freezing-thaw resistance test 100% LiDonit	
Initial mass M_i [g]	7.773	7.743	7.742	7.737
Final mass [g]	7.785	7.755	7.729	7.726
Initial dimensions [mm]	150/150/150	150/150/150	150/150/150	150/150/150
Final dimensions [mm]	150/150/150	150/150/150	150/150/150	150/150/150
Compressive force [kN]	571.5	580.5	477.0	479.7
Section [mm ²]	22500	22500	22500	22500
Initial density [kg/m ³]	2303	2294	2294	2292
Final density [kg/m ³]	2307	2298	2290	2289
Compression strength [MPa]	23.40	23	21.20	21.32
	Average result - 23.2		Average result - 21.26	
Observed loss in resistance [%]	3.90			
Expected loss in resistance [%]	Maximum allowed – 25			

Table 5. Results from the freezing-thaw resistance test (50 cycles) for the sample of concrete containing 100% gravel from 8/16 mm sort and CEM II A-V 42,5R type cement

	Witness sample 100% gravel		Sample used in freezing- thaw resistance test 100% gravel	
	Initial mass Mi [g]	7.890	7.850	7.820
Final mass [g]	7.920	7.950	7.880	7.885
Initial dimensions [mm]	150/150/150	150/150/150	150/150/150	150/150/150
Final dimensions [mm]	150/150/150	150/150/150	150/150/150	150/150/150
Compressive force [kN]	585	580.5	585	590
Section [mm ²]	22500	22500	22500	22500
Initial density [kg/m ³]	2337	2326	2317	2320
Final density [kg/m ³]	2347	2355	2334	2336
Compression strength [MPa]	26.20	25.80	26	26.22
	Average result - 26		Average result - 26.11	
Observed loss in resistance [%]	2.20			
Expected loss in resistance [%]	Maximum allowed – 25			

4. Conclusions

Two types of binders were used in this study. The first (CEM II A-V42,5 R) containing 80-94% Portland clinker and 6-20% thermal power plant fly ash. The second type (CEM III/A 42,5 N-LN) containing 36-65% blast furnace granulated slag and Portland clinker as balance. Tests showed a higher need for water in case of samples obtained with CEM III/A type cement than the other one, and a higher value of compression test (approximately 2-3 MPa) for CEM II/A-V. The two differences, although not important, are clearly a consequence of using industrial wastes in binder production.

Further on, replacement, in various degrees (100%, 75%, 50% and 25%), of 8/16 mm aggregate sort (out of natural 0/4 mm, 4/8 mm and 8/16 mm aggregate materials) with LiDonit (a steelmaking by-product) was realised for multiple tests. Regarding the granulometric curve for all aggregates, all mixtures (with or without LiDonit content) fell between the admissible limits. For all the other tests (water absorption, water to cement ratio, density, compression strength, wear resistance and freezing-thaw resistance), the increase of LiDonit content as

8/16 mm aggregate replacer, resulted in gradually worsening values for the tested samples.

Although LiDonit presents a higher porosity than the natural 8/16 mm aggregate, its crystalline mineralogical content makes it good at impact and compression tests. Also, its obtaining from crushed raw slag leads to polyhedral-shaped granules with sharp edges and corners and many rough faces (apparently a drawback) which along with a higher density develops an important property, namely auto compaction. Thus, although in high amounts the properties of samples are worsened, we can conclude that for some concrete types (using CEM II/A-V in the present study) the replacement of, at least, 8/16 mm aggregate sort is feasible in amounts of 25%. This percentage of aggregate replacement with LiDonit and the replacement of 6-20% Portland clinker, from cement obtaining, with thermal power plant fly ash, makes this concrete recipe feasible, to be used at least in foundations works, and more environmentally friendly.

Further work regarding aggregate replacement with LiDonit in concrete, might be focused on using binders containing 100% Portland clinker. Also, other steel industry by-products might be used as aggregate replacement and all aggregate dimensions can be targeted.

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REINFORCED Al-MATRIX COMPOSITES WITH Ni-ALUMINIDES, PROCESSED BY POWDERS

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ABSTRACT

The paper addresses issues of interest related to the uniform distribution of the reinforcement phase and the continuity of the metal matrix, for two ways of obtaining the powder composites, the hot extrusion and the spark plasma sintering (SPS) respectively. The reinforcement phase is the nickel aluminides obtained by mechanical alloying in ball mills, and the metal matrix is made of aluminum powders. Prior to extrusion, the mixture of aluminum powders and nickel aluminides was pressed and subsequently sintered in environments with high carbon potential, so that in the final product, nickel aluminides, carbide and aluminum oxides were found as reinforcement phases. The obtained results confirmed the hypothesis that, from a blank product with a random distribution of the reinforcement phase, a product with an ordered distribution of the reinforcement phase is obtained after extrusion and that for the same initial proportion of nickel aluminides as reinforcement phase, the composite hardness obtained by hot extrusion is higher compared to that obtained by SPS, the difference being determined by the increase of the proportion of the reinforcement phase by the appearance of aluminum carbide and aluminum oxides during the sintering operation in the high carbon environment.

KEYWORDS: Ni-aluminides, mechanical alloying, hot extrusion, Spark Plasma Sintering (SPS), coated composite particles

1. Introduction

Aluminum and its alloys represent an important class of materials due to their versatile properties. This aspect allows its use in a wide range of applications, many of them having it as a matrix in which hard phases are included, with high thermodynamic stability. The refractory intermetallic compounds in the Al-Ni system are of particular interest due to their intrinsic characteristics, their presence increasing the operating characteristics of the matrices that contain them. In the presence of nickel aluminides dispersed in the aluminum matrix, there is a substantial increase in wear resistance, hardness, oxidation resistance, improvement of carburizing and nitriding processes, as well as thermodynamic stability. Nickel aluminides represent phases with high potential for increasing the performance of metal or light alloys. Of the five aluminides present in the Al-Ni system (Al_3Ni_2 ,

Al_3Ni_5 , Al_3Ni , $AlNi_3$, $AlNi$) [1, 2], the last two are characterized by extremely high thermodynamic stability at temperatures above 1000 °C, associated with ductility, hardness, high mechanical resistance associated with oxidation resistance, carburizing and nitriding [3].

The conclusions of a large experimental research conducted by Gessinger [3], led to the idea that obtaining composites containing intermetallic compounds (IMCs) such as nickel aluminides, through the traditional steps of powder metallurgy (pressing at ambient temperature followed by sintering), does not lead to satisfactory results, for two main reasons: i) the magnitude of the elastic recovery phenomenon after pressing, determined by the nickel aluminides hardness and thus their reduced plasticity; ii) the substantial decrease of the capillary forces in the presence of mechanically allied powders particles of large dimensions (60-100 μm) and with

high hardness, phenomenon that determines the substantial shrinkage reduction during sintering [3].

Consequently, the conventional technologies for the manufacture of such composites should combine the two pressing and sintering steps into one, so that by changing the character of the aluminide from fragile to ductile, it becomes possible to ensure the desired densification and imposed physical and implicit structural features [3, 4].

The main methods of processing composites containing reinforcement phases such as nickel aluminides are hot isostatic pressing, electric current activated/assisted sintering (ECAS), widely known as spark plasma sintering (SPS) and hot pressing (hot extrusion process derived from it) [5].

2. Materials and experimental methods

The aluminium and nickel powders used in this research were obtained by air spraying (aluminium powder, purity ~92 %, manufactured by Zlatna, Romania), or by Sherritt Hydrometallurgical process

(purity 99.9% manufactured by Alfa Aesar part of Thermo Fisher Scientific, Germany). In order to obtain the Al-Ni powder mixtures designed for mechanical alloying, have been used aluminium powder with an average diameter of 12.5 μm and nickel powder with an average diameter of 90 μm , dispersed in equal proportion.

The mechanical alloying was made in ball mills (2.5 l volume capacity), at 85% of the critical speed value (~102 rot/min), so that the released energy would be 8 J/rot (about 13 J/s), at one about 11:1 ratio between the mass of the milling balls and that of the powder mixture, consisting of equal mass proportions of aluminium and nickel powders.

The calculation of the total energy released by the milling bodies took into account the mill geometrical and functional characteristics, the milling bodies and the powder mixture masses subjected to processing, and so on [6-12].

The experimental research steps are presented in the form of a scheme, as shown in Figure 1.

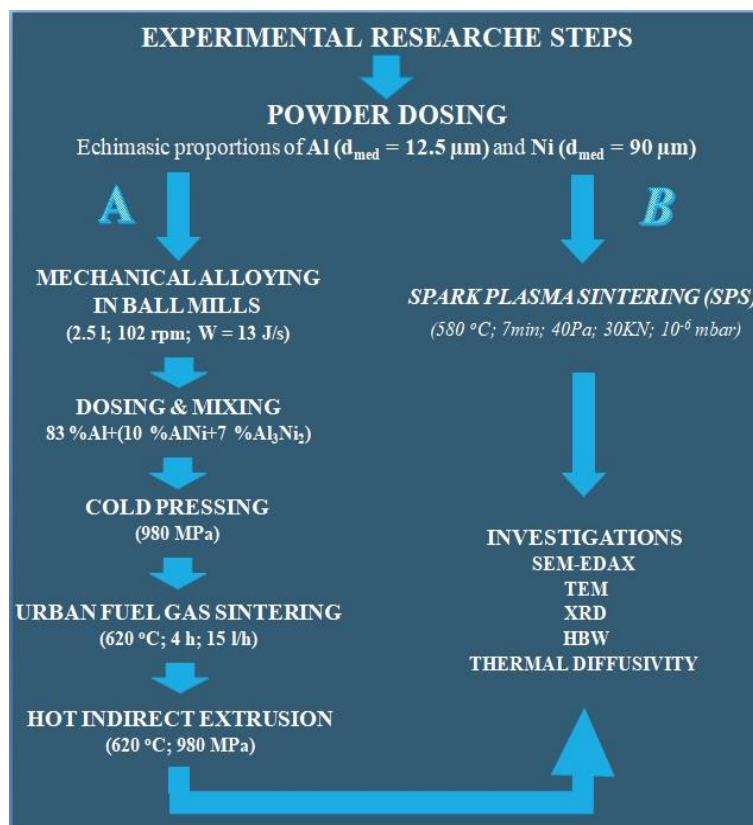


Fig. 1. Experimental research steps

Cold pressing was performed hydraulically (60 tf), with uniaxial and unilateral effort application; the same press was used for extrusion, the extrusion die being heated to 650 °C. Heating for sintering was

carried out in a furnace provided with automatic temperature control (UTTIS Industries-Romania), at a temperature value below that of melting the aluminum matrix (620 °C), maintenance for 4 hours,

in an environment resulting from the thermocatalytic dissociation of urban fuel gas, which contains about 85% methane, at a flow rate of 15 l/h.

SPS was performed on a spark plasma sintering furnace for field assisted sintering technique (FAST), from FCT Systeme GmbH, HPD5 type facility, from Germany.

The results obtained under the different processing conditions, were investigated aiming to highlight the microstructural changes involved and the physical and mechanical properties.

Scanning electron microscopy (SEM -TESCAN VEGA XMU 8 microscope), EDS (EDAX Sapphire type dispersive energy spectrometer with the resolution of 128 kV), X-ray diffraction (APD 2000

diffractometer), transmission electron microscopy (TEM - JEM ARM microscope 200F; the samples were prepared by mechanical thinning, followed by precision ion polishing at small incidence angles, in argon atmosphere, with the aid of a GATAN PIPS System Model 691), appliance were used.

In order to highlight the physical and mechanical characteristics changes, a Heckert hardness tester, series 308/278, was used. For the tests performed, the device was equipped with a tungsten monocarbon ball of 2.5 mm in diameter, applying at a 612.9 N load. Hardness measurements (HBW_m) were performed according to the DIN EN ISO 6506, and the data has been processed according to the "Arghir" methodology [13, 14]:

$$HBW_m = 1/6n(n \times HBW_0 + 3n \times HBW + 2n \times HBW) \quad (1)$$

where:

HBW_m is the average value of macrohardness;

HBW₀ represents the hardness measured in the center of the sample;

HBW is the value of the macrohardness at half sample radius.

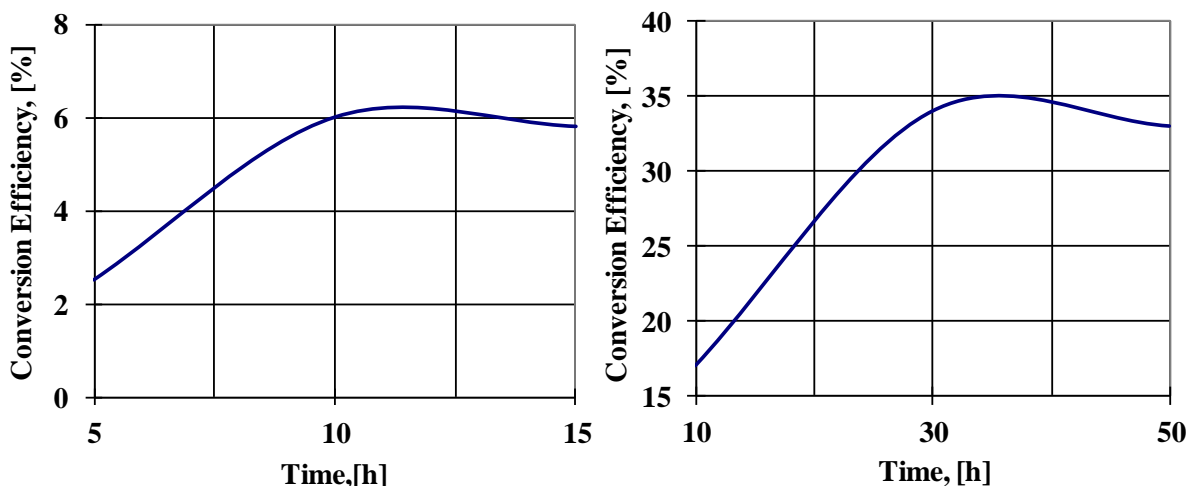
Thermal diffusivity (α) tests were performed on a Netzsch apparatus, model LFA-457, at 20 °C. The principle of design, construction and operation of the apparatus is based on the flash method.

The results of the diffusivity measurements are the average of six tests.

3. Results and discussions

The elemental aluminum and nickel powders conversion into intermetallic compounds (IMCs), during mechanical alloying in ball mills, depends directly on the energy released by the milling balls (W) and the grinding time, as it is shown in Figure 2.

Thus, the increase of the energy released by the milling balls has the first effect of increasing the conversion efficiency (compare Figure 2a with 2b), and as it increases, the ratio between the Ni-rich and the Al-rich aluminides respectively changes [8].



Note - To highlight the effect of the energy low values (<1 J/rot - Figure 2a) on the conversion efficiency, a ceramic mill with a useful volume of 1.5 l was used, the ratio of the balls mass to the load mass was 3:1

Fig. 2. Conversion efficiency variation according to the energy released by the milling balls and the processing time: a) energy of 0.7 J/rot at 102 rpm; b) energy of 7 J/rot at 102 rpm

In the present case, for the energy values of the milling balls below 1 J/rot, the mechanical alloying

will lead to Ni-rich aluminides (Al₃Ni₅) higher values obtaining. At higher values, Al-rich aluminides

(AlNi, Al₄Ni₃, Al₃Ni₂) will be the majority. In time, the production rate of the elemental powders mixture conversion into intermetallic compounds decreases, so that the prolongation of the milling under certain energetic conditions becomes inefficient.

Starting from these conclusions, obtaining nickel aluminides by mechanical alloying in ball mills was performed under the conditions: W = 7 J/rot; n = 85 % ncr = 102 rpm; t = 30 hours. Under these conditions, starting from an equal weight mixture of elemental aluminium and nickel powders, a new powders mixture containing 34 % nickel aluminides (20 % AlNi and 14 % Al₃Ni₂) resulted. This new mixture was used as the reinforcing phase of the powdered aluminum matrix.

