BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI

Volumul 67 (71)
Numărul 3-4

Secția
ŞTIINŢA ŞI INGINERIA MATERIALELOR

2021 **Editura POLITEHNIUM**

BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
PUBLISHED BY
"GHEORGHE ASACHI" TECHNICAL UNIVERSITY OF IAŞI
Editorial Office: Bd. D. Mangeron 63, 700050, Iaşi, ROMANIA
Tel. 40-232-278683; Fax: 40-232-211667; e-mail: buletin-ipi@tuiasi.ro

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BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
BULLETIN OF THE POLYTECHNIC INSTITUTE OF IAŞI
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BULLETIN OF THE POLYTECHNIC INSTITUTE OF IAŞI
Volume 67 (71), Number 3-4 2021

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Publicat de
Universitatea Tehnică „Gheorghe Asachi” din Iaşi
Volumul 67 (71), Numărul 3-4, 2021
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PRELIMINARY RESULTS ON THE ANALYSIS OF MATERIALS USED IN MICRO-ELECTRONICS

BY

IONUȚ ADOMNIȚEI*, ANA-MARIA ROMAN, VASILE MANOLE, CĂTĂLIN PANAGHIE and NICANOR CIMPOEŞU

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Received: September 3, 2021
Accepted for publication: October 20, 2021

Abstract. Presenting the materials used from the beginnings of electronics until today we can see the exceptional evolution that this field has undergone, especially based on the usefulness and infusion of money, in terms of materials, especially those metallic, used for this purpose. The increasingly demanding requirements of the electronics market in general and that of computers in particular have meant that electronic materials are also constantly changing in search of new properties and materials with new features to meet these needs. Starting from the size of a class, computers have evolved in computing power from a few instructions per second to several million instructions per second, reaching the size of a sheet of paper all these developments being possible only based on the advancement of processing technologies. of materials. Starting from the materials initially used in this area of maximum economic interest, in this paper we arrive at the analysis of integrated circuits that present basic cells and connection architectures of micron dimensions as well as a Pentium IV microprocessor in terms of connections. and of the connectors used the chemical elements encountered on the silicon support being aluminum, gold, tungsten, rubidium and light elements such as oxygen, nitrogen or carbon. The current phase of the investigation of the materials used and of the processes of their realization and implementation presented in the paper is a transition to the analysis of nano-circuits that are increasingly taking place in the field of electronics through the tumultuous development of nano-technologies.

Keywords: nano-circuits; electronics; nano-technologies.

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1. Introduction

Semiconductor materials such as silicon and germanium have a diamond-like crystalline structure belonging to the cubic family. Others such as GaAs have a zinc blend structure close to that of diamond. At these, the Ace atoms alternate with the Ga ones and their concentration determines the type of semiconductor and conductivity. The bonding forces that hold the crystal structure are mainly strong forces such as covalent bonds. In addition to these, electrostatic forces such as ionic bonds are also manifested. When the temperature rises, the thermal vibrations can overcome the force of the covalent bonds that break releasing electrons that can contribute to the change of the conductivity of the material (Iancu, 1988).

The operation of semiconductor devices is based on the movement of charge carriers (electrons and gaps) in the material. The energy levels that electrons can occupy in the solid body are arranged inside permitted energy bands, separated by forbidden bands, in which electrons cannot have energy. At temperatures higher than absolute zero, there are always a number of free and empty electrons, due to the breaking of covalent bonds (the phenomenon of generating electron-empty pairs) (Şchiopu and Vasilescu, 1976; Jeludev, 1973; Iancu *et al.*, 1976; Meinhardt, 1999). These carriers are almost free, they do not belong to a certain atom and can move through the crystal lattice, participating in the conductivity of the material. Sometimes they can enter a covalent bond and disappear as free carriers (the phenomenon of electron-empty recombination). In order to increase the conductivity of a semiconductor, impurities (atoms of foreign materials) are introduced by controlled doping, which have a different number of valence electrons than the semiconductor (Hopkins, 1998; Tummala and Rymaszewski, 1989; Baliga, 1988; Jacobsen and Hopkins, 2000; Giesselmann, 1997).

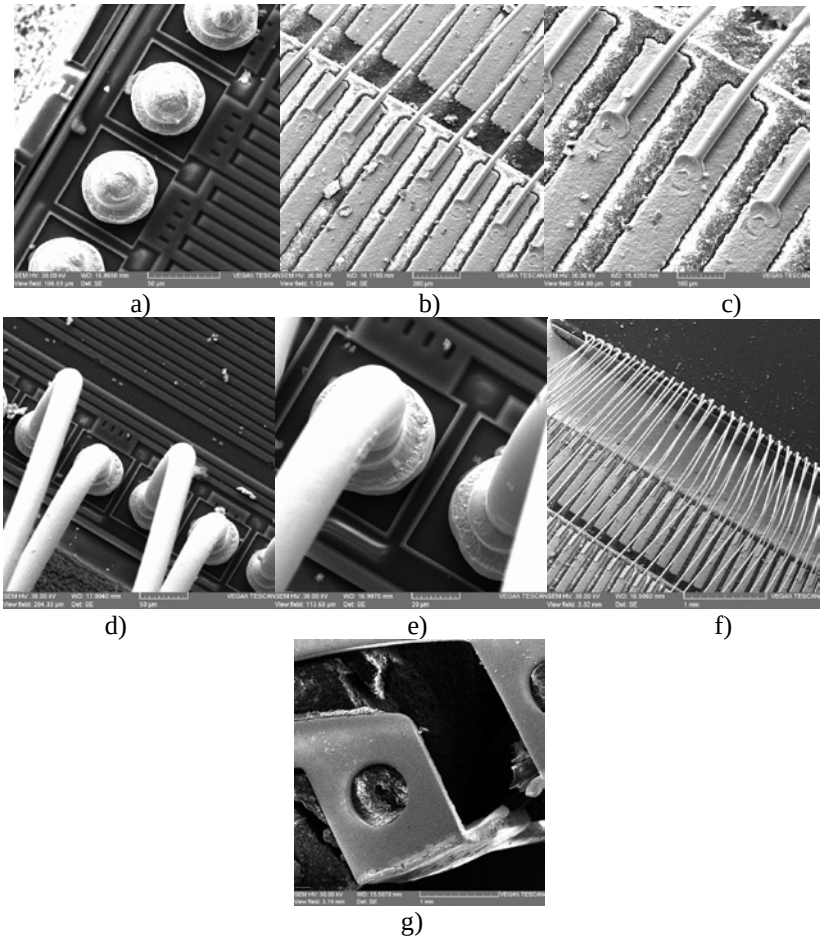
For example, if some base atoms are replaced by group III atoms (Al, Ga, etc.) in silicon that is tetravalent, an electron deficit will result for the covalent bonds. As a result, there will be a higher concentration of gaps (free places) than free electrons. The semiconductor is called the p-type and the conduction is given mainly by gaps. In another situation, when some base atoms are substituted with group V atoms (P, Ga, etc.), there will be free electrons, not fixed in the covalent bonds that will participate in the conduction. In this case the semiconductor is of type n, and the conduction is mainly electronic (Mohan *et al.*, 1995; Trzynadlowski, 1994; Novotny and Lipo, 1996). The materials from group III are called acceptors, and those from group V are called donors. Undoped semiconductors are called intrinsic, and their conduction is given by both electrons and gaps (Von Jouanne, 1996).

2. Experimental Results

The micro-electronic advance, certainly caused by the enormous infusion of capital in this field, was also achieved through the contribution of the electron microscope. Fig. 1 shows some electronic images of the connectors, contact wires and their assemblies taking into account that their dimensions are of the order of microns. Microscopes were performed at magnifications 100, 500, 1000, 5000 and 10,000 times.

The microscopic analysis of these elements used in obtaining electronic parts presents us with several technologies for obtaining them as well as information on the processing methods of the metallic materials used.

Fig. 1 a) shows a contact model in spherical shape used on a support of different material for the centralization of different paths, micron or sub-micron, and to achieve the transfer of electric current.



a) b) c)

d) e) f)

g)

Fig. 1 – Electronic micrographs of contacts used in microprocessors.

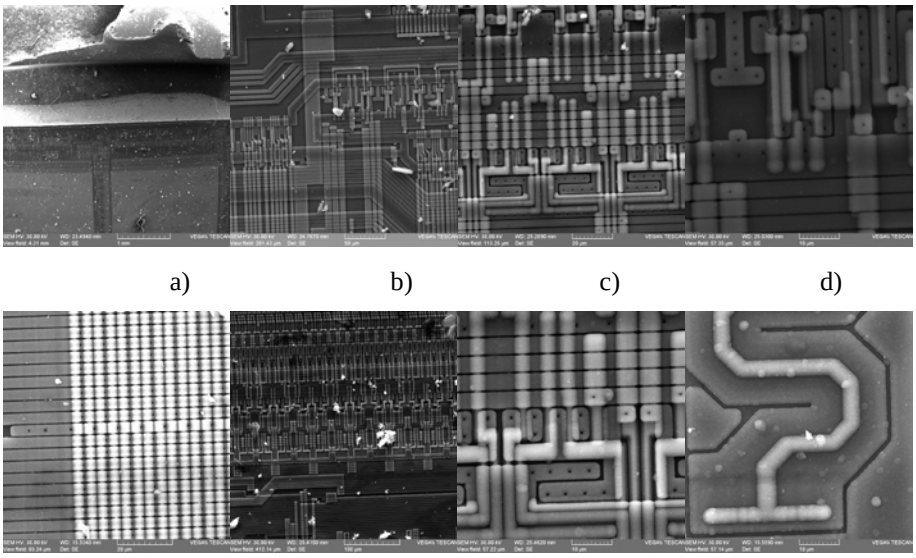
Fig. 1 b) shows another element for connecting and transmitting information, data in the form of electric currents, also small in size and having a connection detail by pressing and melting them in Fig. 1 c). Fig. 1 d) and e) shows the connection of these "mains" for the transfer of electric currents to the marginal architecture that transmits or takes over the information through the connection pins.

Fig. 1 f) shows an overview of the structure of the connecting wires with the observation that they have precise dimensions and locations, the contact between them being totally forbidden. Fig. 1 g) shows a marginal connecting element that makes the connection with the external pins of the microprocessor.

The extremely small dimensions, main contacts between 5 - 10 μm and secondary contacts between 1 and 2 μm make obtaining these pieces a very interesting subject, revealing the fact that at the microscopic level the materials are not only analyzed but are also used for commercial purposes.

Fig. 2 shows the electron microscopes made on an integrated circuit, an integrated video, especially being analyzed the marginal architecture, its connection with the connecting pins.

Fig. 2 a) shows an overview of the element pursued at a scale of 100x magnification, observing at the top the silicon support on which the integrated was made, in the middle the marginal architecture of the connection and at the bottom working cells and central link architecture.



a) b) c) d)

e) f) g) h)

Fig. 2 – Electronic micrographs of an integrated circuit, a video driver, with the presentation of its architecture and especially of the connection structure.