The blank product for hot extrusion was done by pressing (980 MPa). Sintering was carried out in the urban fuel gas atmosphere from the industrial network (about 85 % CH₄), at the following parameters: 620 °C, 4 hours; 15 l/h urban fuel gas). The powder mixture was made up of 50% aluminium powder and 50% mechanically allied powder containing about 17% nickel aluminides (AlNi + Al₃Ni₂).

The formed sinter/composite microstructure (Figure 3) is characterized by a relatively uneven distribution of the reinforcement phase in the metal matrix.

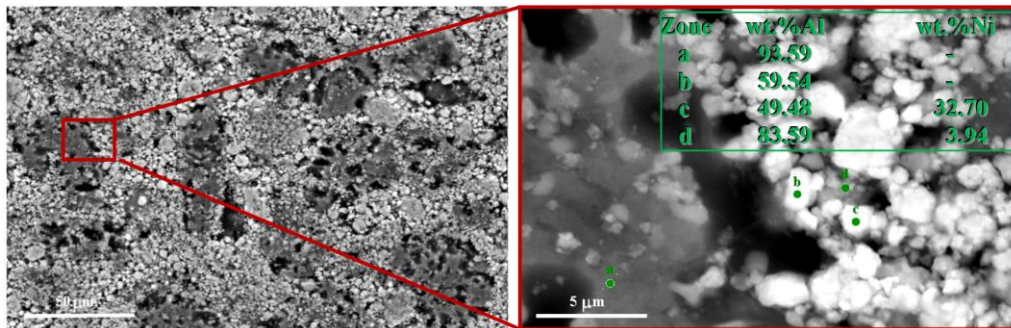


Fig. 3. SEM-EDS images of the aluminium matrix hardened with 17 % nickel aluminides (10 % AlNi and 7 % Al₃Ni₂), with elemental composition details in different interest microvolumes

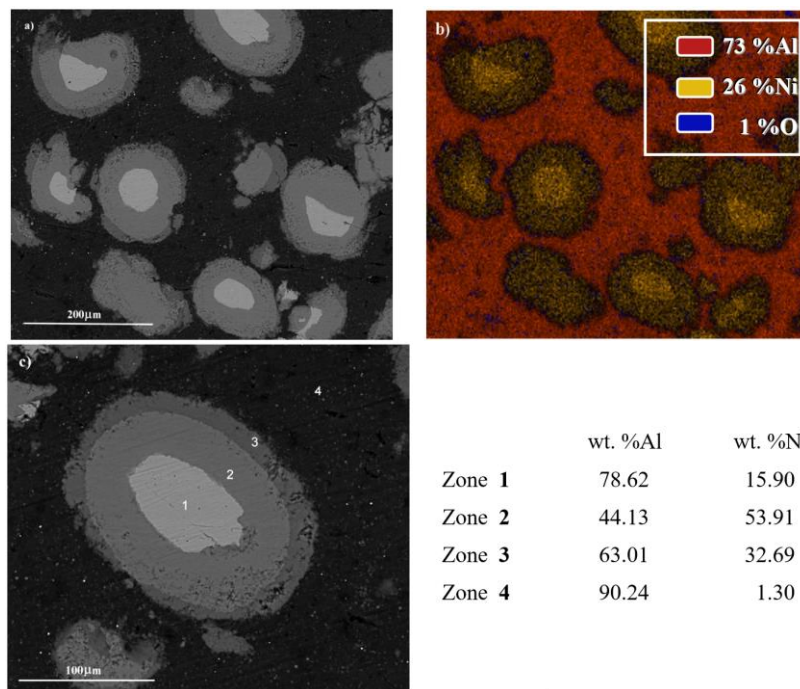


Fig. 4. SEM images of the sintered and hot extruded material: a) image of secondary electrons; b) EDS image for elemental distribution; c) the cross-section composite particle with the Al and Ni elemental distribution, by EDS spectrometry table

Its average macrohardness has values of 58 HBW, the thermal diffusivity at ambient temperature being 4.85 mm²/s (5 % of the value related to the technical purity aluminium), and the thermal conductivity being 29.7 W/mK (12.5 % of the value related to the technical purity aluminium).

By hot extrusion of the pressed and sintered composite (Figure 4), an ordering of the reinforcement phase in the flow direction is obtained

(Figure 4b) and a significant increase of the macroductility of 2.77 times higher than that of the sintered composite.

To this high value of the macrohardness, besides the nickel and oxide aluminides and respectively the aluminum carbide, during the sintering in urban fuel environment formed.

X-ray diffraction pattern (Figure 5) confirms the presence of aluminum carbides and oxides.

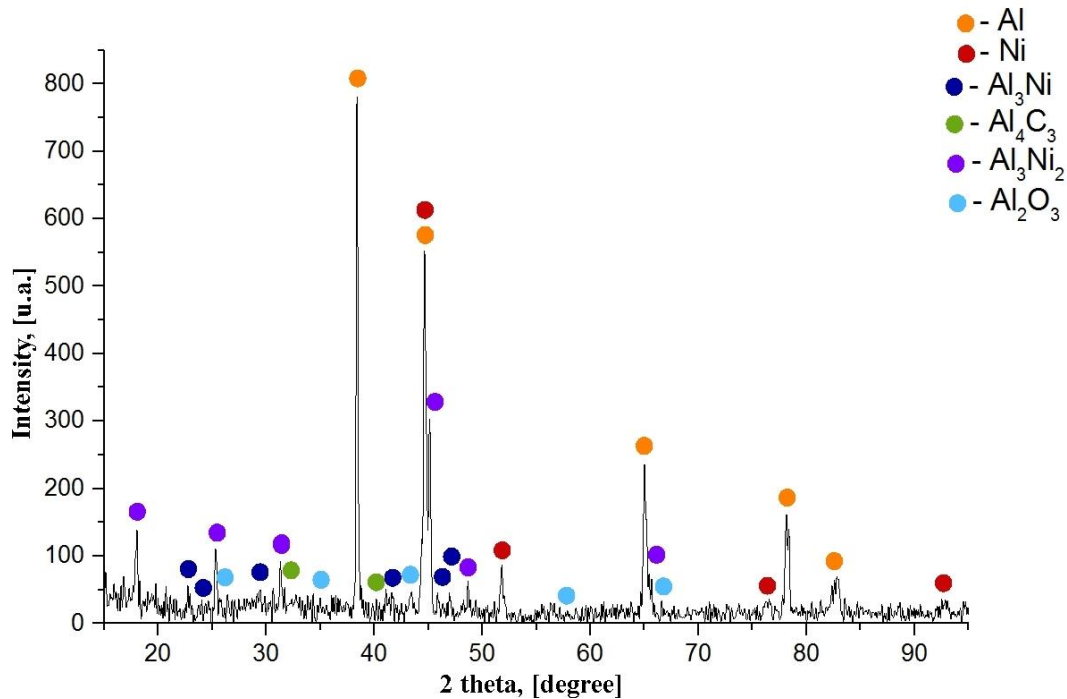
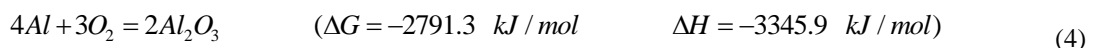
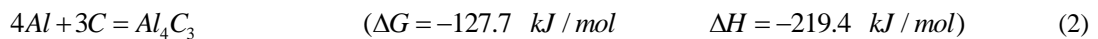


Fig. 5. X-ray pattern of the extrudate with 17 % nickel aluminides (10 %AlNi and 7 %Al₃Ni₂) and aluminium balance

The aluminium carbide and aluminium from a thermodynamic point of view, as it shown in formation and growth respectively is extremely likely the reaction (2-4) [15]:



The carbon required for aluminum carbide synthesis can come from both the magnesium stearate (C₃₆H₇₀MgO₄) decomposition, a lubricant used for mixtures homogenizing and obviously for extrusion, as well as from the methane used as a sintering medium (CH₄ thermocatalytic decomposition products).

The aluminum oxide is formed during sintering and is preferentially distributed within the boundary area, as it is shown in Figure 4 b,c).

High resolution TEM investigations revealed the presence of oxide films at the matrix interface with the aluminum powder particles, respectively aluminides boundary, as it is shown in Figure 6.

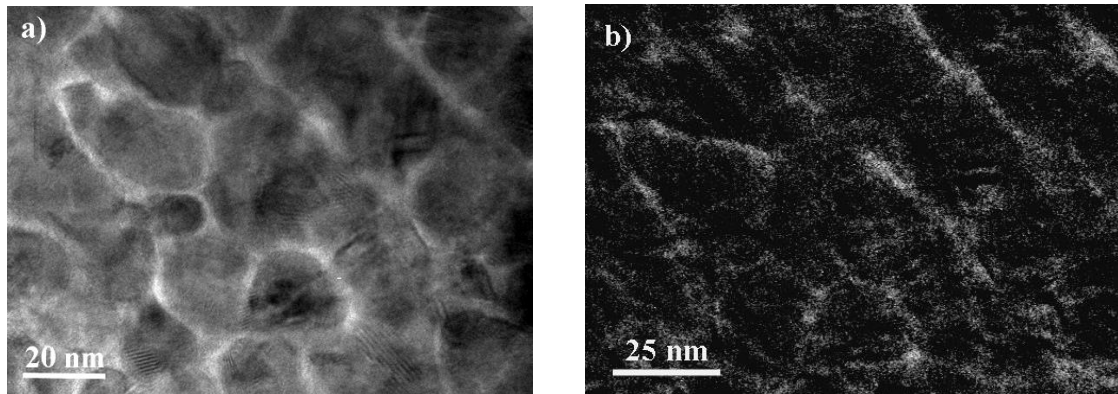


Fig. 6. High resolution TEM images of the aluminum matrix hardened with nickel aluminides: a) high resolution image; b) Oxygen mapping

The particularities of the indirect hot extrusion operation, carried out after sintering, according to the triaxial stress scheme (S1), ensure the possibility of producing blank products without discontinuities [16].

The reinforcement phase (including the oxides initially disposed predominantly at the boundaries) is thus uniformly distributed and preferably oriented in the deforming direction.

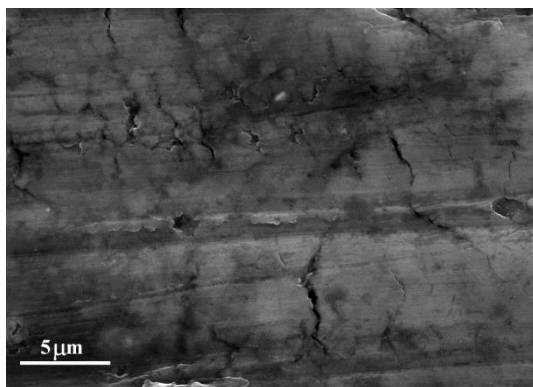


Fig. 7. SEM image of the composite material after the final hot pressing at 350-400 °C, 980 MPa

If the extrusion after the sintering is replaced by a hot plastic deformation, at 350-400 °C (also using the heat stored on the sintering), the spatial stress scheme modification from S1 (triaxial compression) to S3 (compression and two extensions), definitely generates discontinuities in blank, also verified by experiment, the SEM image in Figure 7 being representative.

The SPS ensures the possibility of substantially shortening the general technological cycle of composite materials, resulting in a relatively uniform distribution of the aluminides in the aluminum matrix (see Figure 8).

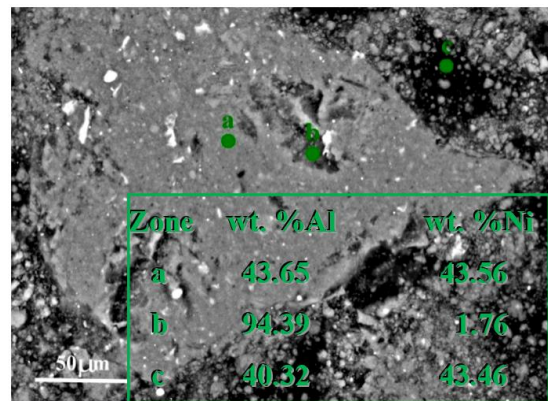


Fig. 8. SEM image of the composite material obtained by SPS in the processing conditions 580 °C, 7 min, 40 Pa, 30 kN and the elemental analysis table by EDS spectrometry in the areas of interest

Macrohardness will increase by about 80% compared to that of composites made by cold pressing and sintering (100 HBW versus 56 HBW), the thermal diffusivity will be reduced by half compared to that of sintered aluminum (41 mm²/s compared to 82 mm²/s).

4. Conclusions

Mechanical alloying in ball mills, at over 8 J/rot value of the energy released by the milling balls, can provide in about 30 hours the conversion yields of the elemental aluminum and nickel powder mixtures in Al-rich nickel aluminides, on the order of 30 percent.

The hot extrusion applied to the semi-finished products made of mixed nickel aluminum/aluminide powders pressed and subsequently sintered in atmospheres with high carbon potential, ensures a high density of the composite and a continuity thereof. At the same time there is an ordering of the

reinforcement phase in the material deformation direction during extrusion.

Under the special conditions of hot extrusion, it is possible to form composite particles with a morphology analogous to the of the coated one.

The average macrohardness of the aluminum matrix composites reinforced with nickel aluminides is about 58 HBW, which is also justified by the presence of carbide and aluminum oxides respectively, phases formed due to the high carbon environment potential, in the presence of oxygen.

The extruded matrix continuity, aluminides, carbides and aluminium oxides hardened, is ensured by the S1 space state tensions, which is characteristic of the extrusion process.

The composites production by SPS allows a considerable shortening of the general manufacture technological flow, a satisfactory matrix continuity level, a reinforcement phase distribution depending on the previous homogenization degree, as well as mechanical characteristics superior to those recorded on the products processed by cold pressing, followed by sintering.

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EVALUATION OF CORROSION RESISTANCE OF IMPLANT-USE Ti6Al4V ALLOY IN HANK BIOLOGICAL SOLUTION IN THE PRESENCE OF MICROORGANISM'S METABOLIC PRODUCT LACTIC ACID

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ABSTRACT

Titanium alloys such as Ti₆Al₄V is the most used alloy used as implant for biomedical purposes. The conditions for a biomaterial to be selected for a particular application in the human body is that this should conform to the physical, chemical and biological characteristics, more precisely to be biocompatible, biofunctional and not ultimately sterilizable. Ti₆Al₄V alloy has mechanical properties suitable for many biomedical applications and has excellent corrosion resistance, which depends on the presence of a stable passive oxide film forming on its surface. Our study aims to evaluate the corrosion resistance of Ti₆Al₄V as a function in time with addition of 5 g/L and 10 g/L Lactic acid in biological solution Hank after exposure at 0 h (at immersion time), after 48 h (from immersion) and 168 h (from immersion). The evaluation of corrosion resistance of Ti₆Al₄V in Hank biological solution with addition of two concentrations of Lactic acid it was done by electrochemical methods in terms of open circuit potential and polarization resistance (R_p). Lactic acid is used in this study because it is a component present in human blood in small quantities and is necessary for the metabolic processes used directly by the heart muscle, brain and nervous system. The increased lactic acid content in muscle appears as weight-bearing exercises.

This is why it is important to know how the presence of lactic acid in larger quantities affects the implants. The study also highlights the importance of using longer testing times and more realistic solutions when testing biomedical materials.

KEYWORDS: Electrochemical corrosion; Titanium alloys Ti₆Al₄V; Lactic acid; Biological solution Hank

1. Introduction

The technological advances that have transformed our world over the last 20 years have been based on developments in Materials Science and Engineering. Materials are evolving today faster than ever in history, allowing engineers to improve the performance of existing products and to develop innovative technologies that will improve every aspect of our lives [1].

The field of biomaterials is essential for the development of surgery, allowing the extension of treatment options, more effective treatments and creating opportunities for less invasive treatment. The selection of the material must be correlated with the

chemical and mechanical properties, while maintaining the biocompatibility and safety [1].

The corrosion resistance of the materials is an essential condition for the metals to be introduced into the human body, because the biocompatibility [1-4] of the metal-tissue must be guaranteed so as to avoid any deterioration of the tissue. Biocompatibility is described as the ability of a biomaterial to perform its desired function in relation to medical therapy, without causing undesirable local or systemic effects to the recipient [1-4]. Implantable medical devices are increasingly important in the practice of modern medicine. Unfortunately, almost all medical devices are affected to a different extent by adverse reactions, including inflammation, fibrosis, thrombosis, and infection. In order to improve the safety and function

of many types of medical implants, there is a major need for the development of materials with physical chemical characteristics of the desired surfaces. Because associated with the implant surface are protein adsorption and conformational changes, which promote immune reactions, rigorous research efforts have been highlighted in the engineering of surfaces of biomaterials (physical and chemical characteristics), surface properties to reduce protein uptake and interactions and subsequently to improve implant biocompatibility [1, 5].

Therefore, the biocompatibility of implants can be regarded as a surface phenomenon of biomaterials and response of biological fluids and human tissues to their interaction and to the reactivity of the material / biological interface [1].

The corrosion of the implants is the deterioration suffered as a result of interactions with the biological environment (electrochemical attack), which causes the release of ions into the environment. It is important to note that no metal or alloy is completely inert in vivo. And the phenomena of corrosion at the interface biomaterial - implant and the biological environment are particularly important in the evolution of dental and orthopaedic implants and can cause implant failures after an initial success. Degradation of a metal implant is undesirable because it negatively alters the structural integrity of the implant [1, 6-10].

Corrosion is one of the most important processes that cause problems for metals and alloys that are used as implants in the body [1-2]. In order to minimize these problems, a better understanding of some of the basic principles involved in the corrosion degradation process of biomaterials is needed. The corrosion of implants in the aqueous environment of body fluids occurs through electrochemical reactions [1-2], and it is necessary to appreciate and understand the electrochemical principles that are most relevant for corrosion processes. The electrochemical reactions that take place on the surface of the surgically implanted alloys are identical to those observed during exposure to solutions that simulate biological fluids in the human body (blood, saliva, etc.).

The electrochemical methods evaluate the properties of the materials in real time in their operation in the environment of use. As an example, are the electrochemical methods of assessing the corrosion resistance of materials and biomaterials in specific environments of use. Electrochemical methods are widely used to characterize materials or biomaterials both from the point of view of their resistance in specific environments of use, biocompatibility or electrocatalytic effects for the efficiency of different synthesis reactions.

Electrochemistry has certain advantages over conventional methods, because it allows the direct generation and identification, in a fast and clean manner, of both stable species and metabolites, with short half-lives, without the need to use laboratory animals or organ extracts. In addition, it can be a powerful tool in interaction studies with specific cellular components, which is more difficult to achieve by in vivo or in vitro methods.

It should also be mentioned that, in general, complete results regarding a certain corrosion process are obtained by using several complementary methods in parallel [2]. Methods for investigating corrosion and kinetics of electrode processes can be electrochemical and non-electrochemical [2, 11-12]. The first category includes the methods in which the disturbance of the studied system and the monitoring of the response given by the system to this disturbance are made with an electrical signal (current, potential, quantity of electricity, etc.) [1-2]. In the second category are methods that use other sizes than electrical ones and which can be used to obtain information complementary to those provided by electrochemical methods (spectroscopic, optical, electron microscopy, X-ray diffraction, etc.) [1-2]. Electrochemical methods are considered to be the most effective for in situ investigations, these being also the most accessible and most commonly used methods for characterizing and evaluating the corrosion resistance and kinetics of an electrode process. The electrochemical methods used can be classified according to several criteria [1-2]. Depending on the speed with which the studied system is disturbed they can be: steady state and non-steady state (relaxation). In the steady state methods, the disturbance of the system takes place at such a low speed that it can be considered in equilibrium, whereas in the non-steady state methods, the disturbance occurs rapidly, following the system's response during its return to a new one steady state.

Lactic acid is a colourless substance produced by almost all tissues of the human body to ensure its proper functioning. Lactic acid is used in this study because circulates in the blood system at any time in small quantities. It is produced by the tissues of the body, mainly the muscles, to obtain energy by metabolizing glucose in the absence of oxygen. Glucose can be used either from the bloodstream or from the form stored by the body, glycogen in the muscles. This process is called anaerobic respiration (without oxygen). Lactic acid (in large quantities) is produced during weight-bearing exercises, and if the amount of it in the muscle is very high, fatigue and muscle cramps occur [13-15].

Our work aims to investigate the effect of Lactic Acid as metabolic product of microorganisms on the corrosion behaviour of Ti6Al4V in Hank biological

solution. The results show that Lactic Acid could improve the degradation process of titanium alloy immersed in Hank biological solution.

2. Materials and methods

Before any experiment for the evaluation of a material, an experimental protocol should be established, comprising all the measurements and the steps necessary for the accuracy of the experiments and the results obtained [1-2]. In general, for the evaluation of the corrosion resistance of the materials and of the corrosion kinetics and mechanism, an experimental protocol may include the following steps [2]:

- The selection of a suitable electrochemical cell so that it is schematized in Figure 1 (with three electrodes). The electrolyte volume must be constant for each measurement [2].

- Choosing and preparing the samples from the tested alloy, respectively Ti6Al4V with a surface roughness and chemical composition as it was received from customer ($R_a = 1.15 \mu\text{m}$) presented in another article [4].

- Correct preparation of test solutions. In the experiment it was used Hank biological solution simulating the blood from the body and addition of two concentrations of lactic acid which is known as one of metabolic product of microorganisms.

The chemical composition of biological fluid used for this study is presented in Table 1.

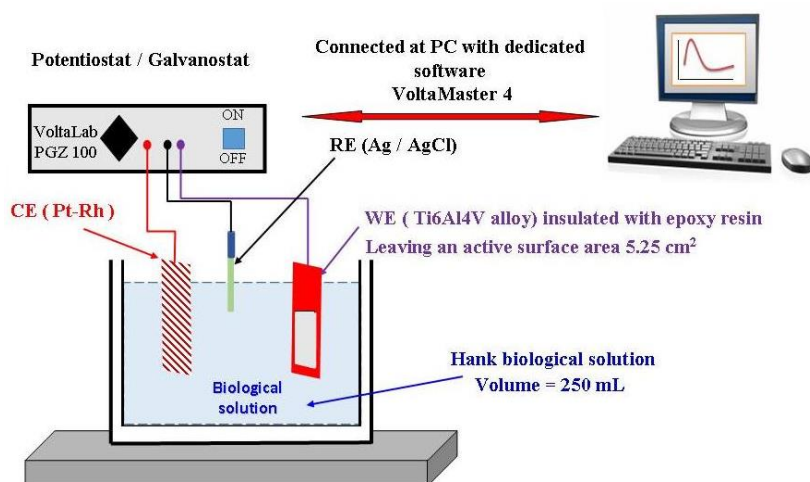


Fig. 1. Schematic representation of electrochemical cell used for corrosion investigation

Table 1. Composition of Hank biological solution without and with Lactic Acid addition

Compound [g / L]	Hank solution	Hank +Lactic Acid 5 g/L	Hank +Lactic Acid 10 g/L
NaCl	8.8	8.8	8.8
KCl	0.4	0.4	0.4
CaCl ₂	0.14	0.14	0.14
NaHCO ₃	0.35	0.35	0.35
Na ₂ HPO ₄ ·7H ₂ O	0.06	0.06	0.06
Lactic Acid	-	5	10
C ₆ H ₁₂ O ₆	1	1	1
MgSO ₄ ·7H ₂ O	0.2	0.2	0.2
KH ₂ PO ₄ ·H ₂ O	0.1	0.1	0.1
pH	7.4	2,67	1,98
Conductivity, [mS/cm]	14.6	14.7	15.6

- Establishing an experimental protocol that includes both the preparation of the samples before immersion

in the test solution and the electrochemical measurements imposed on an electrochemical

workstation. The diagram of the protocol with the programming of the electrochemical measurements

for each type of solution used is presented in Figure 2.

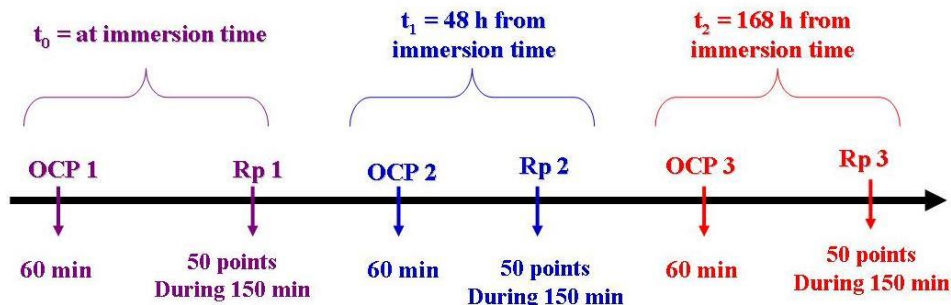


Fig. 2. Schematic representation of experimental protocol used for electrochemical measurements

The two methods used, namely open circuit potential (OCP) and polarization resistance (R_p) emitted from 50 linear polarization (LP) measurements for each sample immersed in each solution, will give some information about the trend of potential evolution of titanium alloy in the tested biological solutions. Measuring the free potential from immersion in the solution according to the set time. The potential of an electrode is measured by reference to a reference electrode [2]. The potential of the reference electrode, E_{ref} , is reproducible and stable over time. The potential of the reference electrode is independent of the solution in which it is used and is the same regardless of the type and experimental conditions that are carried out. For this experiment, the reference electrode Ag / AgCl ($E = 199$ mV vs. the normal hydrogen electrode) was used.

The polarization resistance, R_p , is an important parameter to evaluate the passivation capacity of a biomaterial or to study a uniform corrosion process that occurs on a metallic surface. Each experimental point (polarization resistance and potential versus time) is automatically recorded and obtained from an individual voltammogram, or individual linear polarization, which is automatically, processed using an algorithm introduced in the pilot program and recording of experimental data. These individual voltammograms are saved. This makes it possible to process them with the second Stern method. Between two successive voltammograms the system returns to the free potential.

The polarization resistance was determined by plotting the linear voltammetry curves around the free potential with a small ± 40 mV disturbance and a low scan rate of 1 mV/sec. Fifty (50) such measurements have been programmed to show us an evolution of the polarization resistance over time in the respective corrosive environment.

3. Results and discussion

3.1. Open circuit potential (OCP)

The interface between an electronic conductor and an electrolyte acts as an electrode. As a result of the transfer of charges between the two phases in contact, between the electronic conductor and the electrolyte solution a potential difference is called electrode potential [2].

The variation in potential of the open circuit potential follows the behaviour of a biomaterial in contact with a corrosive liquid environment. After a period of immersion, it stabilizes around a stationary value [2], called free potential or open circuit potential at that time. Corrosion tests should always be initiated with the monitoring of the samples in the respective corrosive test environments [2]. The plot of the $E(t)$ curves for the Ti6Al4V alloy immersed in the three solutions is shown in Figures 3-5, for immersion time 0, after 48 hours and after 168 hours from immersion.

From Figure 3, after immersion it is observed that the open circuit potential of titanium alloy immersed in Hank solution becomes stable at a value of 160 mV vs. Ag/AgCl, while the open circuit potential of titanium alloy immersed in Hank solution with 5 g/L Lactic acid is stabilized at a more positive (noble) value of 430 mV vs. Ag/AgCl having a low decreasing tendency to less noble values. The open circuit potential of titanium alloy immersed in Hank solution with 10 g/L Lactic Acid is stabilized at about 230 mV vs. Ag/AgCl, which is less noble than that of 5 g/L Lactic Acid and a little much positive as compared with Hank solution. It can be concluded that in the very first contact of Lactic acid with titanium alloy surface immersed in Hank solution the effect is to improve the passive capacity and to shift their open circuit potential to more positive (noble) values.

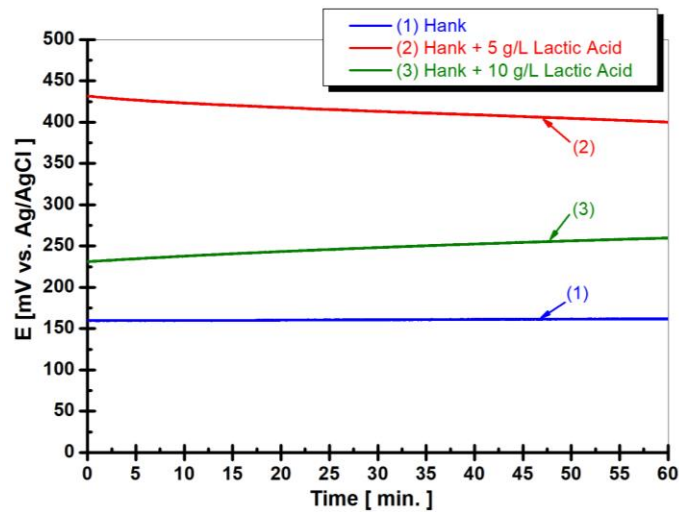


Fig. 3. Open circuit potential of titanium alloy after immersion in: (1) Hank solution; (2) Hank with 5 g/L Lactic Acid added; (3) Hank with 10 g/L Lactic acid added

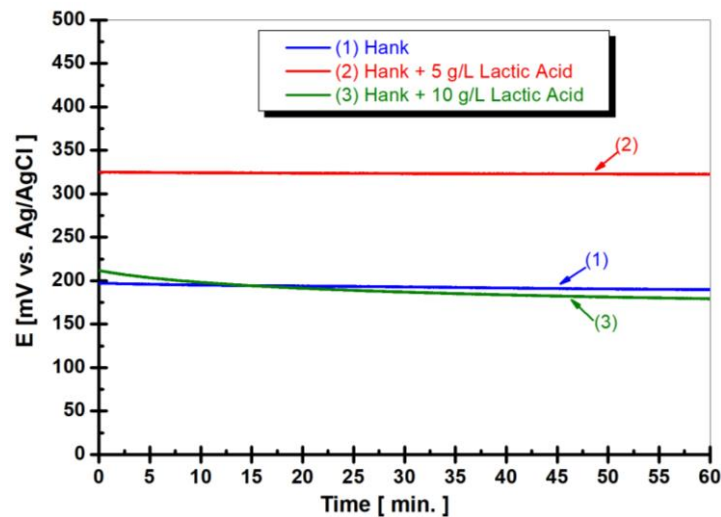


Fig. 4. Open circuit potential of titanium alloy measured after 48 h from immersion in: (1) Hank solution; (2) Hank with 5 g/L Lactic Acid added; (3) Hank with 10 g/L Lactic acid added

After 48 h from immersion time, Figure 4, the open circuit potential of titanium alloy immersed in Hank solution is slowly decreasing to less positive values at 198 mV vs. Ag/AgCl, while the open circuit potential of titanium alloy immersed in Hank with 5 g/L Lactic Acid solution is also decreasing to less noble values but much nobler than Hank solution, respectively at 326 mV vs. Ag/AgCl. The open circuit potential of titanium alloy immersed in Hank solution with 10 g/L Lactic Acid is stabilized at about the same value as Hank solution of 210 mV vs. Ag/AgCl but with a low decreasing tendency to fewer noble values.

After 168 h from immersion time, the open circuit potential showed in Figure 5, of titanium alloy immersed in Hank solution is decreasing to fewer

positive values having a constant value of 160 mV vs. Ag/AgCl as the first time of immersion in this solution. The open circuit potential of titanium alloy immersed in Hank solution with 5 g/L Lactic Acid is stabilized at a much less positive (noble) value of 290 mV vs. Ag/AgCl having a decreasing tendency.

The open circuit potential of titanium alloy immersed in Hank solution with 10 g/L Lactic Acid is stabilized at about the same value as Hank solution of 160 mV vs. Ag/AgCl but with a low decreasing tendency to fewer noble values. It can be concluded that the effect of Lactic Acid is changing during immersion time and therefore will contribute to progression of corrosion process on titanium alloy surface immersed in Hank solution.