Fig. 2 b), c) and d shows the wiring architecture of very small dimensions that is located on the edge of the basic cells of the integrated circuit. The detail from 2 d) highlights the fact that we are not dealing with some simple routes but we are talking about contacts between materials, we observe actuation heating elements as well as systems for interrupting or clearing the miniature routes.

Fig. 2 e) shows the basic structure of the integrated circuit consisting of a very large number of cells located on the silicon support and connected by buses both to each other and to the side architecture. Figs. 2 f), g) and h) give some other examples of micro-wiring encountered especially on the central connection dimension of the two central cell windows.

The integrated circuits made in this case reach the dimensions of the paths up to 0.5 - 2 μm using complex architectures and exceptional realization technologies. The images were obtained by SEM analysis, a 30 kV supply of tungsten filament and a secondary electron detector for image formation and a working distance of 15.5 mm.

In all the images you can see the extremely small dimensions of the electronic elements as well as the finished state of their surface. The microstructures present an exceptional quality of the surfaces, of all the connection elements as well as of the substrate. The connecting elements are not more than 5 μm in diameter and are comparable to human hair.

3. In-Line Analysis of Chemical Elements Belonging to Materials Used in Micro-Electronics

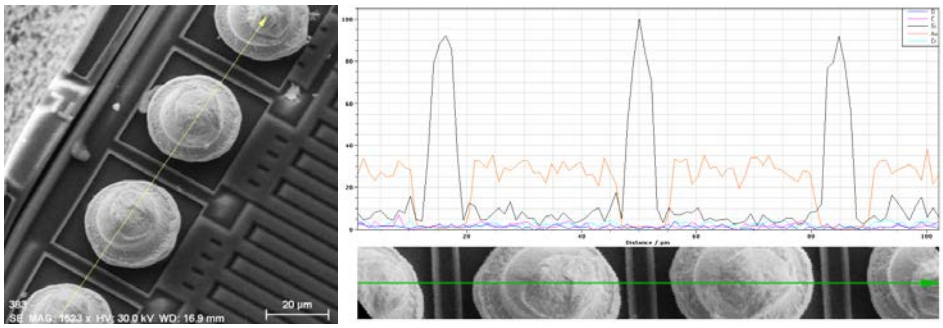
The Line Scan workspace in the Objects group in the workspaces provides the tools for recording a dimensional concentration profile for the selected chemicals. For linear scanning, the Quantax scanning system temporarily takes control of the electron beam to repeatedly scan the surface of the sample along a straight line that is defined in the electronic image display as the scanning line.

During the scanning procedure the fast or complete quantitative results are projected into a profile diagram, which measures the number of individual items in the scan line range. In the case of the EDX detector, the number of chemical elements that can be analyzed simultaneously is unlimited. Due to the updating of the spectrum database, the selection of items can be made at any time, before scanning, during scanning or after scanning.

The profile diagram shows the concentration profiles for the selected chemicals, depending on the color codes. Regarding the test run time for linear scanning, the option of manual or automatic time scanning is valid, as well as the setting of a fixed time.

The distributions of the component elements on a selected line, on some alloys and materials used in electronics are shown in Figs. 3-6.

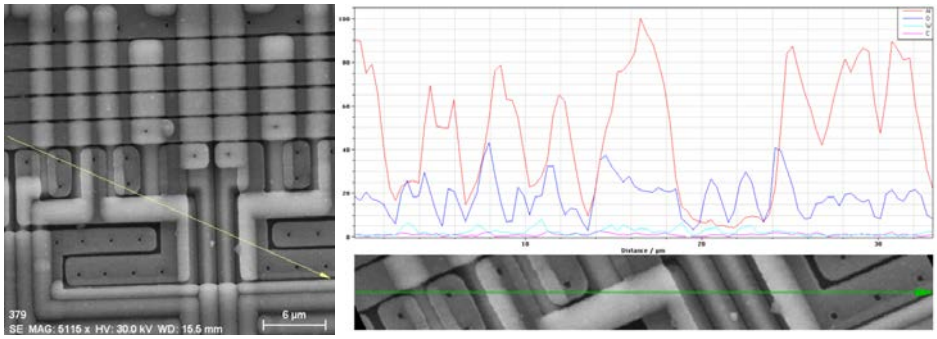
Analysis of the distribution of elements on a selected line, the chosen area being presented in the left microscopy, shows the variation of the selected elements, gold, silicon, oxygen, chromium, aluminum or carbon.



a) b)

Fig. 3 – Distribution of the chemical elements gold, oxygen, silicon carbon and chromium over a selected area a) the selected area and b) the qualitative and quantitative distribution of the elements.

There is an increase in the percentage of gold in all contact areas and a highlighting of the silicon around them, on the support of the mini electronic assembly.



a) b)

Fig. 4 – Distribution of the chemical elements gold, oxygen, carbon and chromium over a selected area shown in Fig. a).

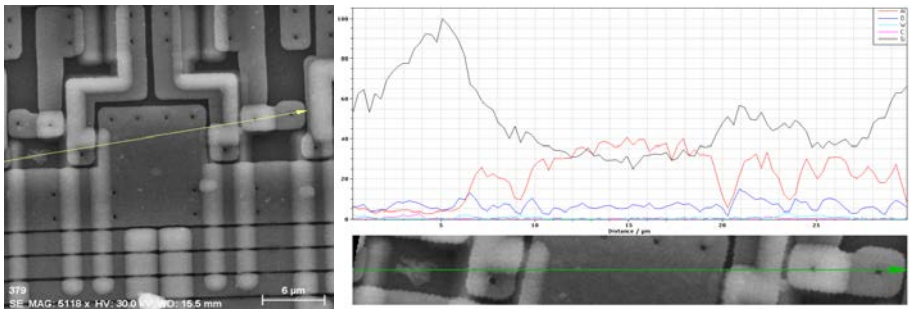
The profile diagram shows the concentration profiles for the selected chemicals, depending on the color codes. Regarding the test run time for linear

scanning, the option of manual or automatic time scanning is valid, as well as the setting of a fixed time.

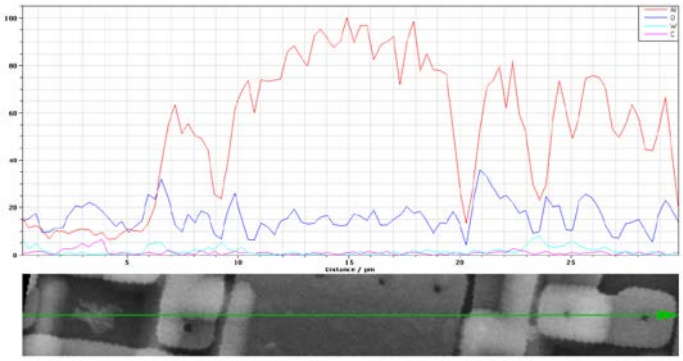
The advantage of using this mode of analysis is given by the fact that alloys or oxides or other combinations of materials that have been used in the realization of the integrated circuit can be highlighted.

In Fig. 5 the analyzed area is 15 μm and comprises different elements of the integrated circuit connection architecture. The composition of the activation or contact elements or the simple ones for transmitting the electric current can be easily observed.

It can also be seen, more obviously on the left side of the image, that these elements are not all located at the same level, some being lower than the others precisely due to the structure pursued by the manufacturer, the silicon aluminum support allowing them any artifice.



a) b)

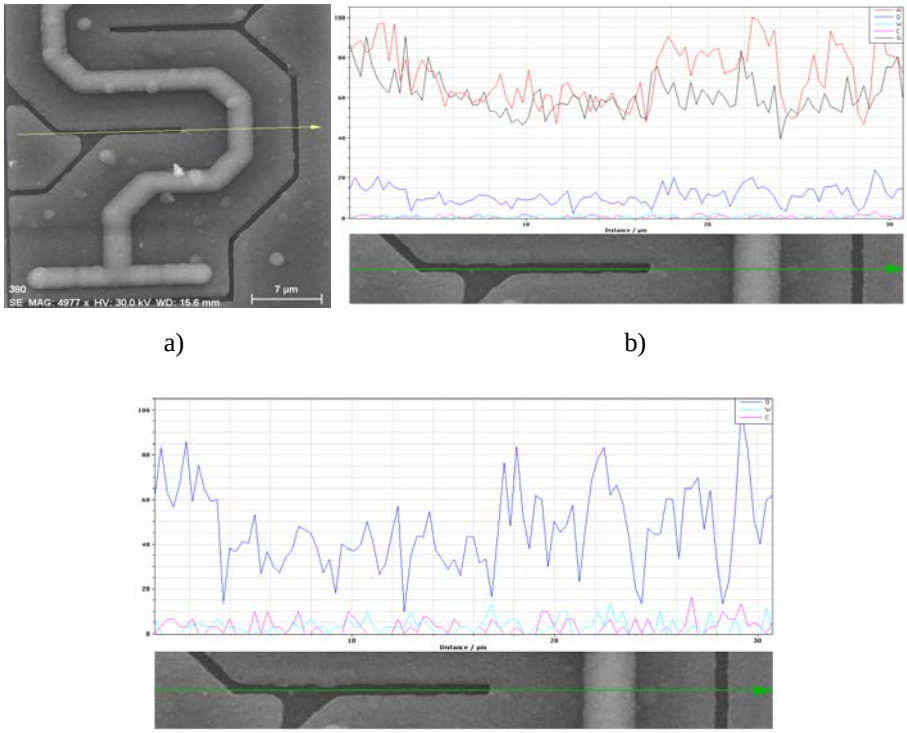


c)

Fig. 5 – Distribution of the chemical elements gold, oxygen, carbon and chromium over a selected area shown in Fig. a) and in b) and c) are shown the variations of the chemical elements, including silicon in b) and without this element with a high percentage in c).

The in-line chemical analysis shows the different bonds in which the component elements participate, observing compounds based on gold, silicon and aluminum and especially oxides. From the analyzes performed it was observed that microelectronics is based on special materials with special characteristics and exceptional properties.

As can be seen from the distributions shown in Fig. 6, the entire architecture of the integrated circuit is based on aluminum, in smaller or larger proportions, in thicker or thinner layers and on silicon as a support. In addition to these elements, tungsten, oxygen and carbon appear in small proportions and variations in the signal.



a) b)

c)

Fig. 6 – Distribution of the chemical elements gold, oxygen, carbon and chromium over a selected area shown in Figure a) and in b) and c) are shown the variations of the chemical elements, including silicon in b) and without this element with a high percentage in c).

Using this micro-technology, it is possible to realize practically any integrated circuit on a very small scale, reaching at this moment the introduction of a microprocessor of over 100 million electronic components.