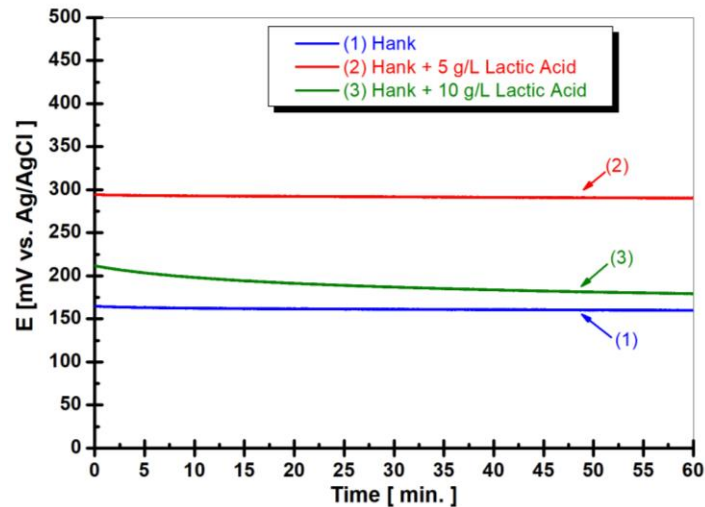


Fig. 5. Open circuit potential of titanium alloy measured after 168 h from immersion in: (1) Hank solution; (2) Hank with 5 g/L Lactic Acid added; (3) Hank with 10 g/L Lactic acid added

3.2. Polarization resistance, R_p

The evolution of polarization resistance resulted from 50 measured voltammograms around free potential for each solution is presented in Figures 6-8 for every period of immersion, respectively: immersion time ($t = 0$ h), 48 h and 168 h.

The polarization resistance (R_p) is determined using the Stern Geary formula, as it is explained in many specialized books [2, 16]:

$$R_p = \frac{\Delta E}{\Delta i} = \frac{\beta_a \cdot \beta_c}{2,3 \cdot (\beta_a - \beta_c) \cdot i_{cor}} \quad (1)$$

where: $-\beta_a$ și β_c are Tafel anodic and cathodic slopes, $(\Delta E/\Delta i)$ tangent to polarization curve in corrosion potential.

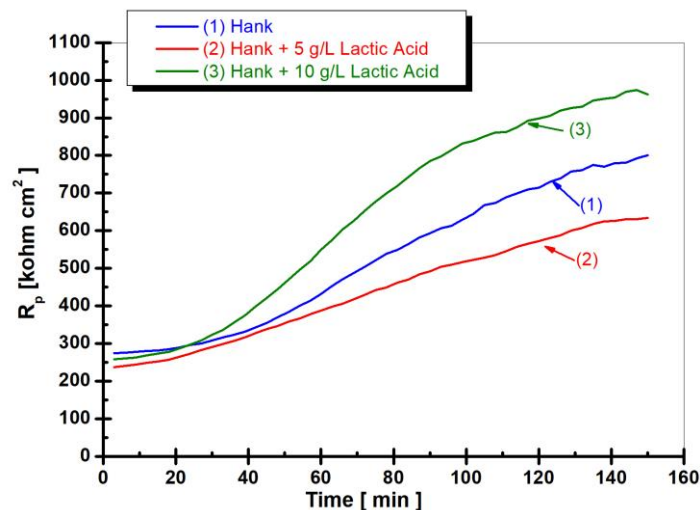


Fig. 6. Evolution of polarization resistance of titanium alloy after immersion in: (1) Hank solution; (2) Hank with 5 g/L Lactic Acid added; (3) Hank with 10 g/L Lactic acid added

As it could be seen from Figure 6 the polarization resistance of titanium alloy immersed in the three types of solution starts at about same values at very immersion time. During measuring period, the polarization resistance of titanium alloy immersed in

Hank solution is shifting to higher values from 275 $kohm\ cm^2$ to 710 $kohm\ cm^2$ showing that the Ti6Al4V alloy in Hank solution forms an oxide passive film which improves the corrosion resistance of the alloy in biological solution. The addition of low

concentration of Lactic Acid of 5 g/L follow the same trend for polarization resistance of titanium alloy as in Hank solution but with slow lower values, from 220 $kohm\cdot cm^2$ to 610 $kohm\cdot cm^2$. This behaviour could suggest that at this concentration the lowering of polarization resistance decreases also the corrosion resistance of titanium alloy immersed in Hank solution with 5 g/L Lactic Acid. Adding a higher concentration of Lactic Acid in Hank solution, respectively 10 g/L can be observed that titanium

alloy immersed in this solution have a higher value of polarization resistance. This behaviour suggests the effect of passivation of Lactic Acid when is present in biological solution. This higher passivity effect could sensitize the titanium alloy surface on localized corrosion. The polarization resistance of titanium alloy immersed in Hank solution with 10 g/L Lactic Acid increases during immersion period, after 48 h, from 230 $kohm\cdot cm^2$ to 900 $kohm\cdot cm^2$, registering the highest values.

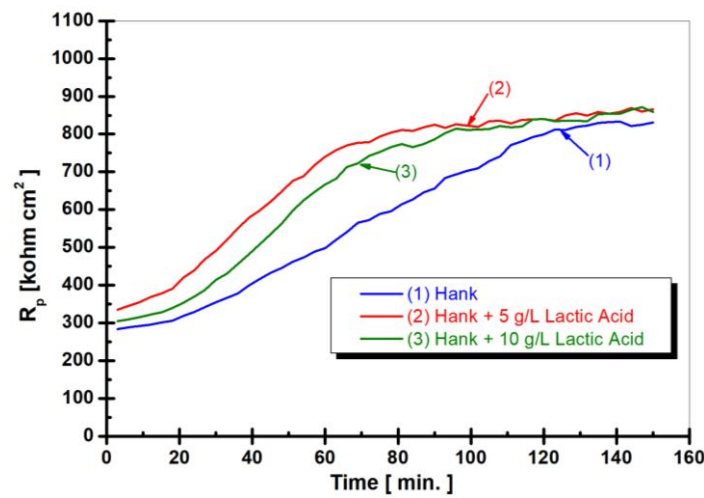


Fig. 7. Evolution of polarization resistance of titanium alloy measured after 48 h from immersion in: (1) Hank solution; (2) Hank with 5 g/L Lactic Acid added; (3) Hank with 10 g/L Lactic acid added

After 48 h the polarization resistance of titanium alloy immersed in Hank solution, Figure 7, show about the same values as at immersion time (Figure 6) from 275 $kohm\cdot cm^2$ to 780 $kohm\cdot cm^2$, confirming a constant corrosion resistance in time. The polarization

resistance of titanium alloy immersed in both Lactic Acid concentration show an increase of polarization resistance from 300 to about 800 $kohm\cdot cm^2$, being close each other.

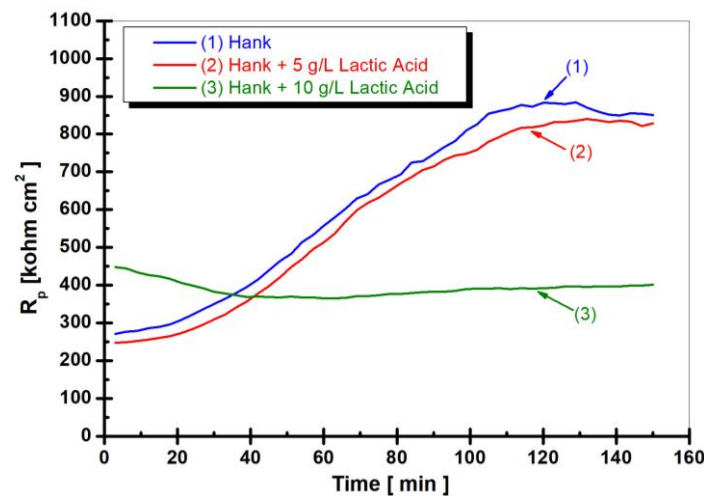


Fig. 8. Evolution of polarization resistance of titanium alloy measured after 168 h from immersion in: (1) Hank solution; (2) Hank with 5 g/L Lactic Acid added; (3) Hank with 10 g/L Lactic acid added

From Figure 8 the polarization resistance of titanium alloy changes dramatically when is immersed in Hank solution with 10 g/L Lactic Acid, after 168 from immersion. While, the polarization resistance of titanium alloy immersed in Hank and Hank with 5 g/L Lactic Acid preserve the same behaviour by increasing from $275 \text{ kohm}\cdot\text{cm}^2$ to $800 \text{ kohm}\cdot\text{cm}^2$, the polarization resistance of titanium alloy immersed in Hank with 10 g/L Lactic Acid shift to lower values from $475 \text{ kohm}\cdot\text{cm}^2$ to $350 \text{ kohm}\cdot\text{cm}^2$ preserving the decreasing tendency.

4. Conclusions

The corrosion behaviour of the Ti6Al4V in Hank biological solution with addition of two concentration of Lactic Acid monitored at different period from immersion time respectively 0 h (at immersion time), after 48 h from immersion time and after 168 h from immersion time was studied in this research work by electrochemical methods.

From the electrochemical methods used for this study, the following conclusions can be drawn:

- From monitoring of the open circuit potential measurement at different periods of immersion time, it is observed that the addition of Lactic Acid in the concentration of 5 g/L and 10 g/L in the Hank biological solution leads to a shift of the potential towards more positive values as compared to the biological solution without addition of lactic acid. It can be concluded that the effect of Lactic Acid is changing during immersion time and therefore will contribute to progression of corrosion process on titanium alloy surface immersed in Hank solution.

- From the evolution of the polarization resistance at time 0, it is observed that the addition of 10 g/L lactic acid in the Hank biological solution leads to an increase in the value of the polarization resistance compared to the biological solution without the addition of Lactic Acid, and in the case of the addition of 5 g/L Lactic Acid in solution can be observed a decrease in polarization resistance compared to the solution containing 10 g/L lactic acid and Hank biological solution. A high polarization resistance value means a low corrosion rate and a low value of the polarization resistance means a high corrosion rate.

- After 48 hours from immersion time it is observed that a change takes place: In this case of the addition of Lactic Acid at a concentration of 5 g/L in Hank biological solution the polarization resistance has the highest value, while that with 10 g/L Lactic Acid decreases in comparison with Hank without Lactic Acid, and the polarization resistance of Ti6Al4V immersed in the Hank solution remains approximately constant.

- From the polarization resistance of Ti6Al4V alloy immersed in three solution after 168 hours from immersion time it can be observed that the value of polarization resistance decreases gradually with addition of Lactic Acid in Hank biological solution.

As an overall conclusion from this study is that the presence of Lactic Acid, one of metabolic product of microorganisms could destabilizes the interface of titanium alloy implant material with biological solution affecting its corrosion resistance by improving the corrosion rate (decreasing the polarization resistance).

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DETERMINATION OF AIR QUALITY, THROUGH THE CUMULATIVE MEASUREMENT OF THE CONCENTRATION OF THE MATERIAL PARTICLES, IN A WORKSHOP FOR MAKING METAL CAST PARTS

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ABSTRACT

Material particles represent a category of air pollutants, which greatly affect human health, and include in their composition, nitrates, sulphates, organic carbon dust and salt. The paper presents determinations of the air quality, from different sectors, of a metal casting workshop. The determinations were made during the technological process of production, as well as during when the workshop does not have a production activity. In all cases, was monitored the variation of material particles (PM) concentrations. The measurements were made with the help of the particle counter, Fluke 985, the results obtained, being compared with the legislation in force, regarding safety and health at work.

KEYWORDS: air pollutants, material particles, air quality, organic carbon dust

1. Introduction

Material particles represent a category of air pollutants, which greatly affect human health. These include in their composition: nitrates, sulphates, organic carbon, elemental carbon, dust and salt. They can come from very different sources and have a number of specific morphological, chemical and physical properties.

The determination of the variability of the PM concentration, during a time interval shorter than one day, can be performed, with the help of continuous measurements. The suspended particles represent a complex mixture of very small particles and drops of liquid [1, 2].

The main sources of origin are:

- Natural sources: volcanic eruptions, rock erosion, sandstorms, and pollen dispersal.
- Anthropogenic sources: industrial activity, population heating system, thermoelectric power plants.

Road traffic contributes to the pollution with dust, produced by the tires of cars, both in stopping them and due to incomplete combustion.

The determinations of the air quality were made in a workshop of casting metal parts, in different workshops, intended for the technological process of forming-casting of castings, in order to determine the

variation of PM concentrations, during the technological process. The monitoring of the air quality problems was carried out in different work areas, respectively, in the area of making alloy in the furnaces, the mould preparation area, the parts casting area, the debating-parts cleaning area, as well as during when the workshop having no production activity.

2. General description of technological processes and flows

Technological processes that take place in the workshop of casting of metal parts are: preparation of mixture for moulds; execution of moulds and cores; filling moulds and preparing them for casting; the casting in the mould; cooling forms; debate of the moulds, regeneration and cooling of the sand; blasting of castings parts; tensioning / normalizing of castings; cleaning castings.

Before casting the steel, is made the wood model gasket, within the modeling workshop, then made the shapes and cores are made of a mixture of quartz sand, binders and auxiliary materials. After pouring the molten metal into moulds, the castings are allowed to cool, then the parts are cleaned, within the cleaning workshop, where the technological

additions, the alloy casting network, the feeder, are removed, by cutting with the oxy-acetylene flame, or is removed mixture, left on the surfaces, of the cast piece. This is done with pneumatic hammers or by blasting.

The workshop for the preparation of the moulds ensures the preparation of the mixture, making the moulds with mixture, their filling with liquid metal, the debate of the pieces after cooling, and their transfer to the cleaning workshop. The moulds and cores, made from mixtures of synthetic binders, with cold hardening, are coated with paint, resin based and water-based paint.

The cleaning workshop ensures the cleaning of the castings, the removal of the casting networks, and the technological additions. Secondary cleaning - it is executed after the heat treatment, in order to deliver the cast parts, to the beneficiary or to mechanical processing.

3. Experimental results

The composition of the dust is extremely changeable and can be associated with the following components: sulphur dioxide, carbon monoxide, nitrogen oxides and hydrocarbon burning residues.

From the point of view of health and the environment, the most harmful dust is made up of particles with a diameter of less than 10 microns, known as PM10. They penetrate deep into the respiratory system, reaching into the lungs, where they store the dangerous substances they carry.

About 60% of PM10 is made up of PM2.5 particles with a diameter below 2.5 microns. In this form, they can enter the pulmonary and blood cells.

Specifically, the body's defence cells, it confuses them with bacteria, and tries to kill them. As they do not represent bacteria, the immune system cannot "kill" them, and the result is a permanent inflammation of the lung tissue. Usually, these powders also contain active substances, which generate a process of lung disease, similar to that caused by smoking or aging. Long-term exposure to fine particulate pollution increases mortality, and the risk of cardiovascular diseases [5, 6].

The effects on human health are the same, and in the case of PM1 particles, which have a diameter of 1 micron.

PM2.5 represents the technical indicator, for the most dangerous suspended powders (dust wires), detectable in the air, especially in large cities. "2.5" refers to the size, and indicates a particle of maximum 2.5 microns. In contrast to the larger powders, classified as PM10 (i.e. particles with a size of at least 10 microns), powders of the PM2.5 category penetrate deep into the lungs, are difficult to remove and cause a reaction of the immune system [8].

This type of particles comes from the dust on the street, the nooks from thermal and industrial plants, the combustion of any kind, traffic or unprotected yards.

The reference method for the sampling and measurement of PM10 and PM2.5 is that laid down in standard EN 12341 "Ambient air. Standardized method for gravimetric measurement to determine the mass fraction of PM10 or PM2.5 of suspended particles" [3, 4].

Table 1. Norms - EN 12341

LAW no. 104 of June 15, 2011 Suspended particles - PM10	
Limit values	50 µg/m³ - the daily limit value for the protection of human health 40 µg/m³ - the annual limit value for the protection of human health

LAW no. 104 of June 15, 2011 Suspended particles - PM2.5	
Target value	25 µg/m³ - annual target value
Limit values	25 µg/m³ - the annual limit value to be reached by January 1, 2015 20 µg/m³ - the annual limit value to be reached by January 1, 2020

The equipment used to determine the air quality inside the parts casting workshop is the Fluke 985 Particle Counter (Fig. 1). The Fluke 985 particle counter is an essential and professional tool, ideal for troubleshooting and monitoring indoor air quality issues, and checking the performance of the HVAC filter, and critical locations for ISO certification 5-9.



Fig. 1. Fluke 985 particle counter

The workshop for casting the parts, is equipped with an installation for the removal and collection of the noxes. This equipment should be located beyond the work area, as it would exceed the noise level allowed by the rules of health and safety at work, in the proximity of work areas.

The workshop is equipped with a Donaldson DFPRO 8 filtration system. Following the installation of the filters for the capture and reduction of powders or noticed visible decreases in the intensity of the noxiousness in the working atmosphere [10, 11].

The paper presents the methods for determining dusts in the air in the working area. The monitoring of the air quality problems was done both during the development of the technological process activities, and while the workshop does not have a production activity, the data being compared, with the norms in force of the EN 12341 standard, "Ambient air". Standardized method, for gravimetric measurement, to determine the mass fraction of PM10 or PM2.5 of suspended particles [12].

The determinations were centralized, by sectors of activity, and represented in the following graphs.

AREA WITH THE MELTING FURNACES

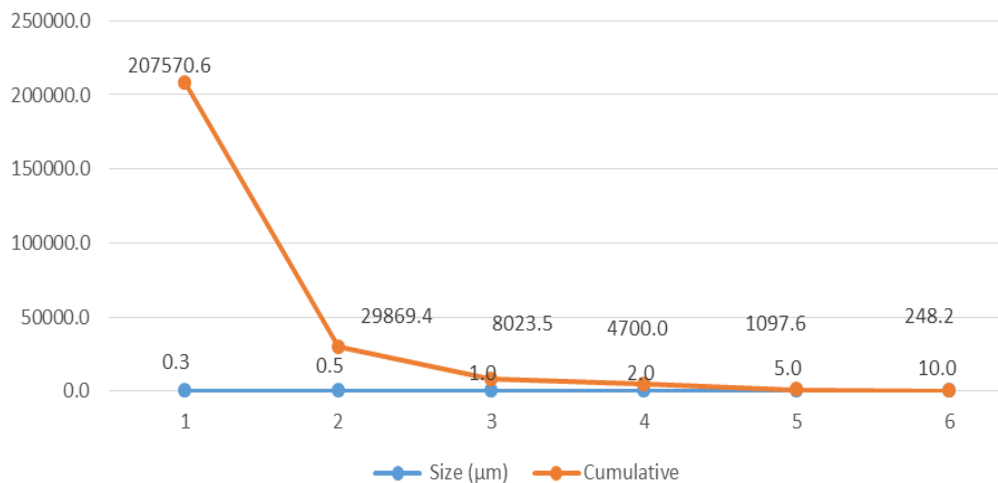


Fig. 2. Determinations of the cumulative values of particles in the alloys making sector

SECTOR FOR MAKING MIXTURES

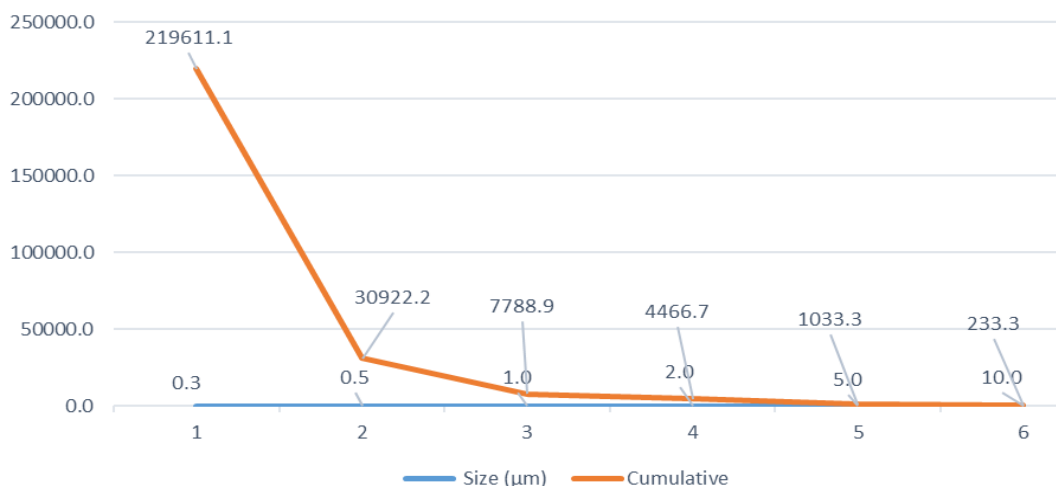


Fig. 3. Determination of the cumulative values of particles in the sector of moulds for casting parts

The coefficient of variability is very high for PM10, and for PM2.5, in the sectors of debating cast parts, and the realization of shapes from casting (Fig.

3, 5). These values show a very large variation during the experimental determination period, between these sectors, in working condition, and in resting state, that

is, in the periods when we have no production activity (Fig. 6). Particles of 0.3 μm are the most dangerous to health. The highest cumulative values of this kind of particles, were obtained, in the sector of debating cast parts from moulds.

Significant differences for PM10 and PM2.5 indices were obtained, between the recorded values, in the two activity areas, respectively in the casting

sector, and the sector in which is making moulds from mixture.

The values obtained for PM10 and PM2.5 indices in air, during the experimental period, in the melting furnace area and in the alloy casting area, were relatively small, below the allowed limit (see Table 1), 50 $\mu\text{g}/\text{m}^3$, according to with GD 592/2002.

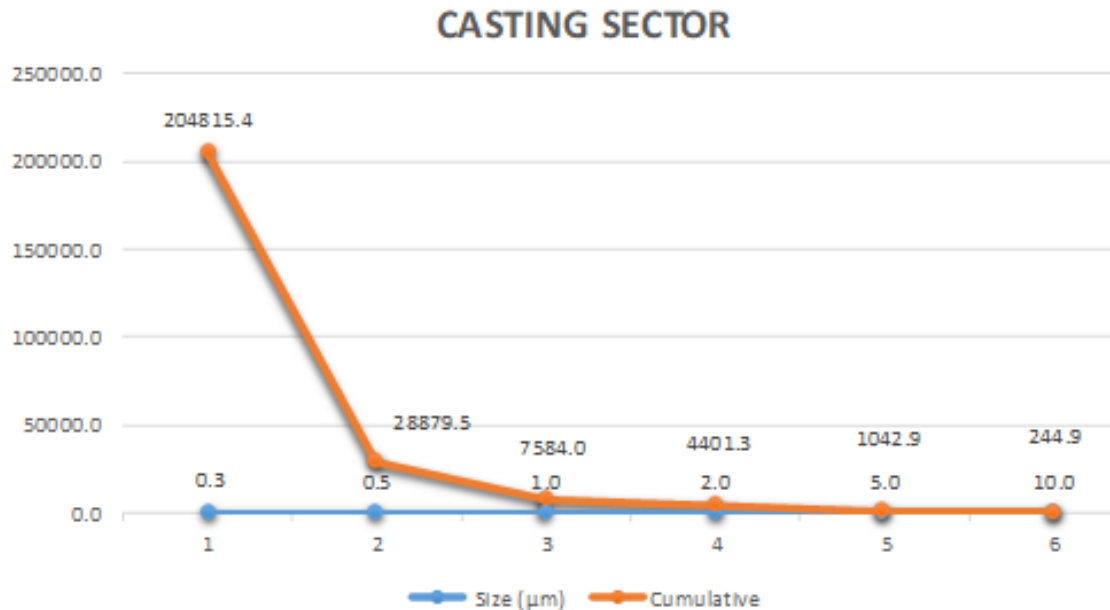


Fig. 4. Determination of the cumulative values of particles in the metal casting sector

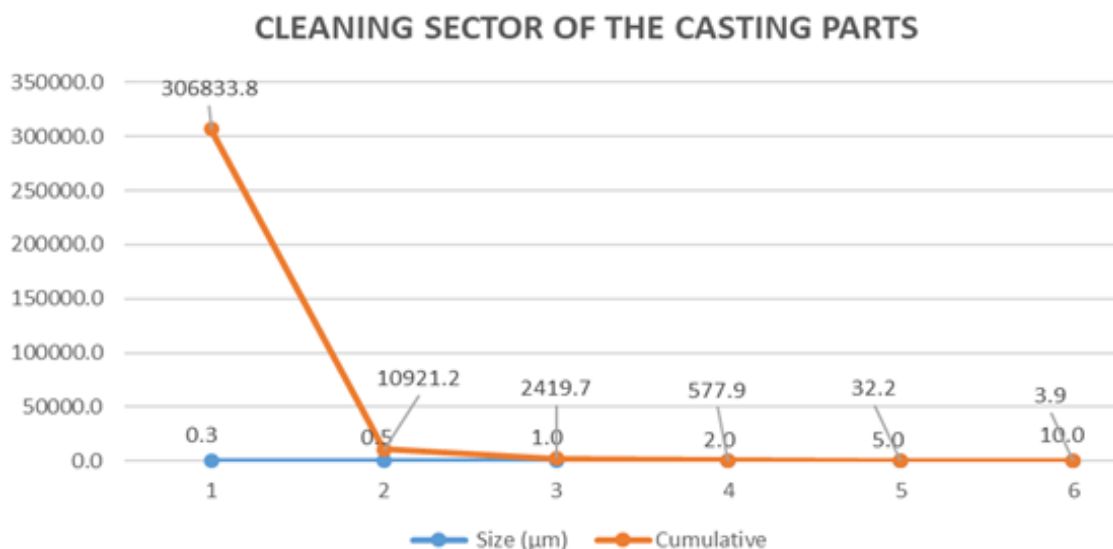


Fig. 5. Determination of the cumulative values of particles in the sector of debating and cleaning castings

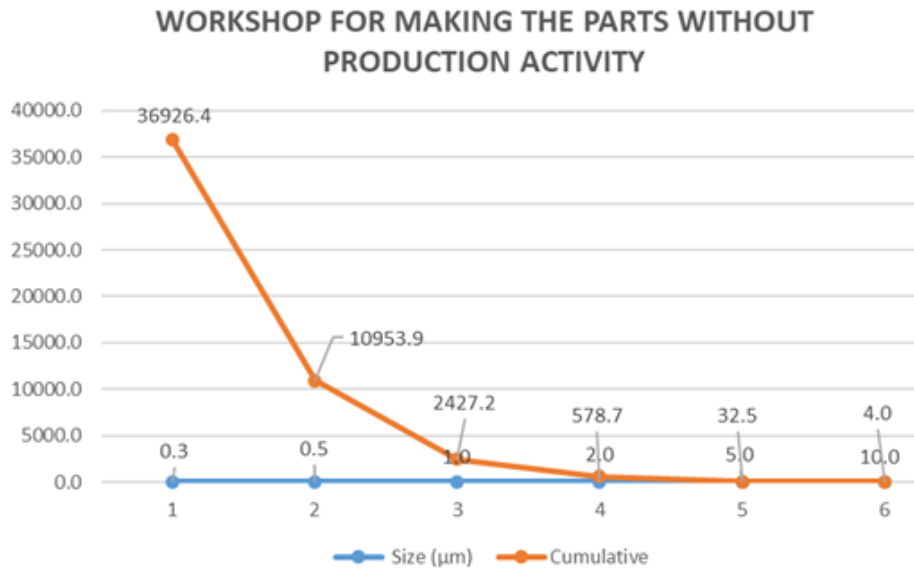


Fig. 6. Determination of the cumulative values of particles while the workshop is without production activity

4. Conclusions

The evaluation of the quality of the air imposed both the investigation of the conditions of the working environment, as well as the evaluation of the quality of the air inside the workshop of casting of the metallic pieces [7, 9].

During the period of experimental determination, there was a great variation, between the sectors of the making moulds from mixture, and debating the castings, in working condition, and in resting state, that is, during the periods when we have no production activity.

The highest cumulative values for 0.3 µm particles it was obtaining in these areas. These particles are the most dangerous for health.

Following the interpretation of the results obtained, in comparison with the norms in force, regarding the health and safety of the work, it is proposed the following organizational measures in the casting workshop.

- training on the need to use goggles and dust masks;
- periodic medical check with thematic detection of the diseases that manifest or are about to be installed in the respiratory system;
- making determinations for the quantity of powders in the workplace atmosphere with the regularity required - maintaining cleanliness to avoid accumulation of dust or other particles that can be entrained by air currents by law;
- appropriate signalling of risks in the workplace.

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BEHAVIOR ON PLASTIC DEFORMATION OF THIN STEEL STRIPS COATED WITH ELECTROLESS Ni-P

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ABSTRACT

Within the present work deformability of Ni-P coatings was analyzed on thin strips of low carbon steel, coated with Ni-P layers in correlation with their structure and chemical composition. Thin layers of 2-7 μm were made at immersion times of 5, 10 and 15 minutes and a variable pH of between 4 and 6, at a temperature of 80-85 °C. The deformability was analyzed by applying the Erichsen Test, which measures the deep deformation capacity of the metallic materials. Following the analysis was established the Erichsen Index (IE) the most used index for assessing the deformation capacity of the sheets.

The microscopic analysis, performed on the surface of maximum deformation, shows a cracking of the layers with a different aspect depending on pH, the duration of deposition and the initial structure of the layer. The results of the Erichsen test show a good behavior at plastic deformation of the strips covered with thin Ni-P layers.

KEYWORDS: layers, Ni-P, electroless, microstructure, Erichsen Index

1. Introduction

Ni-P layers on steel support are obtained by electroless method which consists in immersing the support in a solution containing a nickel salt and a reducer, respectively sodium hypophosphite [1, 2]. The chemical coating process of nickel was first observed in 1844 by Wurtz One hundred years later, in 1946, Brenner and Riddell began experiments to develop such a process that could be applied in practice [2].

The study of the Ni deposition process by this method continued to be of interest and the research carried out led to the development of the process that the inventors initially called electrodeless, then electroless [3].

Compared to the electrolytic coatings, the deposits obtained by the chemical method are usually less porous and more resistant to corrosion (at equal thicknesses) [4, 5]. Almost any surface can be covered: metallic or non-metallic, including polymers (plastics), ceramics. The performances of this type of coverage have led to their use in various industrial fields: cellulose and paper production, plastics, food, petroleum-petrochemical, textile, automotive, aeronautical, electronic, nuclear industry [6, 7].

Deposits obtained by the chemical method are mainly used in applications that require significantly improved characteristics for the deposited layer, the most important being uniformity of thickness, hardness, high resistance to wear and corrosion [8].

These applications may require plastic deformations of the products and it is important to analyze this behavior. In the present work the deformability was analyzed by applying the Erichsen Test, which measures the deep deformation capacity of the metallic materials. Following the analysis was established the Erichsen Index (IE), the most used index for assessing the deformation capacity of the sheets steel, in this case coated with Ni-P layers.

2. Experimental conditions

Ni-P layers were deposited on a thin steel strip (0.18 mm) with low carbon content (0.025%). Samples were cleaned by chemical degreasing in alkalis at 90 °C, pickled in 15% HCl solution and two washes in distilled water at 90 °C. The composition of the baths for Ni-P coatings obtaining are shown in Table 1.

Sodium acetate was added as a complexing agent and as a buffer solution and lead acetate was used as a stabilizer [9].

The working parameters are shown in Table 2.

Table 1. Composition of the baths

Bath components	[g/L]
Nickel Sulphate	20-26
Sodium Hypophosphite	19-23
Sodium Acetate	9-15
Lead Acetate	1-3

Table 2. The working parameters

pH	T [°C]	Time [min]	Stirring rate [rot/min]
4.0- 6.0	80-85	5, 10, 15	300-600

The coating was performed on a laboratory plant consisting in a coating bath, with volume 1 L, thermostated hob and magnetic stirrer, pH meter and thermometer.

3. Experimental results and discussions

3.1. Microstructure and layer thickness

The analysis by optical microscopy of the Ni-P layers, in the cross-section shows that in the case of the thin layers, there is a faithful tracking of the contour of the surface of the steel support (Fig. 1a) and at the increase of the thickness of the layer the roughness fades (Fig. 1b) and the layers become uniform (Fig. 1c) [10]. It is also observed that the Ni-P layer adheres perfectly to the steel substrate, the interface being without discontinuities.