4. Conclusions

The field of alloys and materials for microelectronics is of growing interest based on the multitude of applications in which they are involved.

The in-line chemical analysis shows the different bonds in which the component elements participate, observing compounds based on gold, silicon and aluminum and especially oxides. From the analyzes performed it was observed that microelectronics is based on special materials with special characteristics and exceptional properties.

A leading field of industrial applications obviously requires elements with special properties, finding their properties in elements such as gold, silicon, aluminum, etc.

Going beyond the analysis phase of the micron dimensions, it is clear that the materials were capitalized at this scale, naturally moving to the nanoscale of materials.

Analyzing elements that use successfully, and for some time, micrometric technology makes the transition to what is being pursued and researched in these moments, namely the nanometric structure of materials and the special properties that can be obtained with them.

The information obtained about the chemical elements that are used in these applications, gold, tungsten, silicon, aluminum, etc. increase the interest for the analysis on a micrometric scale and especially of their properties.

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REZULTATE PRELIMINARE PRIVIND ANALIZA MATERIALELOR UTILIZATE ÎN MICRO-ELECTRONICĂ

(Rezumat)

Prezentând materialele folosite de la începuturile electronicii şi până la cele din ziua de azi se poate observa evoluţia excepţională pe care a suferit-o acest domeniu, în special pe baza utilităţii şi a infuziei de bani, din punct de vedere al materialelor, în special cele metalice, folosite în acest scop. Cerinţele tot mai exigente ale pieţei electronice în general şi cea a calculatoarelor în special a făcut ca materialele pentru electronică să se afle, de asemenea, într-o continuă schimbare căutându-se noi proprietăţi şi materiale cu noi caracteristice care să acopere aceste necesităţi. Pornind de la dimensiunea unei săli de clasă, calculatoarele au evoluat ca putere de calcul de la câteva instrucţiuni pe secundă la câteva milioane de instrucţiuni pe secundă, au ajuns la dimensiunea unei foi de hârtie toate aceste evoluţii fiind posibile doar pe baza avansului tehnologiilor de prelucrare a materialelor. Pornind de la materialele utilizate iniţial în această arie de interes economic maxim, în această lucrare se ajunge la analiza unor circuite integrate ce prezintă celule de bază şi arhitecturi de legătură de dimensiuni micronice cât şi a unui micro procesor Pentium IV din punct de vedere al conexiunilor şi al conectorilor utilizaţi, elementele chimice întâlnite pe suportul de siliciu fiind aluminiu, aurul, wolframul, rubidiu şi elemente uşoare cum ar fi oxigenul, azotul sau carbonul. Faza actuală a investigării materialelor utilizate şi a proceselor de realizare şi implementare a acestora prezentată în lucrare se vrea o trecere către analiza nano-circuitelor ce îşi fac loc tot mai mult în domeniul electronicii prin dezvoltarea tumultoasă a nano-tehnologiilor.

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COMPARISON BETWEEN THE EFFECT OF MOLYBDENUM ADDITION TO ALUMINUM GRAIN REFINED BY TITANIUM PLUS BORON ON ITS HARDNESS

BY

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Received: July 27, 2021
Accepted for publication: December 15, 2021

Abstract. Aluminum are the second used materials in engineering and industrial application due to their specific properties, *e.g.* high strength- to-weight ratio, electrical and thermal conductivities in addition to their good corrosion resistance. These alloys could be very attractive but the large columnar grains appeared during solidification have a negative influence on the hardness and surface quality. In this study, a systematic comparison of Mo addition to Al-Ti-B alloy is made between specimens before and after the addition of rare materials (Ti, B and Mo) in the aluminum casting to investigate the enhancement that can be achieved. The master alloys and binary alloys were used for preparing different micro alloys. The effects are investigated through the results. Addition of Mo to Al refined by Ti-B resulted in no further noticed enhancement of the hardness.

Keywords: aluminum; hardness; grain rafiner; master alloy; titanium; boron.

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1. Introduction

Aluminum and most of its alloys solidify with a coarse columnar structure, whereas fine and equaxed grain structure is obtained by the addition of small amounts of Ti or Ti-B into the melt before casting, (Cibula, 1950). When Ti is added alone, its presence in the melt must exceed the peritictic composition of about 0.15% by weight, to obtain a satisfactory enhancement effect on its mechanical properties. However, in the presence of boron, even in ppm order, an important enhancement is obtained at Ti contents as low as 0.005%, (Cibula, 1951). Experience, based on experimental results, has shown that optimum mechanical characteristics properties are achieved using Al-Ti-B master alloys with Ti to B ratio about 5 (Jones and Pearson, 1976). It has been reported that boron has the greatest enhancing effect on the Mechanical Properties efficiency of Ti in the aluminum casting although boron itself has not good impact when added alone. The ternary Al-Ti-B master alloy in common use contains 5% Ti and 1% B, wt. and has two crystalline intermetallic compounds, namely: small crystallites of titanium debride and larger crystals of TiAl3, (Zaid and AL-Dous, 2006; Zaid and Hussein, 2005; Zaid and Hussein, 2006). The ternary AL-5%Ti – 1%B master alloy is usually about five to six times more efficient than a binary Al-Ti master alloy (Zaid, 2001).

The increasing and increasingly efficient use of additions of Al-Ti-B master alloys has been justified from the technological and scientific point of view, although this mechanism is still a controversial matter and further work needs to be carried out before it is determined. Suggestions have been made to explain the mechanism, (Zaid, 2006). It was reported that these effects and enhancement in the mechanical properties of aluminum are due to the nucleation of Al by the aluminide particles, or by boride particles, (Zaid and Al-Qawabah, 2011; Zaid *et al*., 2011) or by TiB2 particles coated with TiAl3 "duplex particles", (Abdel-Hamid and Zaid, 2000) has discussed the mechanism and showed that a high local Ti-concentration exists in the vicinity of TiB2 particles making high efficient nuclei for Al grain. Recently, the local Ti-enrichment associated with TiB2 particles has also been suggested by others (Pearson, 1979).

In this study, a systematic comparison of addition Mo to Al-Ti-B alloy mechanical properties of cast aluminum components is made between specimens before adding the rare materials (Ti, B and Mo) and after adding these materials in the aluminum casting to investigate the improvement & the enhancement that can be achieved by Mo addition.

2. Materials and Method

2.1. Materials

The following materials were used throughout this work:

– Commercially pure aluminum 99.8% purity of the chemical composition shown in Table 1.

Table 1

Chemical Composition (wt. %) of Commercially Pure Aluminum

Element	Fe	Si	Cu	Mg	Ti	V
Wt %	0.09	0.05	0.005	0.004	0.004	0.008

Table 1

(*Continuation*)

Element	Zn	Mn	Na	Al
Wt %	0.005	0.001	0.005	Rem

– High purity molybdenum of 99.98% purity titanium and aluminum powders of 99 99% purity were used in manufacturing Al-Ti and Al-Mo master alloys which were later used for manufacturing the different micro alloys. Graphite crucibles were used for melting and graphite rods were used for agitation.

– An Electric furnace was used to melt the Aluminum and its alloys, the furnace can reach to 1400 C as a maximum Temperature, with high furnace chamber with five sided heating for very good temperature uniform -LH Model. Hollow rectangular brass mold was used to prepare the specimens with 5 mm inside diameter and 55 mm external diameter, graphite crucible and graphite rods were used for stirring, and for the tensile tests was used universal testing devise-2000 (KN) Universal Testing Machine type EM. LaboPol 30 Grinding/Polishing machine (50-500 rpm). Digital Microscope, AmScope type, PN ME300TZ-3M 40X-1000X

– A hardness test is performed by pressing a specifically dimensioned and loaded object (indenter) into the surface of the tested specimens. The hardness is determined by measuring the depth of indenter penetration or by measuring the size of the impression left by an indenter using micro hardness tester model HWBM-3 device.

2.2. Method

The commercially pure bundles of the Al wires, supplied & tested by the POLITEHNICA University of Bucharest, were pickled in HNO3 to remove the oxide layer and any other contaminant, then melted in a graphite crucible

inside an electric furnace at 800°C and then poured to solidify in hollow rectangular brass rods of 10 mm inside width and 55 mm external width and 3 mm thickness, 10 mm width and 240 mm length specimens dimensions Fig. 1.

The Al-3% Mo and Al-5% Ti binary master alloys were prepared by adding the calculated amount of Mo to the predetermined amount of molten aluminum in the graphite crucible at 850^{o}C for Al-Mo binary master alloy, stirred by the graphite rod for one minute and brought back to the furnace for 20 minutes, brought out and stirred again for one minute and then poured to solidify in the thick brass rods. Finally, the specimens prepared to be of 3 mm thickness,10 mm width and 240 mm length. The two prepared master alloys were used for preparing the Al-Ti and Al- Ti-Mo and Al-Ti-B-Mo micro alloys.

The Vickers's micro hardness survey was carried out by taking the average of ten values along the metal regions, using the digital micro hardness tester model HWBM-3 at 100 gm force.

Fig. 1 – Aluminum alloy specimen.

3. Results and Discussion

The Vicker's micro hardness survey were carried out by taking the average of ten values along the HAZ and away from it along the base metal regions, using the digital micro hardness tester model HWBM-3 at 100 gm force.

Examination of the general specimens appeared that there are not high enhancement effects of Mo addition on the hardness. It can be seen from the histogram of Fig. 2 and according to the experiment data Table 2 that addition of 0.15% Ti to the aluminum decrease the hardness about 58% and adding 3% Mo

alone resulted without enhancement of the hardness. The maximum increase is at adding Ti and B addition with enhancement percentage reached 15%. This enhancement in the hardness can be related to the grain size effect and appeared toghether with the grain refinement.

3.1. Hardness Results

Table 2
Effect Addition Ti, B and Mo on Al - Vickers Microhardness

Ref	Micro Hardness (Hv)
Al	60.1
Al-0.15% Ti	25.2
Al-3% Mo	56.1
Al-0.05% Ti-0.01% B	68.9
Al–0.05% Ti–0.01% B–0.1% Mo	56.5

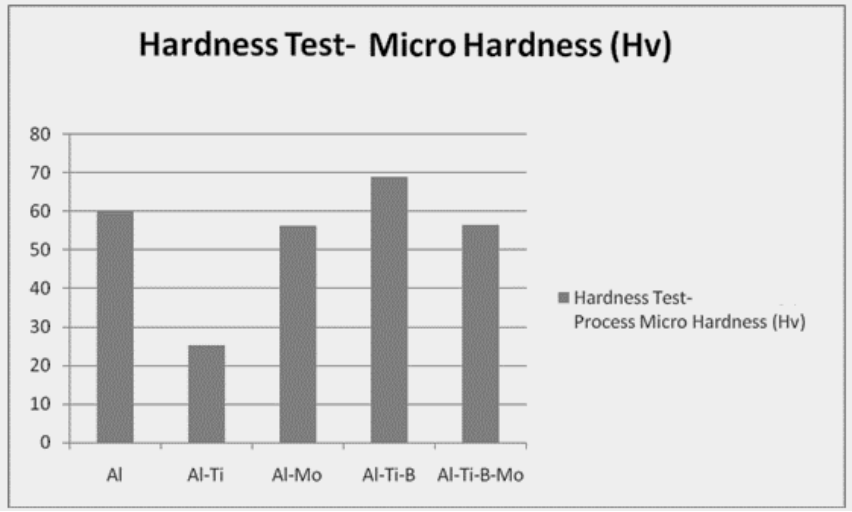

Fig. 2 – Effect of Ti, Ti+B and Ti+B+Mo addition on the Vicker's microhardness.

Fig. 3, Fig. 4 and Fig. 5 present the microstructure photograph pictures for Al, Al-Ti-B and Al-Ti-B-Mo respectively.

Grain refiners resulted in change the grain size by increasing or decreasing, which affects the hardness values which indicate changes in the grain boundaries size and shape, and in addition to it, gives also indications about the thermal stress and the solidifying process and its parameters.

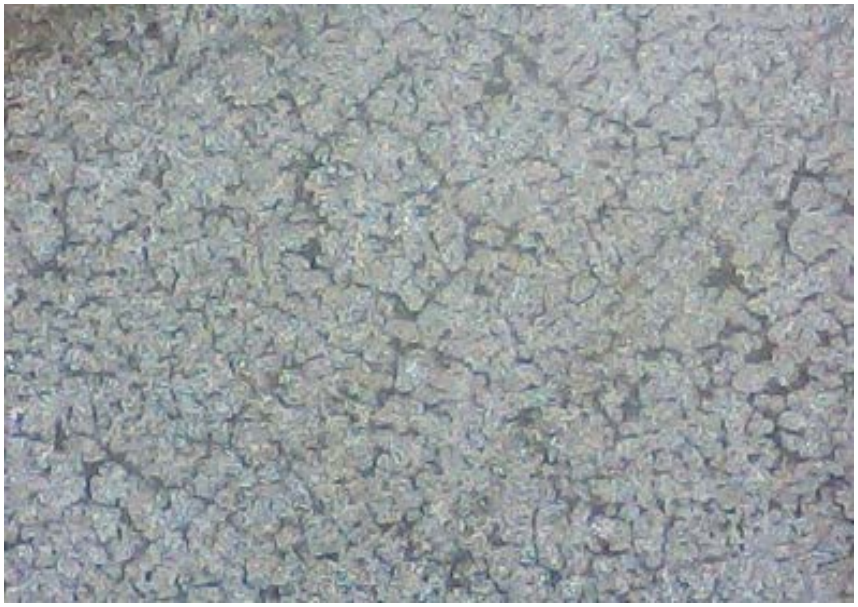

Fig. 3 – Photomicrograph of the microstructure of Al specimen, X 120, 200 µm.

Fig. 4 – Photomicrograph of the microstructure of Al-Ti-B specimen, X 120, 200 µm.

Fig. 5 – Photomicrograph of the original microstructure of Al-Ti-B-Mo specimen, X 120, 200 μm.

4. Conclusions

From the results of the research work in this paper, the following points are concluded:

– Addition of Ti to commercially pure aluminum resulted in decreasing the hardness with a percent reaching up to 80%.

– Addition of Mo to commercially pure aluminum resulted in no high enhancement on the hardness values.

– The addition of Ti-B to Al has resulted in increase of its Vickers micro hardness.

– Addition of Mo to Ti-B aluminum resulted in no high enhancement on the hardness values.

In summary, grain refinement of Al and Al grain refined by Ti, Ti-B and the addition of Mo to Al grain refined by Ti or Ti-B to the melt before solidification is a very powerful technique which overcomes the discrepancies resulting from their solidification in columnar structure of large grain size which is appeared in addition Ti-B, whoever adding one rare material gives poison effect on hardness and adding 2 elements in some cases there is no enhancement.

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COMPARAȚIE PE BAZA EFECTULUI ADĂUGĂRII MOLIBDENULUI ASUPRA DURITĂȚII, LA RAFINAREA GRĂUNȚILOR DE ALUMINIU PRIN TRATARE CU TITAN ȘI BOR

(Rezumat)

Aluminiul este al doilea material utilizat în inginerie și aplicații industriale datorită proprietăților sale specifice, de exemplu: raport mare rezistență pe densitate, conductibilitate electrică și termică mare la care se adaugă o bună rezistență la coroziune. Aceste aliaje pot fi foarte atractive, dar grăunții lor columnari de dimensiuni

mari care apar în timpul solidificării au o influență negativă asupra durității și calității suprafeței. În acest articol este realizat un studiu sistematic comparativ al adăugării de Mo la aliajul Al-Ti-B folosind probe înainte și după adăugarea de materiale rare (Ti, B, și Mo) în aliajul de aluminiu turnat, pentru a investiga înbunătățirea, care poate fi obținută. Aliajele principale și cele binare au fost folosite pentru a prepara microalieri diferite. Sunt investigate efectele. Adăugarea de Mo la Al rafinat cu Ti-B nu a adus nici o creștere a durității.

BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
Publicat de
Universitatea Tehnică „Gheorghe Asachi” din Iaşi
Volumul 67 (71), Numărul 3-4, 2021
Secţia
ŞTIINŢA ŞI INGINERIA MATERIALELOR

BIBLIOGRAPHICAL AND EXPERIMENTAL STUDY CONCERNING THE WELDING OF THIN PARTS MADE BY FEMNSI SHAPE MEMORY ALLOYS

BY

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Received: July 27, 2021
Accepted for publication: December 8, 2021

Abstract. The paper presents and analyses the various ways of joining by welding of thin parts made by FeMnSi, alloy that shows the shape memory effect. The originality is being given by the way of obtaining the semi products, namely they are obtained by powder metallurgy with a 50% powders mechanically alloyed. This particular characteristic puts a strong imprint on the processing of semi products by welding as well as on the final structure of components and joint itself. An another specific problem of the welding technology is the establishing of the optimum parameters of processing, given the initial specific structure. A large part of the effort made in the experimental study was allocated for establishing the working parameters. The structure of the obtained joints, visually accepted, has been analysed by microscopy- optical and scanning electron microscopy as well as chemical analysed by X rays spectroscopy, EDX. There have been obtained clean joints, homogenous, characterised by a size – thickness, less then of the initial semi product, but with a structural homogeneity obviously superior.

Keywords: shape memory alloys; alloys with shape memory effect based of FeMnSi system; TIG welding; welding current; optic microstructure.

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1. Introduction

The shape memory effect alloys (SME) are alloys having remarkable properties, properties that tightly depend both on chemical composition and of the processing procedures applied.

The welding and the connected procedures enable the joining of semi products or of finite products in the conditions of keeping a convenient geometry of the finished product – there are no special processing, section reduction etc. On the other hand, welding, in the majority of cases it supposes a thermal cycle or a thermo-mechanical one, of various amplitude, that affects in a sensible way the material or materials to be joint. The most frequent modification is on the structure at microscopic level, modification that can be followed by variation of chemical composition, induced locally by the phenomena associated with the temperature variation or due to an exterior mass transfer, filler material that is similar to the joint but not identical.

The particularities of the shape memory alloys suggests from the beginning the selection of some welding procedures that modify as little as possible the chemical composition, respectively welding procedures that do not need the use of filler material.

We have started from the hypothesis that the alloys that show the shape memory effect have been neglected from the point of view of the processing by welding. The documentation proved that there was and still exist a preoccupation for their welding, but the interest for various alloys being considerable different. Simultaneously, even if there are being reported or comprised in synthetic works information about various tentatives of welding of even appreciations concerning the weldability, information about the working regime applied are few and fewer are those containing concrete data.

The shape memory alloys consists of three main families: first NiTi based alloys (those who put into evidence the property itself), second the Cu based alloys and third the FeSiMn alloys.

All of three groups have in common the existence of the transformation of the mother phase – the high temperature phase, austenite, in martensite during cooling but also the presence of the inverse transformation, martensite to austenite without the formation of an intermediary phase.

The phase transformation can develop either under the effect of temperature, either under the effect of an adequate effort capable to induce transformation. The level of dependence on temperature of the deformation is demonstrated and sustained by thermo dynamical criteria: it can be demonstrated that the undercooling necessary to initiate the transformation in the case of SME alloys is 5...30°C, by comparing with the martensitic transformation specific for steels that is about 200°C.

The transformation that takes place during cooling is named the direct transformation and that corresponding to heating is named the reverse transformation.

The thermo mechanical behavior of SME alloys is defined by three ways of answers at the environment variation temperature or force: first, the simple shape memory effect, second, the pseudo elasticity effect and third the double shape memory effect.

Fundamentally, at the atomic network level, the structural modification austenite-martensite is of "military type", an ordered displacement, fast, without diffusion, of the atoms from a network to another "related network", possible to be attained by this relative displacement system on shorter distances comparing with the diffusive jump. For keeping the capacity of change of the structure it would be necessary the maintaining as much as possible the crystalline network, or the obtaining/recovering of this state. Obtaining or consolidating the structure can be achieved by the education process, a suite of thermo mechanical treatments adapted to the characteristics of the alloy.

On the other hand, it is well known the unwanted effect brought by the welding processing on the structure of a material: growing of grains, separations of elements, formation of chemical compounds etc. In these conditions it can be expected that the welding will modify substantially the behavior of SME alloys or to impose special technological measures.

2. Bibliographic Study

A bibliographic investigation concerning the welding of SME alloys confirms that the most consistent number of studies is dedicated to the star alloy, Nitinol. Fig. 1 shows that they were attempts for both procedures with melting and in the solid state.

It is easy to understand that the welding of SME alloys is more and more requested by those interested in such materials, fact that leads now, towards an obvious interest for this difficult field. The same picture demonstrates, indirectly, the number relatively small of studies on welding the SME alloys and the growing interest manifested starting from the years 2000.

The problems arisen by welding does not discourage the studies in this field. A special attention is being oriented towards the joining of wires, products used on a large scale in medicine and who, by mechanical joining methods become over sized (Kramar *et al*., 2019; Quintuno and Miranda, 2012; Oliveira *et al*., 2017).

Between the welding procedures given in the literature, no matter the composition of the alloy, the WIG procedure and the laser beam detaches in what concern the frequency. The attempts of joining using the electron beam, plasma or by electrical resistance or in solid state, by friction are poorly represented. A justification can be found in the price of the procedure that is

high, in the small sizes of the semi products or in the late approach of some of the procedures.

It must be remarked the small sizes of semi products, wires or plates.

It is preferable to weld with laser beam, sources Nd: YAG or fiber, characterized by small wave length comparing with the CO_2 laser, characteristic that leads at a better absorption and generates a narrow welding.