The thickness of the layer is influenced by pH. As pH increases, the thickness of the layer increases due to the increase of the nickel reduction reaction

rate. Lowering the pH, below 4, leads to a significant decrease of the layer thickness, the deposition process becoming very slow [11]. In addition to the pH, the sample exposure time in the electroless bath significantly influences the layer thickness. As can be seen in Figure 1, the layer thickness at pH 4.95 and at a working temperature 83 °C is doubled when increasing the immersion time from 5 (Fig. 1a) to 15 (Fig. 1c) minutes. Research has shown that the layer thickness can be also increased by applying a higher stirring speed or introducing completely dry samples into the electroless bath. These influences have not been verified yet on a sufficient number of samples allowing safety outcomes. High stirring speed provides better removal of the hydrogen formed around the sample preventing pH decrease during the process [12]. Clean and dry samples may have an activation energy higher than in the presence of a water film on the surface, thus facilitating the deposition process.

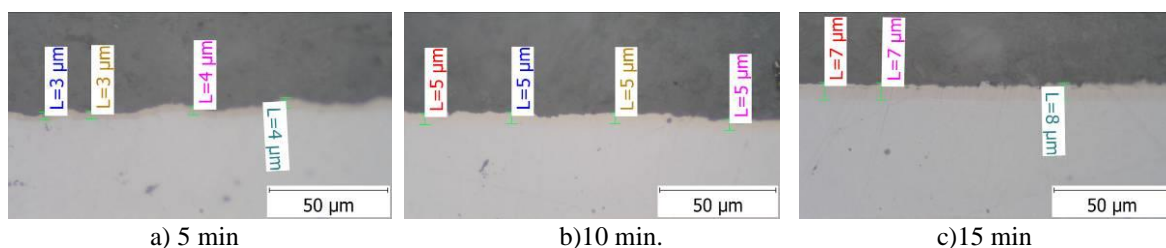


Fig. 1. The influence of immersion time on layer thickness, pH = 4.95, 83 °C

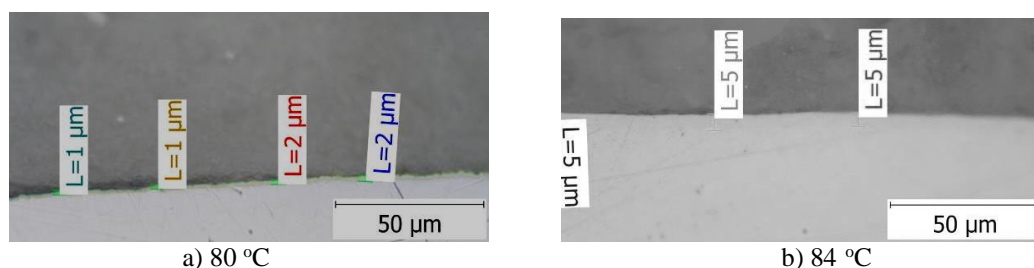


Fig. 2. The influence of electroless bath temperature on layer thickness

As is known from the literature, increasing the electroless bath temperature favors the deposition process. Figure 2 shows that an increase in temperature by 5 °C can provide an increase up to 3-4 μm of the layer thickness at the same pH and work duration. Electroless method does not allow, however, a working temperature higher than 90 °C with the risk of destabilizing the bath [2].

3.2. Testing Adhesion and Plasticity by Erichsen Method

Erichsen test measures the capacity of deep deformation of metallic materials or deformability. The test consists of deformation by a punch with a hemispherical head up of a sample until it breaks in

order to determine the maximum of the depth of the indentation left by the penetrator. The penetration depth in millimeters is the Erichsen Index (IE), the most widely used index for assessing the capacity of steel strips deformation [13, 14].

At steel strips coated with metals this test can give indications on deformation capacity of that product (steel strips coated with a layer) and on the layer adherence to the steel support. The test on thin steel strips of 0.18 mm, coated with Ni-P, obtained in different conditions of nickel plating, was carried out on a test device by using a ball $\phi = 15$ mm. Erichsen index was rated as the average of three measurements. Table 3 shows the values obtained for the samples tested depending on the obtaining conditions.

Table 3. Erichsen index depending on nickel plating parameters

Sample code*	pH**	t*** [min]	IE median
E1	6.6	5	6.67
E2	6.6	5	6.70
E3	5.11	5	6.61
E4	5.11	15	6.19
E5	4.32	15	6.41
E6	4.32	15	6.50

* There was a special nickel-plating for the samples dimensionally corresponding to the test

** The bath pH dropped freely as a result of successive coating of the samples

*** Immersion time

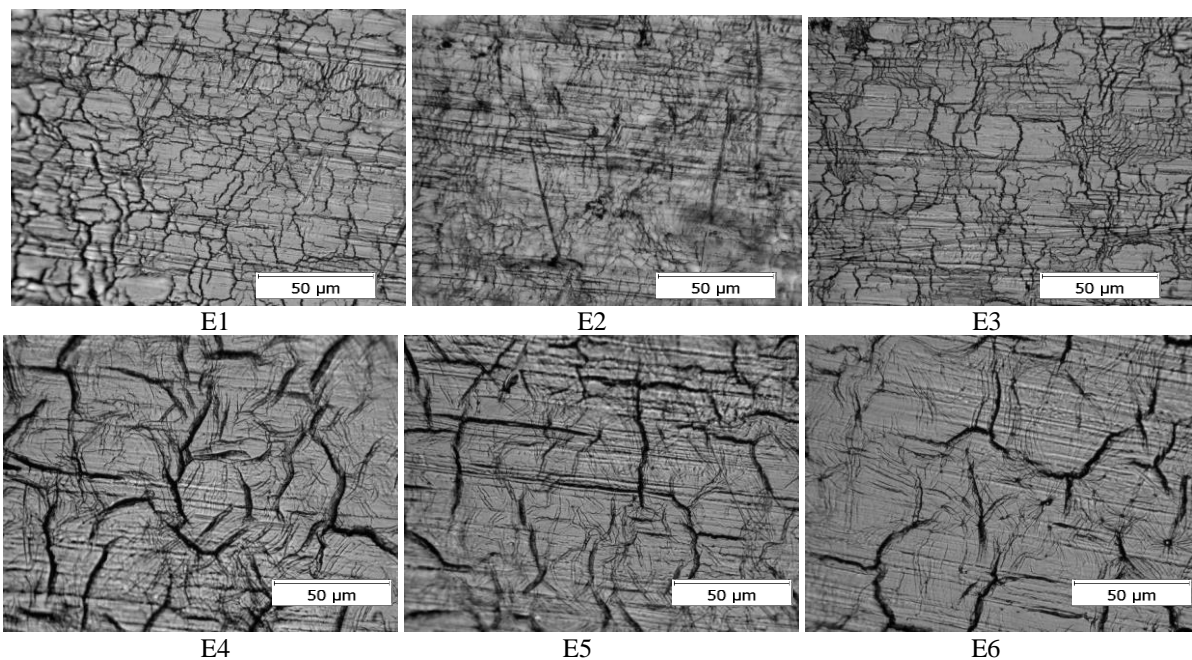


Fig. 3. The appearance of the surface on maximum deformation area of the Erichsen tested samples

The microscopic analysis, performed on the area of maximum deformation, reveals a cracking of layers of different appearance depending on the pH and duration of deposit, as presented in Figure 3. It can be noted that samples made at high pH and duration of 5 minutes (code E1, E2, E3) due to a finer structure, also visible from the surface morphology analysis, shows a fine network of cracks. The samples obtained at 15 minutes immersion time and medium and low and average pH (code E4, E5, E6), which revealed microscopically a bigger granulation, showed a coarse network of cracks. The same difference is observed in function of the immersion time as seen at E3 and E4 samples obtained at the same pH. All samples, regardless deposition conditions, present numerous slip lines.

Macroscopic analysis of Erichsen tested samples does not reveal exfoliated layer, cap surface is smooth, just like the cracked area, as shown in Figure 4. This result shows a very good adhesion of Ni-P layers to steel support which is also highlighted by microscopic analysis in cross section showing a layer - steel interface free of discontinuities.



Fig. 4. Macroscopic aspect of Erichsen deformation

Erichsen test results show a close behavior to the plastic deformation of thin strips coated with Ni-P thin layers. Small variations can be correlated with greater thickness of layers obtained at deposition times of 15 min. vs those obtained at 5 min.

4. Conclusions

- Thin films of 2-7 μm Ni-P deposited, by electroless method, on cold rolled thin strip were obtained.
- Microstructural analysis reveals uniform layers in a continuous and clean interface with the support band.
- Macroscopic analysis of samples subjected to Erichsen test does not reveal exfoliated layer, cap

surface is smooth just like the fissured area. This result shows a very good adhesion of layers Ni-P to the steel support.

- Microscopic analysis performed on the area of maximum deformation of the Erichsen samples show that samples made in 5 minutes shows a fine network of cracks and samples obtained at 15 minutes immersion time show a coarse network including numerous slip lines. Erichsen index value shows a similar behavior to plastic deformation of strips coated with Ni-P thin layers.

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PROJECT MANAGEMENT IMPLICATIONS ON CLIMATE CHANGE

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ABSTRACT

At the moment, project management is a field in development and increasingly used in all economic sectors. Thus, we can specify that the project management plays a major role in order to consolidate a competitive advantage and achieve the organizational performance. In order to achieve long-term goals, it is necessary for the projects to consider several aspects, among which the mode and context of their implementation and the identification of the answers to the needs of the companies and organizations that implement the projects, as well as the follow-up of the measures / recommendations for solving certain problems. Further, in this article we will present the involvement of the project management, as well as funding sources in the field of climate change that may have major implications for agriculture.

KEYWORDS: project management, climate change, financial instruments, EU funds, cost-benefit analysis

1. Introduction

Climate change is a defining issue of our time, and we are at a defining moment, from changing weather patterns that threaten agricultural production to rising sea levels that increase the risk of flooding, the impact of climate change is global and has no broad precedent. Without taking action and identifying solutions at the moment, adapting to the impact of climate change will entail high costs and procedures will be more difficult. According to research in the field, the notion of project refers to the fact that it has a temporary character, since from the beginning of the project, that is, in the planning phase, the terms of development and scope are defined, as well as the resources established. The project manager and the members of his team within the project can play an essential role in meeting the proposed objectives and reaching the final result.

2. General concepts concerning project management (PM) and project management office (PMO)

Project management consists of planning, organizing and managing the tasks and resources that pursue a certain objective, under the conditions of time constraints, resources and costs. From this perspective, defining the objectives of the project

acquires a major importance for according to these we establish the methods used. Looking at project management as a discipline it can be specified that it involves two different modes of management. One of the most common ways of using it is the management of the execution stages of a project, and the other is the project management from forecasting / planning until its completion. According to the PMBOK Guide on project management (4th edition, 2008), the project management processes fall into five groups, namely: forecasting / planning, organizing, coordinating, training and controlling-evaluation.

Further, a figure representing the definition of the project is represented, as well as the processes and steps required to reach the final result.

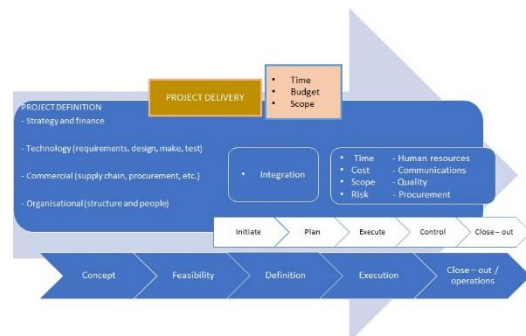


Fig. 1. Description of the steps in order to achieve the final result of a project

PMO is a place where we consolidate all the knowledge, practices, experiences and resources of the project management in an organization / company.

In addition, the PMO has the role of identifying the best practices in a company / organization. Companies looking for greater efficiency and tighter project management are opening project management offices (PMOs).

The PMO has several tasks, including ensuring the implementation of procedures, practices and operations - on time, on budget and in the same way.

PMOs need to ensure the success of projects and programs and this is essential because organizations provide value through projects and programs.

3. EU funds and financial instruments relating to climate change

In order to efficiently implement strategies to adapt to climate change, investments are needed to support the application of strategies, policies and recommended measures.

In general, climate financing that is beneficial to the agricultural sector can be realized with the help of central and local public administration budgets, European, national, local funds, as well as the private sector, international development assistance, donor states and regional development banks.

At the same time, it should be mentioned that "many projects are being implemented in developing countries, the associated financial flows are a new and largely untapped source of income for the improvement of livelihoods" (Peskett *et al.*, 2007).

"investments can start in terms of reducing greenhouse gas emissions", as well as adaptation to climate change and can support additional private investments" (European Environment Agency, 2017). In order to recognize the needs of investments in the field of climate change, The EU has committed at least 20% of the budget of the European Union for the period 2014-2020. This budget results in several EU funds that can be made available to local authorities to finance actions / measures to reduce greenhouse gas emissions and to adapt to climate change. The financing available is represented in the form of non-reimbursable grants, financial instruments and financing available for assistance for project development (PDA) and technical assistance (TA), but also consultancy services available for specific EU financing instruments.

Source: Financing climate action: opportunities and challenges for local and regional authorities, Commission for the Environment, Climate Change and Energy, European Committee of the Regions (2017).

The above figure shows a brief description of the EU financing instruments available to local authorities to finance measures / actions to reduce greenhouse gas emissions, but also to adapt to climate change.

At the same time, it should be mentioned that those EU funding instruments that support the implementation of climate actions, but have a precise destination (companies, organizations or other institutions) are not part of the scope of the above presentation.

Further, will be present briefly some details regarding the financing programs of the projects in the field of climate change: ESIF (European structural and investment funds (ESIF) consists of providing a financing source in the field of climate change, reducing greenhouse gas emissions or adapting to climate change), (European Commission, 2017).

The ESIF family is composed of five distinct funds:

- o ERDF (European Regional Development Fund);
- o European Social Fund (ESF);
- o Cohesion Fund (CF);
- o European Agricultural Fund for Rural Development (EAFRD);
- o European Maritime & Fisheries Fund (EMFF).

The Managing Authority of each Member State that co-manages or implements projects / programs deals with the granting of grants or financial instruments for the final beneficiaries. Within the INTERREG program, URBACT III aims to support sustainable urban development integrated in the cities of Europe through an exchange of knowledge and

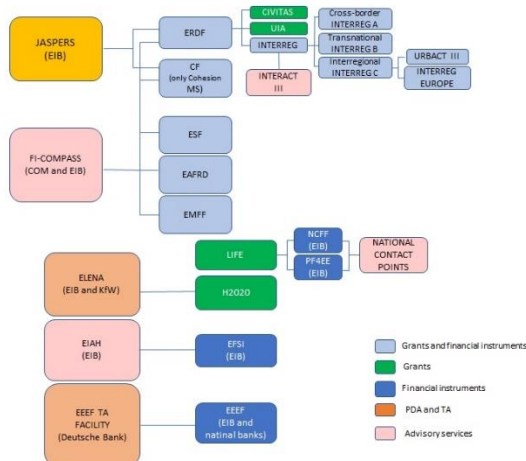


Fig. 2. Description of EU funding instruments available to local authorities

Climate finance is essential for both local and regional and national authorities because

better cooperation between Member States (URBACT, 2017).

The INTERACT III program wants to offer consultancy on various issues, but also how to use financial instruments within INTERREG. (INTERACT, 2017).

In addition, ERDF finances the CIVITAS program and the actions of urban innovation (UIA).

Civitas has the role to implement actions and measures regarding sustainable urban mobility in the EU.

The UIA aims to identify solutions and recommendations for urban challenges that range from the integration of migrants to the energy transition (Covenant of Mayors for Climate & Energy, 2016).

JASPERS (Joint Assistance for Support Projects in European Regions) provides support to authorities and promoters in preparing and implementing ESIF projects (JASPERS, 2017).

FI-Compass is a consulting service made available to managing authorities.

In addition, ESIF includes integrated territorial systems, which allow managing authorities to correlate different priority axes and operational programs for financing integrated urban and territorial strategies.

In addition to ESIF there are other EU funds specific to the field of climate change: LIFE, HORIZON 2020 (H2020), the European Fund for Strategic Investments and the European Fund for Energy Efficiency.