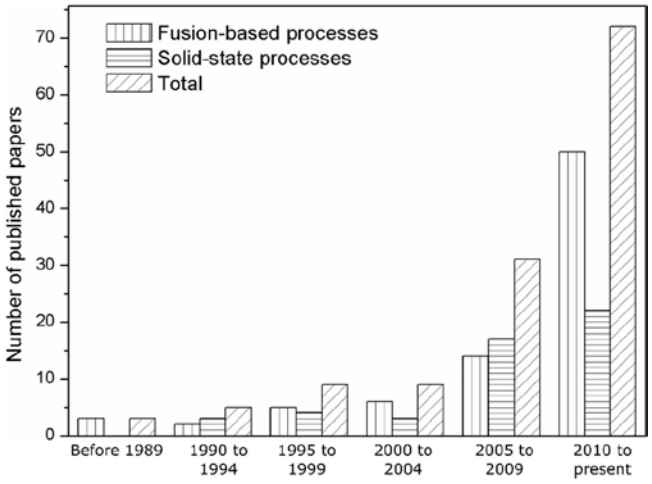


Fig. 1 – Number of articles published concerning the attempts of welding of NiTi alloy along the time (article published in 2017, probable the data included in the study are from 2015...2016) (Oliveira *et al*., 2017).

The final problems are linked to the structural homogeneity (the welding contains a complete range of structures from fine grains to dendritic formations, due to rapid cooling) together with a grain growing inside the thermal influenced zone (TIZ). Another aspect is the one linked to the presence of precipitates on intermetallic compounds: Ti_2Ni, Ni_3Ti and Ni_4Ti_3. The frequency of occurring and the type of precipitates depends on the previous processing of the material: the Ni – rich precipitates are present in the cold deformed materials prior to welding, while annealed welded alloys are considered without structural modification in the TIZ, Oliveira providing a consistent number of sources, (Oliveira *et al*., 2017).

It worth mentioning the interest for heterogeneous welding or semi-heterogeneous (quasi-dissimilar – the same alloy, different structural state – austenite/martensite of components at the environmental temperature (Oliveira *et al*., 2017; Crăciunescu, 2018).

In the case of Fe based alloys the bibliographic resources are incomparable poorer. If Cladera (Cladera *et al*., 2014) reminds, linked by the FeMnSi only the melting procedures, respectively TIG (WIG) welding, the electron beam and the laser, Mehta in 2019 (Mehta and Gupta, 2019) includes a

large number of procedures also those in solid state. Unfortunately also in this case the Fe based alloys are only remembered, mentioning the fact that the laser beam procedure is benefic, reducing significantly the TIZ, and this advantage is significant in the case of the laser with Nd: YAG active medium and fiber.

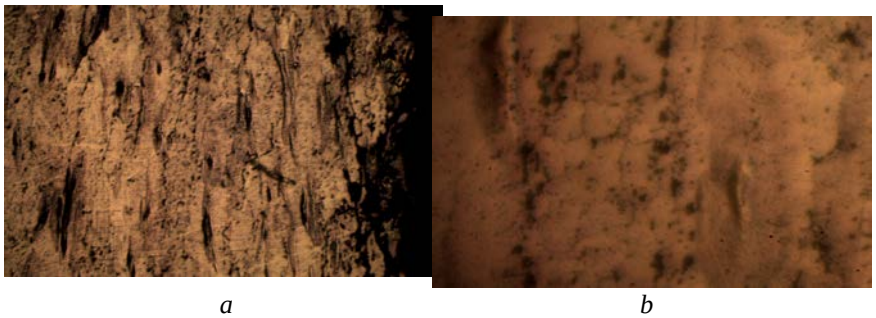
Mentions regarding the welding of Fe based alloys are also included in the paper (Sadati and Javadi, 2016) where the unaltered of the base material is emphasized as well as the preserving of mechanical qualities verified by bending tests. A paper destined to the welding of Fe based alloys is (Lin *et al*., 2000). It compares the weldings achieved by TIG and laser on two chemical compositions, Fe30Mn6Si and Fe30Mn6Si5Cr from the point of view of the structure obtained after welding as well as the corrosion resistance before and after welding. The laser welding is considered also in this case better that the one achieved by TIG – fine structure in the weld, mentioning also a Mn loss by vaporization. Technological details linked by the procedure are not given, even if in the majority of works the initial state of the semi products is mentioned: deformed, annealed etc.

3. The Objectives and Experimental Conditions

It has been used an SME alloy having the composition Fe14Mn6Si9Cr5Ni, elaborated by powder metallurgy, 50% commercial powders, 50% powders mechanically alloyed. After the sintering process the material was hot deformed by rolling. The sample used were in this state, laminated and thermally untreated.

The samples were characterized by close geometrical sizes – length of about 50 mm, width 5…6 mm and average thickness about 0.85 mm with small tolerances on the length.

A problem was linked to the deformation in the longitudinal plane of the samples, they showed an uneven arching and an eventual heat treatment would not guarantee a better flatness. The samples shown an adherent layer of oxides, layer that needs the removing a consistent thickness for obtaining the metallic luster.



a *b*

Fig. 2 – The characteristic microstructure of metal before welding: *a*) x10; *b*) x50.

The microstructure of the material before the welding is characterized by the specific texture obtained after rolling, Fig. 2*a*.

The micrograph shown in Fig. 2*b* details structural elements: they are visible colonies of fine, equiaxial grains, between the formations that have preserved the secondary texture of rolling; they are also visible small inclusions. Having in mind that the alloy is made by the powder metallurgy technique, it can be supposed that the dark formations are oxides and/or pores.

For obtaining the weld it has been adopted the TIG procedure. It has been used a TELWIN equipment, a welding invertor, maximum current 170 A, electrodes in the range 1…4 mm, possibilities o work in direct current or in pulse current. During the experiment it has been demonstrated that the equipment is capable do deliver very small currents, 4...6 A.

The main, general parameters used during the experiment were: direct current, direct polarity, non-fusible electrode with the diameter 1 mm, conical tip at 60°, nozzle with gas diffuser (ensures the laminar flow of the shielding gas and thus it achieves higher stability in terms of protection), shielding gas – Argon 4.8. The working parameters – welding current, variants of current type – constant or pulse will be explained for each sample achieved.

The aim was to find a welding regime capable to produce suitable welds from a visual point of view as well as the analysis of the modifications occurred at structural level.

4. Establishing of Working Parameters

In order to establish the corresponding parameters, test were performed with the electric arc following the meting mode and penetration level. Tests were performed with low values for the current, in the variant with direct current, without pulses. For I_S = 5 A the alloy was superficially melted and non-uniform. Doubling the welding current value lead to a continuously solidified bath, penetration present, non-uniform. In such conditions the first attempt to weld has been achieved using a current I_S = 5 A. The choice of the welding current value was made on the basis od tests described and also by extrapolation, using the values from the literature for NiTi alloy, 4 A at a thickness 0.2 mm. It was considered that the assimilation is valid based on the relatively close thermo physical characteristics.

The attempts of welding obtained with a current of 15 A, respectively 10 A, direct current, non-pulsed, did not enabled the joining of samples, the arc moving randomly on the two components, having as effect the intense melting of one component and the total lack of melting for the other, or the breaking of the materials. Finally the use of pulsed current was adopted. In this variant there were used successfully two regimes

The first regime adopted: $I_{s\,max}$=16 A, $I_{s\,min}$=0.5 x $I_{s\,max}$ =8 A, $t_{I\,max}$= $t_{I\,min}$=1s, without any other technological measures. It has been obtained the first suitable

weld, with small areas not penetrated at the root, Fig. 3*a*. The last variant was: $I_{s\ max}$=22 A, $I_{s\ min}$=0.6 x $I_{s\ max}$≈13A, $t_{I\ max}$=0.5 s, $t_{I\ min}$=1.1 s. Supplementary in this case there was used a support plate made of Cu.

Results are shown in Fig. 3.

a *b*

Fig. 3 – Macroscopic aspect of welds obtained with pulsed arc. *a*) Weld with pulsed arc, without Cu support plate; *b*) Weld with pulsed current on Cu support plate.

Fig. 4 – Reduction of section to the sample weld, I_s=10 A.

As a conclusion, it is recommend to use pulsed direct current, the variant that ensures a good thermal input for the formation and maintaining of the liquid bath. The effect of supporting the samples and implicitly of the bath remains to be studied. A general remark regarding the area exposed to the electric arc is the reduction of the thickness of the samples. The reduction reaches, in some areas, 40% from the average thickness measured before welding. The reduction of height of molten and solidified materials using electric arc in the absence of additive material is a reality but such dimensional contractions are not reached, Fig. 4.

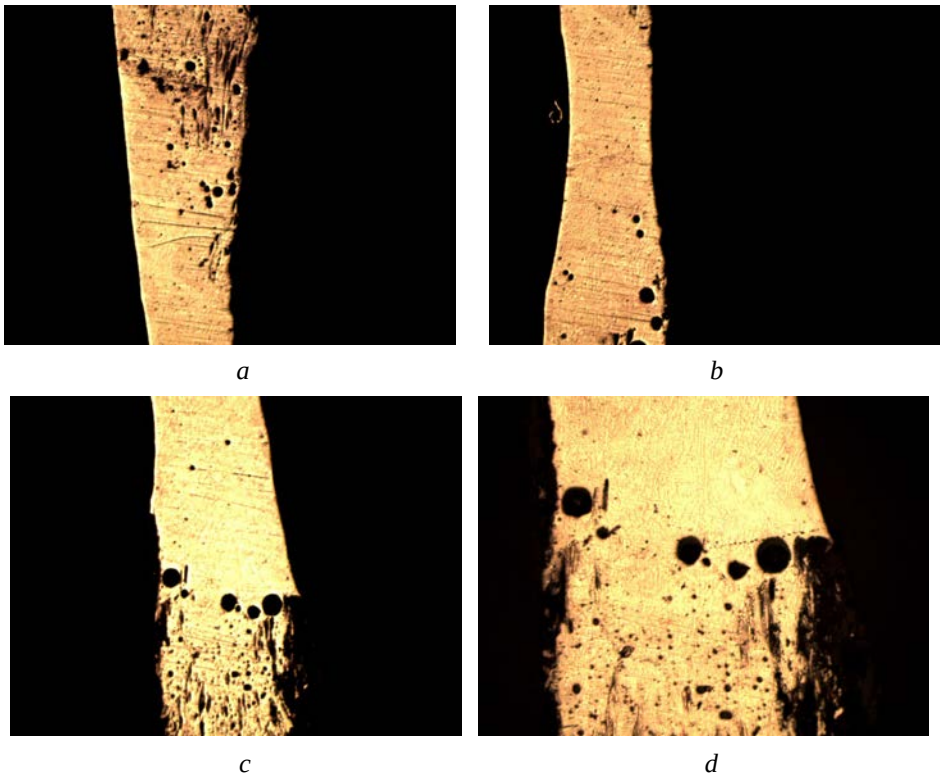
5. Microstructural Modifications

For the microstructural analysis the samples were prepared by grinding, polishing and reagent attack 1.2%$K_2S_2O_5$+1%NH_4HF_2 (penta sulfide of K and ammonium fluoride).

As previously mentioned, Fig. 2, the base material shows an oriented structure, obtained after plastic deformation by rolling. The oriented structure is visible starting with relative low magnifications due to the inclusions which are present in the metal.

Common to all microstructural analyzed samples is the “compaction” of the material near the area exposed to the arc, the metallic solidified bath zone. In this area an obvious porosity is present because the relative homogenous metallic mass.

The major porosity is present in the adjacent area near the bath, the passage area, area where the structural modifications are hidden by the multitude of pores, Fig. 5.



a *b*

c *d*

Fig. 5 – The Microstructure of weldt samples. Weldt sample D.C. 16A/8A: *a*) passage zone x5, *b*) Welding, x5; Weldt sample D.C. 22A/13A *c*) x5; *d*) x10.

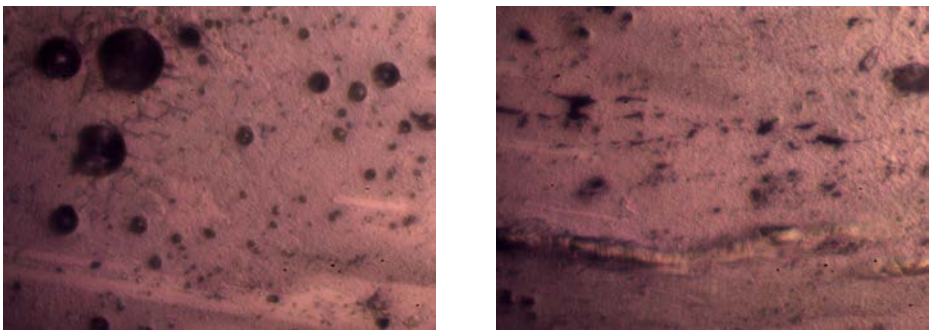
Taking into account the distribution of the porosity as well as its dependence on the quantity of introduced heat during welding on can formulate a series of affirmations and hypotheses.

After the sintering process the remnant porosity is not eliminated completely during the plastic deformation. By exposing to the thermal field

specific to welding the remnant gases have the possibility to move by diffusion, making pores. Inside the welding, as a result of temperature and liquid phase of metal, a part of gases exit the metallic mass, elimination that is more consistent if the energy induced during welding is more consistent (the porosity in the welding 16A/8A is more important than the one inside the sample 22A/13A).

The effect of the input energy in samples can be seen also in the passage area and also in the TIZ. Inside the passage area the porosity is accentuated, together with the energy growing the coalescence is intensified resulting in massive pores, Fig. 5*d*.

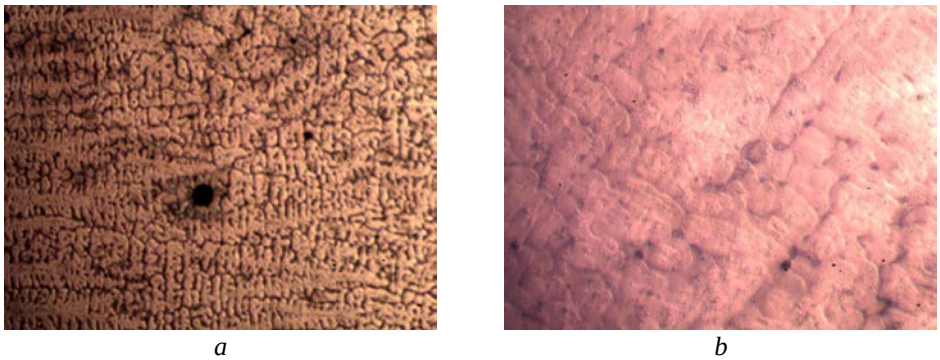
Concentrating on sample 22A/13A and the characteristic areas of it the hypotheses are confirmed, Fig. 6, where the increasing of pores is obvious in the passage area and the partial fibrous appearance kept in the thermal influenced zone.



a *b*

Fig. 6 – Microstructure in sample 22A/13A: *a*) passage area, x100; *b*) thermal influenced zone, x100.

Unlike these areas, the weld shows a dendritic, homogenous structure, Fig. 7, with sparse and, general small size pores.

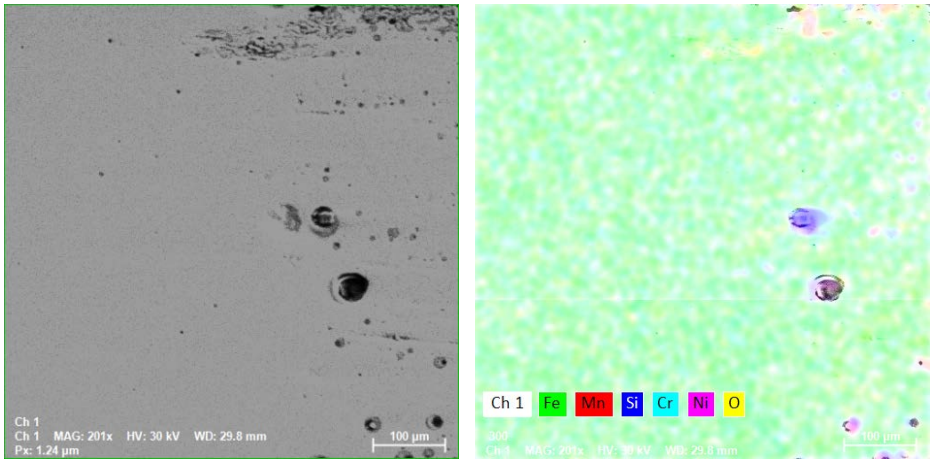


a *b*

Fig. 7 – Micrographs of the welded seam: *a*) x50; *b*) x100.

The modification of chemical composition – analyzed by the EDS are an effect of the loss of alloying elements due to evaporation, mostly Mn (from 14% to 12%) associated with an enhancement in oxygen content. Here it can be also seen the uniformity in the distribution of main elements in the welded seam – the passage zone, Fig. 8.

The image analysis highlights the massive presence of oxygen in the areas with "inclusions" but also the distribution almost homogenous on the surface. It is possible and likely that the presence of oxygen to be secondary to the sample exposure and chemical attack.



a *b*

Fig. 8 – Microstructure and chemical analysis of the weld: *a*) SEM image, x200; *b*) distribution of elements inside the weld, EDS.

6. Conclusions and Recommendations

On the basis of welding attempts made on thin samples of shape memory alloy Fe14Mn6Si9Cr5Ni obtained by sintering, with 50% alloy obtained by mechanical alloying the following conclusions can be made:

– without stating that the alloys in this family, achieved by sintering, are weldable in the plastic deformed state, one can affirm that they can be welded;

– for welding of thin semi products made by alloys in this family the experiment recommends the use of a pulsed direct current welding regime, the minimum value of the current being between 1.5…2A/0.1 mm, the maximum value less than the double of minimum value;

– also it can be also recommend the use of a Cu support plate for the metallic bath;

– weldability involves the ensuring of some desired properties, but this thing has not yet been proven, in addition, after welding, the reduction of the

cross section of semi-products is a fact that can be considered as an inconvenience;

– the presence of large pores in the passage area represents another impediment in sustaining a real quality of the achieved welds on alloys in this family.

It should be noted that this feature is probable specific to the state after primary rolling. It is possible that through a degasing treatment followed by a new plastic deformation the alloy acquires adequate properties after welding. This hypothesis is supported by the homogenous, chemically uniform structure, obtained after processing by welding.

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STUDIU BIBLIOGRAFIC ŞI EXPERIMENTAL PRIVIND SUDAREA PIESELOR SUBŢIRI DIN ALIAJE CU MEMORIA FORMEI PE BAZĂ DE FeMnSi

(Rezumat)

Lucrarea prezintă şi analizează modalităţi diferite de îmbinare prin sudare a pieselor subţiri din aliaj pe bază de FeMnSi, aliaj ce prezintă efect de memorie a formei. Originalitatea este dată de modul de elaborare al semifabricatelor, respectiv acestea sunt obţinute prin sinterizare cu un procent de 50% pulberi aliate mecanic. Această

caracteristică îşi pune amprenta puternic asupra procesării prin sudare a semifabricatelor precum şi asupra structurii finale a componentelor şi a îmbinării propriu-zise. O altă problemă specifică tehnologiei de sudare este stabilirea parametrilor optimi de prelucrare, dată fiind structura iniţială specifică. O mare parte a efortului în cadrul studiului experimental a fost alocat stabilirii parametrilor de lucru. Îmbinările obţinute, vizual acceptate, au fost supuse analizei structurale microscopice – microscopie optică şi microsopie electronică cu scanare, precum şi analizei chimice prin spectroscopie de raze X, EDX. S-au obţinut îmbinări curate, omogene, caracterizate de o dimensiune – grosime, mai mică decât cea a semifabricatului iniţial, dar cu o omogenitate structurală evident superioară.

BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
Publicat de
Universitatea Tehnică „Gheorghe Asachi” din Iaşi
Volumul 67 (71), Numărul 3-4, 2021
Secţia
ŞTIINŢA ŞI INGINERIA MATERIALELOR

STUDY CONCERNING THE OBTAINING OF THE FILAMENT FOR 3D PRINTERS FROM GRAINS OF RECYCLED POLYETHYLENE TEREPHTHALATE

BY

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Received: July 27, 2021
Accepted for publication: December 7, 2021

Abstract. In the context of the growing need to reduce global pollution, the move to clean industries is still a must. An important step in this direction is the implementation of processes that have a pronounced ecological footprint, such as those that use recycled materials. This paper presents a possible use of a well-known recyclable material, namely polyethylene terephthalate (PET) to obtain various products through "3D printing technology". The use of this plastic material for 3D printing requires filaments, and the possibility of making them from recycled materials is being investigated here. After the initial presentation of the main properties of the material and its history, the paper presents a sketch of the technology for obtaining filaments, intended for 3D printing, using as raw material recycled polyethylene terephthalate (PET). The paper also briefly presents the main steps in the PET recycling process. The phenomena generally involved in 3D printing and also those directly involved in the use of PET filament are reviewed. The important thermal properties of PET, on the basis of which the material can be used as a filament for 3D printing, were determined using data from the literature. The paper also briefly describes the equipment used to obtain thermoplastic filaments. To determine the properties of the material, after obtaining recycled PET filaments under various conditions, tests

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were performed on samples of recycled PET granules and samples of recycled PET filament by differential scanning calorimetry (DSC) and were compared. The results confirm the preservation of the properties of PET after recycling and after obtaining the filament for 3D printing, so implicitly the possibility of using it to obtain products through 3D printing technology.