4. The role of cost-benefit analysis

The cost-benefit analysis consists of a process of evaluating the advantages and disadvantages of a project.

The economic analysis (cost-benefit) aims to evaluate the impact of the project on the well-being of the company / organization.

The main purpose of carrying out the economic analysis of an investment project is to provide information for the decision makers regarding the expected contribution of the project to the welfare of the company.

Thus, the analysis contributes to providing a means of identifying, quantifying and capitalizing on the types of impact that have emerged within a project. Also, if appropriate, the environmental impact will be established.

Cost benefit analysis "can be used to collect information on the consequence of a project, and to help organize the debate, by linking different opinions of various groups on what should be done to different opinions about the parameters of the analysis. CBA should therefore be understood as a

complement and a tool to open consultations and discussions, not as a replacement for them." (Hallegatte, 2016).

The purpose of the economic analysis of the potential impact and investments in climate change is to identify, quantify and highlight both the possible impacts of climate change on the costs and benefits of the project, as well as possible measures that can contribute to reducing these effects.

Regarding the achievement of the analysis result, it will be relevant if climate resistance could be implemented, especially in situations where several technical options for climate resistance are available, and the most appropriate option for the effects resistance. climate change should be recommended to decision makers. Also, the economic analysis can contribute to indicating the most opportune moment of the investments of resistance to the effects of the climatic changes.

The cost-benefit analysis is done through some stages, and the most important are the identification and quantification of the potential impact of the project. The field of climate change may introduce a note of uncertainty in the economic analysis of a project, but uncertainty is not a novelty in economic analysis. The necessity of writing the scenarios was and is necessary, and the degree of fulfilment can be known if ex post analysis is performed.

5. Identification of a management perspective in the field of climate change

In terms of emergency management, extreme weather phenomena, unlike other "traditional" phenomena that occur in the short term, cause short and medium term disasters with an identifiable pattern or a predictable path that is easy to anticipate and follow, but also easy to respond to the immediate action and establishing well-defined procedures for returning to the initial situation.

At the same time, climate change must be treated as a moving phenomenon in the short and medium term. Climate change may be able to produce more prolonged events with high probability and major impact on agriculture or the economy. Currently, climate change is a threat that is difficult to manage by local or county authorities around the world.

In this regard, it is proposed to impose measures, strategies and plans to reduce greenhouse gas emissions and to adapt to climate change.

We cannot help but think that regardless of the measures we will take locally, nationally or internationally, there is a high probability that the effects of climate change will become the biggest challenges for human safety and well-being.

Further, will be presented an emergency management perspective regarding climate change that has the role of providing a conceptual framework for stakeholders. The perspective will be able to be built around the management processes, such as forecasting and planning, coming to support the development of a guide for the elaboration of climate policies. In the forecasting stage (before planning), an assessment of the types of risks and vulnerabilities is required. It can be specified that these evaluations may be limited depending on the specific parameters. The assessments are conducted in a single jurisdiction and for a limited period of time (for example, 10 years). These parameters may be insufficient in terms of the impact of long-term climate change (50 or 100 years). At the same time, the risk assessment must also take into account the geographical characteristics, moving from a global perspective to a local one, as climate change acts, to a large extent, locally.

National and international entities must provide mechanisms for integrating local planners and their assessments into a global network and for connecting local planners and specific disaster threats that will vary from location to location, to a wider global nexus than climate change analysis and expertise.

In the field of climate change, the risk assessment process must correlate with the expertise of specialists, researchers, experts in international relations and other relevant persons who can add value in the evaluation.

The assessment of risks and vulnerabilities is followed by the forecasting / preparation and planning phases.

Preparation (forecasting) involves building capacity (technology and personnel), expertise (training) and resources to respond effectively in the interest of public safety and protection of community infrastructure in the face of the effects of climate change.

For example, sea level rise could flood low-lying areas of the globe, and populations living in those areas will have to migrate to other safe places.

An adverse event that leads to migration to other areas can cause long-term effects, affecting other generations.

Climate change has led to the loss of agricultural land, and the urgent need is to adapt agricultural crops (resilience to climate change).

To achieve a high degree of sustainability, each community must assess its environmental resources and risks, and then choose the level of risk they are willing to bear and define the losses that are unacceptable and those that must be avoided and ensure that all community development policies and activities comply with all requirements and recommendations. Given that the effects of climate

change may be adverse, even devastating in some situations, it is necessary for all communities to be prepared for the management of situations in the event of the occurrence of events that can manifest in a very short time and cause major damage.

Some techniques for minimizing and reducing risk are already being widely used. At the same time, the authorities have adopted an inconsistent approach regarding the emergence of the risks caused by climate change that are occurring more and more regularly and unexpectedly.

In this regard, it should be specified that the decision makers should promote the correlation between the efforts to reduce or minimize the risk and the impact of climate change.

In most cases, responding to the effects of climate change and reducing them are considered two separate phases in managing emergency situations.

But, considering the time period of the global climate disaster already underway, the possibility of mitigating and creating communities more resistant to danger is, in fact, an appropriate response mechanism. This should provide a renewed impetus for reducing greenhouse gas emissions. It offers a double meaning for decision makers in order to highlight disaster reduction and resistance as a policy priority.

In fact, it should be a policy priority at local, national and international level.

In this respect, the decision-makers can contribute to the efficiency and management of climate change mitigation efforts and their response to them.

The main priority of the decision-makers must be the study and understanding of the potential impact of global climate change and the responsible improvement of mitigation and adaptation measures where necessary and feasible.

In this sense, a common approach or perspective in order to develop climate policies can help to achieve coherence and efficiency in the field of climate change.

6. Recommendations

With a view to a good management of financing in the field of climate change, the following steps can be recommended:

- allocation of additional resources to finance measures / actions to adapt to climate change and reduce greenhouse gas emissions;

In this way, central public authorities should continue to use financial sources and ensure that existing public investments function effectively.

Nationally, the existence of a financial fund for climate change can be highlighted, which will become an easier way of accessing the financing when needed, but also an easier attraction of the

financing sources. All these will be able to contribute significantly to the realization of as many climatic actions. This financial fund should be managed by an existing institution, such as the Ministry of Finance / the Ministry of European Funds.

- implementation of economic and financial instruments in order to stimulate private sector investments in a green ecological economy, considering the extension of activities in front of financial constraints;

Central public authorities and the Government are largely dependent on subsidies to support climate development initiatives and a low carbon economy.

Obviously, it is clear that climate change will lead to a thorough preparation to prevent natural disasters and will require more resources globally, as well as the ability to combine or integrate efforts in jurisdictions and even internationally, when it is necessary to respond to disasters.

- evaluation of the impact of climate change in all sectors of activity;

- conducting studies to identify the risks and vulnerability of the danger in relation to the projected impact on climate change;

- identify and prioritize actions aimed at mitigating the risks and vulnerabilities identified to reduce the impact of climate change;

- increased protection and improvement of the environment and the role it plays in creating communities resistant to danger and reducing the impact of future disasters;

- improve response capabilities for all-natural disasters and expand resources to cope with the expected impacts of global climate change;

- support regional, national and international cooperation to assess risks and vulnerabilities and to respond to increasingly probable and unprecedented mega-disaster scenarios;

- identify progress and update climate change impact assessments.

7. Conclusions

Through this article is desired to increase the importance of climate finance and implement risk management for climate change. At the same time, a perspective has been suggested that may support decision-makers in assessing and responding to climate change.

Given that the planning, mitigation and response are best implemented within the community, decision makers need to adopt an emergency management perspective.

In conclusion, it can be mentioned that this article lays the foundations of an approach that will allow decision makers to interact and think about identifying measures that can be achieved through an analysis (for example, cost-benefit analysis) in the field of climate change. Climate change plays an important role and we must take into account the management of extreme weather events that can cause major damage, but also define it as a natural disaster in order to implement the preparation and planning of the best solutions to reduce gas emissions with greenhouse effect and adaptation to climate change.

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ADVANTAGES AND DISADVANTAGES OF CHEMICAL METHODS IN THE ELABORATION OF NANOMATERIALS

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ABSTRACT

Reducing the size of macroscopic systems to nanometers can be achieved by top down synthesis by different chemical or physical methods. The bottom-up approach is a method in which the components of the atomic or molecular dimensions are assembled together to form nanoparticles. The bottom-up method is used for the elaboration of nanoparticles, because it allows the control of their size. This article presents a review of the advantages and disadvantages of chemical methods for the development of nanomaterials.

KEYWORDS: top-down, bottom-up, methods, elaboration, advantages, disadvantages

1. Introduction

The methods of synthesis of nanometric structures include two approaches, depending on the precursors used:

- top down
- bottom-up

In the first category, the "top down" synthesis, nanoparticles are obtained by reducing the size of macroscopic systems at nanometers. The reduction of the particle size can be achieved through different physical or chemical methods.

The methods of synthesis of "top down" are sought to be replaced or improved due to imperfections in the structure of the obtained material. This is a major limitation because the surface chemistry and other physical properties of the nanoparticles are strongly dependent on the structure of the material. In addition, they may contain significant amounts of impurities. The particles have a relatively wide distribution of different sizes and shapes.

Following the studies of the bibliographic references, the following advantages and disadvantages are presented in the Table 1.

Table 1. Advantages and disadvantages of "top down" synthesis

<i>Advantages</i>	<i>Disadvantages</i>
✓ large-scale production;	✓ size distribution (10-100 nm);
✓ it is possible to deposit on a large substrate;	✓ expensive technique;
✓ no chemical purification is required.	✓ various particle shapes;
	✓ controlling the deposit parameters is difficult to achieve.

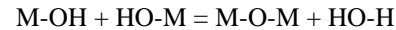
The bottom-up approach is that method in which the components of atomic or molecular dimensions are assembled together to form nanoparticles. The bottom up method is much more used for the elaboration of nanoparticles, because it allows to control their size. The bottom up approaches have

proved to be more versatile, which is why a multitude of nanoparticle synthesis techniques have been developed following the principle of self-assembly [1]. Following the studies of the bibliographic references, the following advantages and disadvantages are presented in the Table 2.

Table 2. Advantages and disadvantages of "bottom up" synthesis

Advantages	Disadvantages
✓ obtained nanoparticles, nanotubes;	✓ large-scale production is difficult;
✓ the deposit parameters can be controlled;	✓ chemical purification of nanoparticles is required.
✓ it is possible to distribute the narrow size (1-20 nm);	
✓ cheaper technique.	

2. Methods of elaboration



2.1. Sol-gel method

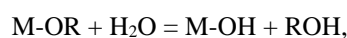
The sol-gel method was first described by the chemist Ebelmen [2] in the mid-19th century. The soil is a colloidal suspension of oligomers ("oligomer = monomer molecular complex" whose diameter is several nanometers). Thereafter, this "soil" may be developed by chemical reactions, i.e. polycondensation or polyesterification, forming alcohol molecules in the bridges, until gel formation. This freezing process offers many advantages for producing large materials with homogeneity and purity at lower temperatures than conventional methods. Thus, the gel obtained is subjected to the drying process and the resulting product is transformed into xerogel, followed by a heat treatment that will eventually form powders [3, 4].

The sol-gel method does not involve melting or sintering powders to produce ceramics, but uses a solution containing reactive precursors such as alkoxides or metal salts. The precursors for the preparation of a colloid consist of a metal or metalloid element surrounded by various ligands. Metal alkoxides (R-O-M) are similar to alcohols (R-OH) with a metal atom M, replacing hydrogen H in the hydroxyl group. They are the class of chemical precursors most commonly used in soil-gel synthesis, because they are subject to hydrolysis depending on the amount of water and the catalyst present.

The sol-gel method makes it possible to obtain various materials, especially in the form of films, fibers, monoliths or submicron powders.

The sol-gel technique is based on two classic chemical reactions of nucleophilic substitutions: hydrolysis and condensation according to the following:

The hydrolysis is reproduced by the following reaction:



The condensation is given by the reactions below:



where: M represents a metal cation such as silicon, titanium or zirconium and the organic R alkyl group.

Researchers have become aware of the potential of the sol-gel method to provide new advanced functional materials, based on various micro and macrostructures. Thus, Shek *et al.* (1999) obtained by the sol-gel method of tin oxide, SnO₂ nanocrystals with a particle size close to 3.5 nm [5].

Piccaluga *et al.* (2000), Huang *et al.* (2003) made composite nanopowders containing elementary nano-Ni-SiO₂ and Fe-Al₂O₃ particles. Bruni and his colleagues (1999) synthesized the following oxides using this method: Fe₂O₃-SiO₂, NiO-SiO₂ or 3Al₂O₃-2SiO₂, thus verifying that the sol-gel technique is a good way to produce nanocomposites containing inorganic nanoparticles [6]. Andrei Jitianu and his collaborators have developed nano-sized SnO₂ clusters using sol-gel technique [7]. S. Mahshid and his team synthesized TiO₂ powders by this method [8]. In the 2001 paper, Gash and his colleagues developed nanostructured iron oxide (III) monolith (Fe₂O₃) by the sol-gel synthesis method with the iron chloride (III) reagent [9]. Research continued later and Tang and colleagues (2004) synthesized thin magnetite films (Fe₃O₄) using the same procedures and reagents, but found that pure magnetite could not be synthesized by using iron (III) chloride as a precursor due to the formation of impurities of hematite (α-Fe₂O₃) and magnetite (γ-Fe₂O₃) [10]. In 2013 Shaker and his colleagues obtained sol gel magnetic nanoparticles (Fe₃O₄) technique and showed that the crystallinity was improved at a higher treatment temperature and therefore the particle agglomeration decreased dramatically [11]. Khodadadi and his colleagues developed sol-gel method of Al₂O₃ nanocrystals and Fe-doped Al₂O₃ nanocrystals [12]. Sun and his associates successfully reported soluble gel-soluble ZnO thin films at a relatively low temperature (≤200 °C), which can function as an efficient transport layer in inverted solar cells [13]. Copper oxide nanostructures were synthesized by this method using different concentrations of copper nitrate [14]. Research conducted by Tayseir. M., and his collaborators in 2017 led to the sol-gel synthesis of hydrophobic

silicon nanoparticles containing zirconium, highlighting the influence of zirconium content on the texture, structure and morphology of the synthesized silica [15]. Following the studies of the bibliographic

references, the following advantages and disadvantages of this process are presented, presented in Table 3.

Table 3. Advantages and disadvantages of the sol-gel method

<i>Advantages</i>	<i>Disadvantages</i>
✓ can produce a thin coating to ensure excellent adhesion between the substrate and the top layer;	✓ the contraction that occurs during processing;
✓ can produce a thick coating to provide protection against corrosion;	✓ residual hydroxyl and / or carbon groups;
✓ it has the capacity of sintering at low temperatures, between 200-600°C;	✓ long processing time;
✓ simple, economical and efficient method to produce high quality coverage;	✓ fine pores;
✓ synthesizes high purity products, because the organo-metallic precursor of ceramic oxides can be dissolved in a specified solvent and hydrolyzed in a soil and subsequently a gel, the composition can be highly controllable.	✓ use of organic solutions that can be toxic.

2.2. Polymer precursor method (PPM) – Pechini method

The method was proposed in 1967 as a technique for depositing titanium and niobium

dielectric films and alkaline-earth metals in condensation production. Later, the process was customized for the synthesis of oxide materials in the laboratory.

Table 4. Advantages and disadvantages of the Pechini method

<i>Advantages</i>	<i>Disadvantages</i>
✓ versatility;	✓ use of toxic ethylene glycol and organic reagents; ✓ the lack of stable citric complexes of elements (bismuth, silicon, etc.), as well as the partial or complete regeneration of one of the components during the pyrolysis of the polymer gel (for example: copper, lead, zinc, ruthenium, etc.).
✓ almost complete independence of the process conditions of the positive ion chemistry contained in the final material;	
✓ the relatively low temperature of the precursor, due to which the process can occur almost completely without sintering.	