Keywords: plastic materials recycling; filament extrusion line for thermoplastic materials; vitreous transition; DSC thermograms.

1. Introduction

Polyethylene terephthalate (PET) is the most frequently used thermoplastic polymer in the world and it is better known in the textile industry under the commercial name of "polyester". This is an artificial colourless, transparent and semi-crystalline material used on large scale for obtaining fibres used in the clothing fabrication because it is an effective moisture barrier.

This material has a wide applicability both in bottling liquids and packaging (named PET for these cases) as well as plastic for engineering when it is combined with other materials as fiberglass or carbon nanotubes for obtaining composites.

The most important characteristics of PET are:

– chemical resistance – it does not react with water or with food and is hygienic, motives for its use in food packaging;

– a very good ration weight/resistance;

– high breaking resistance, including shock resistance, makes it a very good replacement for glass, as a container;

– transparency (Exconde *et al*., 2019);

– large scale availability as an economic recyclable plastic;

– it is not biodegradable, (good or bed depending from the perspective and destination);

– thermo plasticity.

1.1. Very Short History

Polyethylene terephthalate (PET) was polymerised for the first time in the years 1940 by the chemists from Du Pont which worked for developing polymeric materials for obtaining textile fibres.

For obtaining PET mono ethylene glycol and terephthalic acid are used.

Even the fabrication of this material has oil as a starting point, approximately 40% of the energy involved is internally stocked and such it is available after recycling.

According to PET resing.org "the studies for the lifecycles of PET have demonstrated constantly that the material is extremely durable, with an average positive environment profile".

According some reports the actual global demand for this materials generates worldwide a market of 56 millions of tones.

The main final user of this material are the textile industry that consumes more than 60% from the total quantity.

Other major uses are oriented toward bottling and packaging, together representing about 30% from the requested quantity (Choudhary and Sangwan, 2019).

1.2. Obtaining Polyethylene Terephthalate (PET)

The polyethylene terephthalate as most of the plastic materials is usually obtained by the distilling oil in fractions. Some of these low-mass fractions combined with various catalysts in special conditions produce plastic materials (usually by polymerisation or polycondensation). In the case of PET the raw materials used are mono ethylene glycol and terephthalic acid and the peak temperature involved for polymerisation ranges between 225°C and 255°C.

From the 3D printing technology point of view PET is a strong and flexible materials with a high rate of success for the parts obtained. The most suitable use is for objects that must combine flexibility and hardness for example mechanical parts or enclosures for electronic equipment. More over, emitting less odours is an another advantage for PET in 3D printing comparing with ABS (acrylonitrile- butadiene -styrene) or with the well known PLA (polylactic acid) (Exconde *et al*., 2019).

Recently, a series of researches signalled that the ultrafine particles emitted during the 3D printing process can be toxic to humans. This is one of the reasons why it is recommended to use air filtration systems or frequently ventilation of manufacturing spaces (Nwogu *et al*., 2019).

1.3. The Mechanism of PET Recycling

The polyethylene terephthalate (sometimes called polyterephthalate of ethylene PETE) or PETP is the most frequent thermoplastic polymeric resin from the family of polyesters.

The packages made from PET can be recycled and used for fabrication of new recipients, thermo formable packaging and are also in application in the shape of fibres in carpets and clothing. It can be used in various combinations in composites for construction elements.

The empty PET package thrown away by the consumer after usage become for the recycling industry “post consumer PET”. In the EU the environment protection lows require for the local administrations to collect separately different types of waste. In other countries there are lows concerning the depositions of containers applied also for PET bottles (Nwogu *et al*., 2019).

After collecting PETs are being sorted according colours (Nwogu *et al*., 2019) and then, packed in bales are sent to a collector/recycler. It processes the bales by grinding and obtaining flakes. Some of them make special preparations for meeting the quality requests for food packaging. These preparations consist in obtaining a very high grade of purity of the material by eliminating label materials by washing glues, separating paper and all other extra materials by melt filtration.

1.4. Methodology of Fabrication for Granules for Filaments

Recycling the post-consumer polyethylene terephthalate (POSTC-PET) involves a series of scientific fields and a transversal approach. The fields connected in this technology of recycling are the physics and chemistry of polymers, process engineering and fabrication engineering.

The first step in achieving recycled PET involves virgin PET synthesizing, including the thermal transitions and processing.

The second phase is focussed for enhancing the molecular weight of the recycled material (R-PET) involving melting at specific temperatures and pressure and obtaining granules.

For obtaining good results the row material, PET recycled in the shape of flakes, must be clean and dry. The presence of humidity must be less then 100 ppm to minimize hydrolysis during melting.

The granules can be use for obtaining various semi products including filaments, fibres, bottle preforms etc. the process involving mainly melting and extrusion.

1.5. Significant PET Properties for 3D Printing

Specific for the 3D printing, in general, is the bringing of the materials in a viscous flowing state and conducting it on a predefined designed trace followed by controlled solidification of it, leading finally to the obtaining of the designed shape and necessary properties. From these reasons it is very important the knowing of viscous properties and rheology of used materials.

In the case of PET the achieving of viscous state involves its heating. The viscosity depends on the temperature level and pressure, parameters also very important in polymerisation and polymer stability. All elements implied are important and for ensuring the success of 3D printing operation is dependent by the ensuring through the printing head and the equipment as an ensemble of heating-cooling conditions, of maintaining temperature and pressure during printing.

PET used for 3D printing can be considered from these points of view a complex fluid. So the known elements applied: at low pressures the viscous fluids flow at big strains not only by sharing but also other ways of deformation.

The apparent flowing, named also plastic deformation is a very complex phenomenon. Some consider that the plastic deformation of vitreous fluids suppose the localisation of the deformation and its evolution toward the forming on sharing stripes.

Fig. 1 shows the structure of local sharing regions during the simulated creep by plastic deformation modelling.

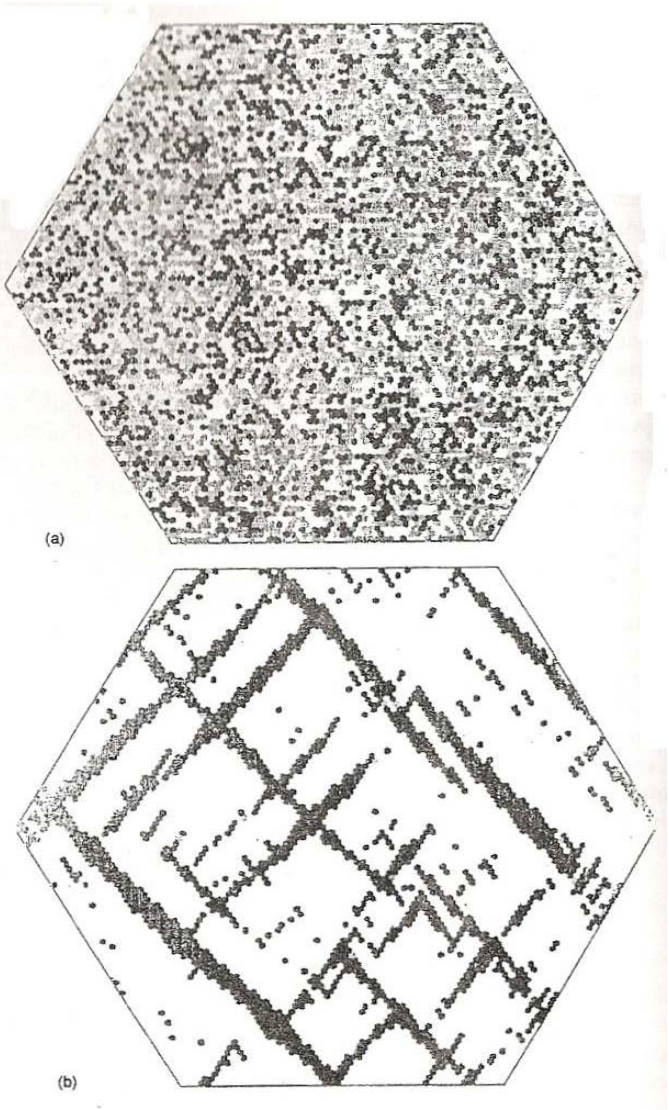

Fig. 1 – Plastic deformation regions (dark) described by the creep model of a fluid (*a*) at high temperature over the vitreous flowing temperature (Tg); and (*b*) at a low temperature, in vitreous state (Larson, 1999).

At high temperature the highly deformed regions are not spatial correlated Fig. 1*a*. At low temperatures the high shared regions accumulate in stripes Fig. 1*b*.

2. Thermal Characterisation of PET

Because the thermic properties of recycled PET are very significant for the 3D printing it is obvious that they have to be determined in a precise manner.

Among the techniques used for thermal analysis, the differential scanning calorimetry (DSC) is considered to be the one, that ensures the best measuring precision for such an attempt (Kaiser *et al*., 2015).

This method is destined for the identification of thermal effects linked to the phase transformation that take place in materials under the influence of a thermal field.

It is known that at the transition from one state to another, when a redistribution in the arrangement of particles in a given material takes place the thermodynamic properties of the material change. These thermal effects can be studied as a function of temperature or time during the application of a well defined temperature programme.

The DSC analysis technique can be used to investigate a large variety of materials:

– compact solids – plastic materials, rubber, resins, metallic materials, ceramics, glass, composite materials, organic materials etc.;

– powders – pharmaceutical products, minerals;

– textile fibres;

– viscous samples;

– liquids.

Among the phenomena that can be determined using the DSC analysis technique there are being mentioned (Wagner, 2009): - melting, solidification, solid state transformations; vaporisation, sublimation, adsorption, glass transition, dehydration, decomposition, oxidation, polymerisation. For all of them there can be determined the characteristic temperatures levels or ranges, the enthalpy and the caloric capacity.

A large number of phase transformations in materials are accompanied by a heat release (exothermic reaction) or heat absorption (endotherm reaction).

The first order transformations, that take place at a strictly determined temperature, implying latent heat, are detected on DSC like maximum exothermic or endotherm (Ekeren, 1998).

The second order transformations are those that take place in a range of temperatures and which are not associated with heat releasing or absorption. At these transformations the variations consists in the symmetry of the system and as examples we can mention: compressibility, caloric capacity, volume dilatation coefficient etc. The glass transition in polymers is also a second

degree transformation. In this case sudden modifications of specific heat can be put into evidence on the DSC thermograms as a changing of the linearity if the recorded signal (Paladi, 2013).

In Fig. 2 is shown a thermogram in the coordinates heat flux-temperature for a three layers thermo-contractible envelope made from PET (Lacatusu *et al*., 2019).