The method is based on an intense mixing of the positive ions in a solution, the controlled transformation of the solution into a polymeric gel, the removal of the polymeric matrix and the development of an oxide precursor with a high degree of homogeneity [16]. During the synthesis process, metal salts or alkoxides are introduced into a solution of citric acid with ethylene glycol. The formation of citric complexes balances the difference in the individual behaviour of the ions in the solution, which leads to a better ion distribution and prevents the separation of the components in the later stages of the

process. Polycondensation of ethylene glycol and citric acid begins at over 100 °C, resulting in the formation of citrate polymer [17]. When the heating temperature exceeds 400 °C, oxidation and pyrolysis of the polymeric matrix begins, which results in the formation of an amorphous oxide and a carbonate precursor. Subsequent heating of this precursor results in the formation of the required material with a high degree of homogeneity and dispersion. Today, the Beijing method is widely used in the synthesis of dielectric, fluorescent and magnetic materials,

superconductors and high temperature catalysts, as well as for oxide films and coatings [18, 19].

Following the studies of the bibliographic references, the following advantages and disadvantages of the polymeric precursors' method presented in Table 4.

2.3. Microemulsion method

Microemulsions are isotropic solutions, macroscopically homogeneous and thermodynamically stable, containing at least three components, namely a polar phase (usually water), a nonpolar phase (usually oil) and a surfactant. At the microscopic level, the surfactant molecules form an interphase film that separates the polar and nonpolar domains. This interface layer forms different microstructures, ranging from oil droplets dispersed in a continuous aqueous phase (oil / water microemulsion) to a bicontinuous phase with water droplets dispersed in a continuous oil phase (water / oil microemulsion).

The latter can be used as nanoreactors for the synthesis of low polydispersion nanoparticles (Julian *et al.* 2006, Destree *et al.* 2008, Zhong-Min *et al.* 2007, Wanzhong *et al.* 2006) [20-23].

Different types of microemulsions are known, such as water in oil (A /U), oil in water (U/A), water in sc-CO₂ (A/sc-CO₂), oil in sc-CO₂U/sc-CO₂). The microemulsion method is one of the versatile preparation techniques that allows the control of the properties of particles such as size, geometry, morphology, homogeneity and surface area (Hu *et al.*, 2009, Pileni, 2003) [24, 25].

Many published studies discuss different aspects of microemulsions (Pileni, 2001, Pileni, 2007, Pileni, 2008, Lopez-Quintela and co-workers, 2004, Cushing and co-workers, 2004, Shervani and co-workers, 2003) [26-31].

The microemulsion method was used for the synthesis of colloidal compounds, as follows: colloidal Fe₃O₄, colloidal AgCl, nanocrystalline Fe₂O₃, TiO₂, Al₂O₃ and YBa₂Cu₃O₇ (Boutonnet and

co., 1982, Ayyup and co., 1988, Hou and Shah, 1988, Lal and co. his, 1998, Zhang *et al.*, 2002) [32-39].

The term microemulsion was proposed by Schulman *et al.* (1959). They prepared a quaternary solution of water, benzene, hexanol and K-oleate, which was stable, homogeneous and slightly opalescent. These systems became clear as soon as a short-chain alcohol was added. In 1943-1965, Schulman and his colleagues described how to prepare these transparent systems. Basically, a coarse (or macro) emulsion was prepared and the system was then titrated to form a transparent solution by the addition of a co-surfactant (the second surfactant). Most of the work reported by Schulman concerned systems with four components: hydrocarbons (aliphatic or aromatic), ionic surfactants, co-surfactants (generally carbon chain 4-8 aliphatic alcohol) and an aqueous phase [40]. He proposed that the surfactant and co-surfactant, when properly selected, form a mixed film at the oil / water interface, resulting in an interphase pressure that exceeds the initial positive interfacial tension. To summarize, the basic observation made by Schulman *et al.* was that when a co-surfactant is titrated in a coarse compound microemulsion from a mixture of water / surfactant in an amount sufficient to obtain micro-droplets, the result can be a system that is low viscosity, transparent, isotropic and very stable. The titration from the opaque emulsion to the transparent solution is spontaneous and well defined. It has been found that these systems are made of spherical micro-droplets with a diameter between 600 nm and 800 nm. It was not until 1959 that Schulman proposed to name microemulsions of these systems. Previously, he used terms such as transparent water and oil dispersion, oleopathic hydromicels or hydroopathic oleomycetes. From this moment, microemulsions have found a wide range of applications, from oil recovery to nanoparticle synthesis, as reported by Chhabra *et al.* (1997) [41].

The advantages and disadvantages of the microemulsion method are summarized in the following Table 5.

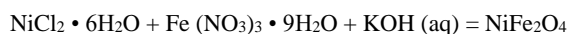
Table 5. Advantages and disadvantages of the microemulsion method

Advantages	Disadvantages
✓ they are easy to prepare and do not require an energy contribution during synthesis;	✓ large amount of surfactants;
✓ the preparation is due to better thermodynamic stability;	✓ temperature stability influenced by microemulsion, pH;
✓ the formation of the microemulsion is reversible;	✓ limited solubility capacity for substances with high melting points.
✓ thermodynamically stable;	
✓ low viscosity compared to emulsions.	

2.4. Hydrothermal method

The hydrothermal method consists of obtaining nanomaterials through hydrolysis reactions at high temperatures of the various compounds directly in an autoclave. The synthesis can have as precursors products obtained previously at room temperature based on the crystallization of the phases under high temperatures and pressures. Hydrothermal synthesis can be performed both at temperatures and at pressures below the critical point for a specific solvent over which the differences between liquid and vapor disappear and under supercritical conditions. The solubility of many oxides in hydrothermal salt solutions is much higher than in pure water (such salts are called mineralizers). There is also a group of solvothermal synthesis methods, related to hydrothermal methods; this group of methods is based on the use of organic solvents and supercritical CO₂ [42]. Substantial improvement of the hydrothermal method facilitates the use of additional external factors to control the reaction environment during the synthesis process. From now on, this approach is implemented in the methods of microthermal hydrothermal synthesis, hydrothermal-ultrasonic, hydrothermal-electrochemical and hydrothermal-mechanochemical. The hydrothermal method is a simple and versatile method for the synthesis of inorganic nanomaterials at high temperatures and pressures. Thus, it is possible to obtain the nanoparticles by adjusting the processing conditions, including temperature, pressure or concentration of precursors. The main parameters of the hydrothermal synthesis, which define both the

process kinetics and the properties of the resulting products are the initial pH of the solution, the duration, the temperature of the synthesis and the pressure in the system [43]. The synthesis is carried out in autoclaves that are stainless steel cylinders, which can withstand high temperatures and pressures for a long time. A precursor solution, often in the presence of a hydrolysis agent, is autoclaved at a certain temperature for a certain period of time. In a typical hydrothermal process, the aqueous solution of the precursor and KOH is mixed and introduced into the autoclave maintained at 70-200 °C for 10-24 hours depending on the process and then cooled in air at room temperature. The resulting precipitate is collected by filtration, washed and finally dried. For example, nickel ferrite particles prepared by hydrothermal processes led to size distribution particles from 40-90 nm, as reported by Cheng *et al.* [37], according to the reaction:



Some of the most popular nanomaterials produced by the hydrothermal method are synthetic zeolites. A prerequisite for their production is the presence in solution of surface agents (SAAs) that actively influence the morphological evolution of oxide compounds in hydrothermal solutions. The choice of the synthesis conditions and the type of surfactants can ensure the production of targeted pore nanomaterials with a pore size, controlled in a wide range of values [44]. The advantages and disadvantages of the hydrothermal method are summarized in the following Table 6.

Table 6. Advantages and disadvantages of the hydrothermal method

Advantages	Disadvantages
✓ the ability to synthesize substances that are unstable near the melting point;	✓ high cost of equipment;
✓ the ability to synthesize large crystals of high quality.	

2.5. Sonochemical method

The sonochemical method is one of the recently discovered techniques that offers a versatile way to obtain nanostructures for different applications. This represents the use of high intensity ultrasounds, which induce synthesis conditions distinct from other conventional methods such as hydrothermal synthesis, spray pyrolysis method and wet chemical method (Bang and Suslick, 2010; Suslick, 1990; Suslick and Price, 1999).

These specific conditions are generated during acoustic cavitation, which produce high temperatures and high pressures in the center of the bubbles formed

in the solution. The bubbles are obtained when the solutions are exposed to high intensity ultrasound. The reaction conditions in the sonochemical method are as follows:

- the speed of noise in the liquid should be in the range 1000-1500 ms⁻¹;
- the ultrasonic wavelength is required between 10 cm and 100 μm;
- the frequency range from 20 kHz to 15 MHz is required.

Suslick in his 1989 paper points out that cavitation is the formation, growth and implosive bursting of bubbles in a liquid. Cavitation collapse produces intense local heating (~ 5000 K), high

pressures (~ 1000 atm) and enormous heating and cooling speeds (> 109 K/sec) and fluid jet flows (~ 400 km/h) [39].

Two types of materials, such as volatile and non-volatile precursors, have been used in the sonochemical method as a raw material for the production of nanomaterials through different reaction mechanisms (Xu *et al.*) [45].

If volatile compounds are used as precursors in the sonochemical method, it is called primary sonochemistry, and if non-volatile compounds are used, it is called secondary sonochemistry.

In primary sonochemistry, free metal atoms are generated from volatile organometallic compounds by bond dissociation, facilitated by the high temperature produced during bubble collapse. The obtained atoms are injected into the liquid phase and subsequent nucleation gives rise to nanoparticles of various materials in the presence of a suitable template. In the latter case, the sonochemical reactions occur just outside the balloon, which is subjected to the reaction with the radicals. Radicals diffuse into the liquid, result in a reaction and generate nanomaterials.

Using this method, different metal oxide nanoparticles have been developed, and the number of papers that report data on their synthesis and application is quite large. Among the metal oxides, the synthesis and applications of the transition metal oxides, and in particular TiO₂, ZnO and Fe₃O₄, have attracted the interest of the research. The nanocrystalline TiO₂ anatase (6 nm) with the BET specific surface area of 300 m²g⁻¹ and the direct band difference of 3.31 eV were prepared sonochemically (Gonzalez-Reyes *et al.*) [84]. It was then subjected to heat treatment from 400 to 900 °C for 2 hours to produce the desired anatase-rutile ratio. During the elaboration three stages were observed in the heat-treated samples:

In the first stage, the anatase granules coagulate as a result of the temperature of the heat treatment, increasing the structural homogeneity and crystallinity, both phenomena producing a reduction of the specific surface. In the second stage the coexistence of two phases (anatase and rutile) are separated by a transition region, called an interface. In the last stage a process takes place in which the rutile nuclei evolve into a new form of equilibrium without the presence of the anatase phase, minimizing the total energy of the surface and the border, by the diffusion of mass transport. In this last stage, the rutile phase has the only function of growth and densification.

To encapsulate Fe₃O₄ nanocrystals into fibers using sonic-chemical synthesis followed by a reflux procedure (Yang *et al.*) [46], a method was developed by adapting the use of tetraethylortosilicate, ammonia, Cd²⁺ and thioglycolic acid to a synthesis.

Conducted by ultrasound, the Fe₃O₄ nanoparticles were coated with a thin shell. Ultrasound treatment plays an important role in preventing Fe₃O₄ agglomeration. The monodisperse Fe₃O₄ particles in the fibers showed a superparamagnetic behaviour. The ZnO, NiO₂ and MnO nanowires were successfully synthesized by the sonochemical method in solutions at room temperature. The reactants used are (M(Ac)₂·2H₂O, sodium hydroxide NaOH and H₂O/C₂H₆O as carrier in polyethylene glycol matrix. Parameters (NaOH solution concentration, ultrasonic strength and sonication time) influenced the morphology of the nanostructures (Aslani and collaborators) [47].

Askarinejad and his colleagues investigated the epoxidation of styrene and cyclooctene with anhydrous tert-butyl hydroperoxide on prepared nanocatalysts (Co₃O₄ and Mn₃O₄).

The results of the conversion activity were compared with conventional Co₃O₄ and Mn₃O₄. Under optimized reaction conditions, the nanocatalysts showed higher catalytic performance compared to conventional catalysts [48].

Titanium oxides (TiO₂) with honeycomb structures have been successfully replicated from a bio-template using a sonochemical method. The bio-templates of cedar wood type were irradiated under ultrasonic wave in TiCl₄ solutions and then calcined at temperatures between 450 and 600 °C (Zhu *et al.*) [49]. Photocatalytic activities were evaluated by measuring the percentage of methylene blue degradation using UV-VIS spectroscopy. The calcination temperature has a strong effect on the photocatalytic activity.

ZnO nanoparticles were successfully developed by ball milling through solid-liquid reactions, assisted by ultrasonic wave. Ultrasonic waves have been found to be a key factor promoting the transformation from Zn(OH)₂ to single-phase ZnO nanoparticles (Ding and Ting) [50].

CuO nanoparticles were sonically prepared from copper acetate and sodium hydroxide in the presence of polypropylene glycol and polyvinyl alcohol (Ranjbar-Karimi *et al.*) [51]. Variations of several parameters and their effects on the structural properties of nanoparticles (particle size and morphology) were investigated. A 0.05 M solution of copper acetate in the presence of polypropylene glycol gave the best results. Mn₃O₄ nanoparticles were prepared using an isochemical method without requiring pH adjustment (Baykal *et al.*) [52, 56]. The synthesized material was identified as a tetragonal. The magnetic evaluation revealed a blocking temperature of 313 °C, above which the material behaves paramagnetically. The asymmetric coercive field is attributed to the interaction between ferromagnetic Mn₃O₄ and the antiferromagnetic Mn

oxide at the nanoparticle surface. Binding of a semi-essential amino acid, L-arginine, on the surface of the nanomagnetite, created a stable aqueous suspension using the step-by-step synthesis method (Theerdhala and co-workers) [53]. The initial concentration of the amino acid was shown to play an important role in particle sizing. It was found that lower concentrations of arginine favour the formation of elongated tubular structures, whereas at higher concentrations, elongated structures were less prominent and it was found that arginine is adsorbed on the magnetite surface. The formation of uniform α -Fe₂O₃ nanoparticles has been reported and their magnetic properties have been investigated by Koo and his colleagues [54].

Sonochemical synthesis resulted in the formation of α -Fe₂O₃ spherical nanoparticles with an average diameter of 60 nm. ZnO microspheres were prepared by sound-chemical synthesis at room temperature using carbon spheres as a template (Xiaohua *et al.*). The diameter of the hollow spheres obtained is about 500 nm, and the walls are composed of numerous nanocrystalline ZnO aggregates with diameters of 90 nm. A growth mechanism has been proposed for the formation of ZnO microspheres, in which carbon spheres play a crucial role in the formation of hollow ZnO microspheres [55, 57, 58].

The advantages and disadvantages of the sonochemical method are summarized in the following Table 7.

Table 7. Advantages and disadvantages of the sonochemical method

Advantages	Disadvantages
✓ improves reaction rate;	✓ extension of problems;
✓ involves high energies and pressures in a short time;	✓ inefficient energy;
✓ no additives needed;	✓ low yield.
✓ reduced number of reaction steps.	

3. Conclusions

There are two types of approaches to the synthesis of nanomaterials: top down and bottom-up. The "top down" synthesis, nanoparticles are obtained by reducing the size of macroscopic systems at nanometres. The "bottom-up" method is much more used for the elaboration of nanoparticles, because it allows to control their size. In order to elaborate the nanomaterials, the chemical methods allow the control of the reaction parameters so that particles of nanometric dimensions are obtained. In the literature there are studies on the advantages and disadvantages of chemical methods [56]. Some of these specific advantages and disadvantages consist of: sol-gel synthesis has many advantages for producing high quality materials with homogeneity and purity at lower temperatures than conventional methods, and as a disadvantage it has a long processing time, Pechini method has the advantage that it is widely used in the synthesis of dielectric, fluorescent and magnetic materials, superconductors and high temperature catalysts, as well as for the deposition of oxide films and coatings, and as a disadvantage the use of organic reagents that can be toxic. The microemulsion method allows the control of particle properties such as size, geometry, morphology, homogeneity and surface area. The disadvantage of the microemulsion method is the large amount of surfactants used. One of the advantages of the sonochemical method is that it involves high energies

and pressures in a short time, and the disadvantage is the low efficiency.

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