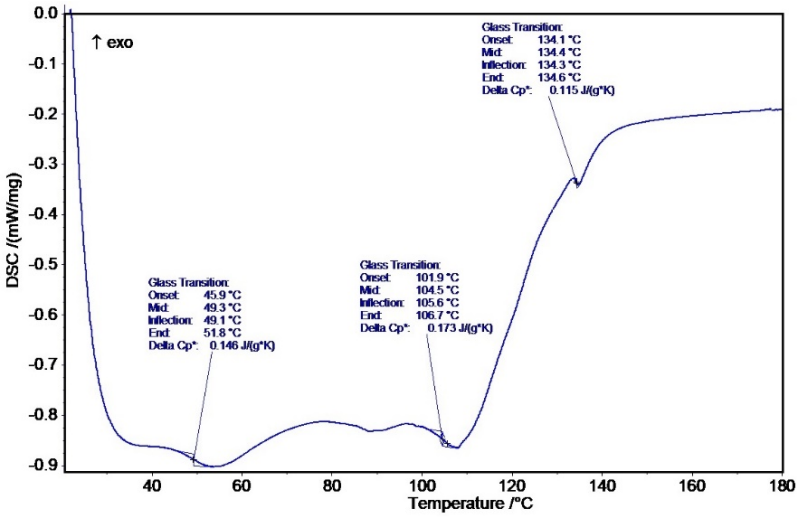

Fig. 2 – DSC thermogram at the heating of a fragment of a three layer thermo-contactable envelope made from PET, showing multiple glass transitions (Lacatusu *et al*., 2019).

Three glass transitions can be seen, corresponding to the three layers. The glass transition is identified by an endotherm step during heating. These three transitions took place between the following temperature ranges:

(i) 45.9 and 51.8°C (with an average temperature of 49.3°C);

(ii) 101.9 and 106.7°C (with an average temperature of 104.5°C) and

(iii) 134.1 and 134.6°C (with an average temperature of 134.4°C).

The transformation were accompanied by heat variation of 0.146, 0.173 and respectively 0.115 kJ/ (kg × K).

3. Filament Extrusion Line

3.1 General Characteristics

The production lines destined for obtaining filaments for 3D printing have a high automation level and integrate operations starting from the row materials until the final product.

A general view of such a line is shown in Fig. 3.

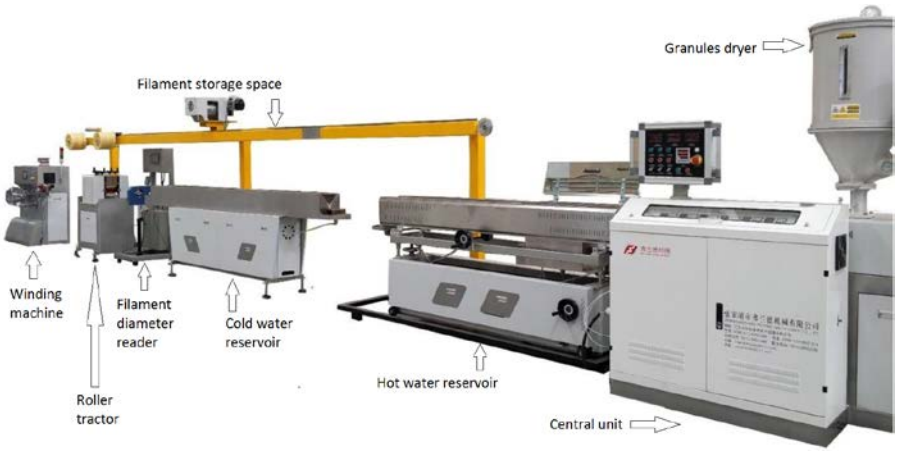

Fig. 3 – General view of a production line for PET filaments for 3D printing.

The equipment comprises: a dryer for granules, an extrusion system having special conceived dies, a hot water reservoir and a cold water reservoir, a roller tractor, a filament storage space and a winding machine. All components are being integrated with a programmable logic controller (PLC) and conducted by a software. The production line is compatible with all thermoplastic products (Sava and Bujoreanu, 2021).

3.2. Operation Flux

1. After drying, the granules are introduced into a helical conveyor by a supplying device and are being transported, compressed, homogenised and forced toward a die to form the filament.

2. After extrusion the filament is shaped in hot water and then quickly cooled in the cold water reservoir. At the end of the cooling reservoir there a dehydration device that removes 90% of the surface moisture from the filament.

3. The filament enters the horizontal tensioning support which uses an automated tension control system to even out the tension.

4. The filament reaches the winding machine using the roller tractor. The winding machine ensures the correct arrangement of the material along the line and also ensures easy access to the spool for replacement (Sava, 2021).

3.3. The Laboratory Analysis

The laboratory analysis consisted of tracing the thermograms of the materials using a differential scanning calorimeter (DSC). The thermograms were recorded only during heating in order to study the behaviour of the material along the filament extrusion line. The purpose of the experiments was

to determine the transition temperatures for the vitreous phase and for melting, in order to establish the fluidization conditions of the raw materials (granules).

The thermograms were made on PET granules with various colorants. For example, Fig. 4 shows the DSC thermogram for green PET granules.

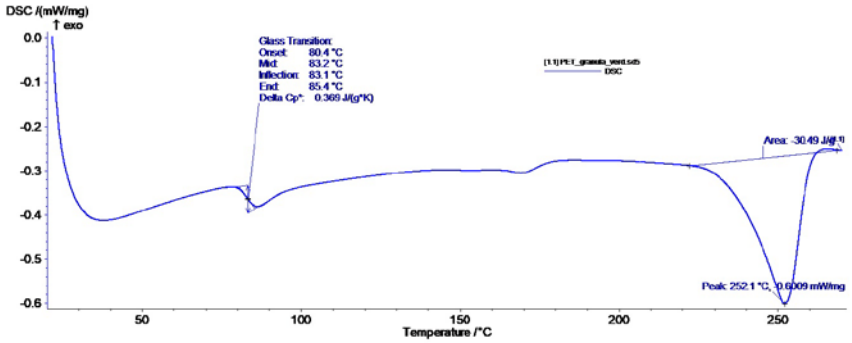

Fig. 4 – DSC thermogram at the heating of some green color PET granules (Sava and Bujoreanu, 2021).

During heating one can see in the range between 80.4-85.4°C, first a step associated with the glass transition. The PROTEUS software associated with the calorimeter, computes automatically an absorbed heat (0.369 J/g x grd). After it one can see a small endothermic minimum that can be associated with the crystallisation of some amorphous segments in the structure of the polymer. Finally in the range between 220-265°C, one can see an endothermic minimum that represents the melting of the material. The quantity of heat absorbed during melting is 30.49 J/g. It results that the minimum temperature of heating of green granules is about 220°C.

The second study was made on transparent granules, without colouring additives. A DSC thermogram for this situation is given in Fig. 5. The same transformations can be seen during heating.

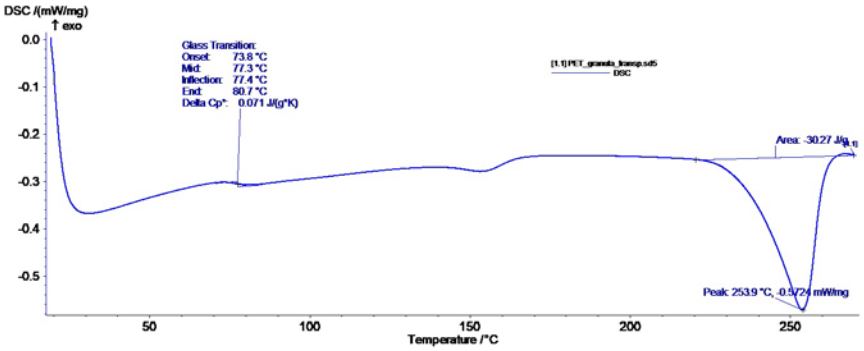

Fig. 5 – DSC thermogram at the heating of some transparent PET granules (Sava and Bujoreanu, 2021).

By comparison with the green granules, the transparent ones showed lower intensity transformations during heating. Thus, the glass transition absorbed 0.071 J/(g x grd) and took place at a temperature about 6 degrees lower, melting absorbed 30.27 J/g and the corresponding transformation point was 5 degrees higher.

There were made filaments from the two types of PET granules and samples were taken and subjected to another DSC test. A representative thermogram for the filament made by green granules is illustrated in Fig. 6.

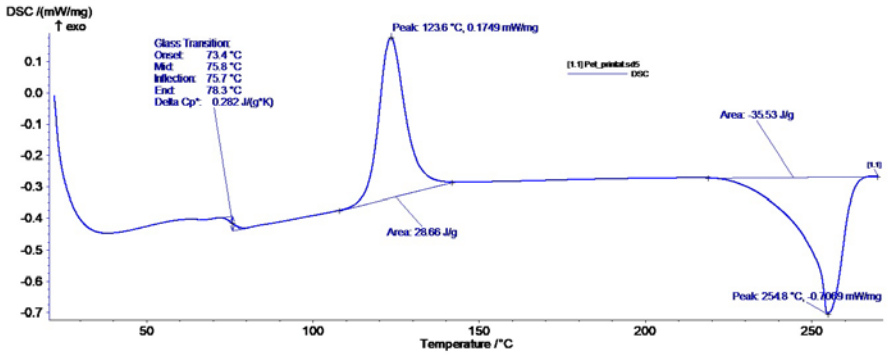

Fig. 6 – DSC thermogram at the heating of a fragment of filament for 3D printing made by green granules of recycled PET (Sava and Bujoreanu, 2021).

Unlike the row material granules the filament showed a glass transition in the range between 73.4-78.3°C that absorbed a specific energy of 0.282 J/(g x grd) and a melting point located around 254.8°C absorbing 35.53 J/g. In addition the filament produced by green granules show an exothermic maximum located at 123.6°C that can be associated with crystallisation/ solidification phenomenon of the analysed material (Sangerlaub *et al*., 2019).

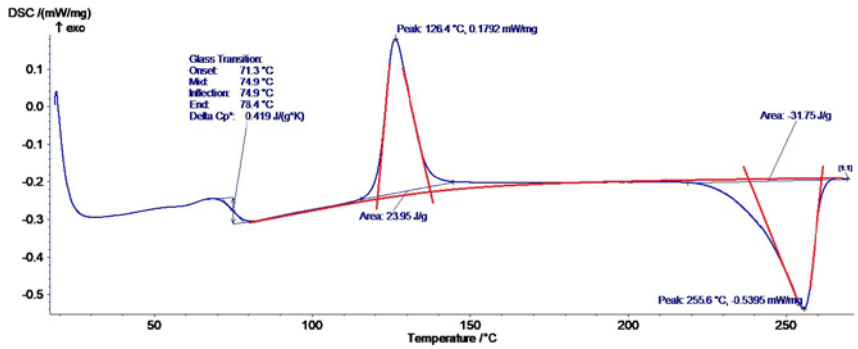

Fig. 7 – DSC thermogram at the heating of a fragment of filament for 3D printing made by transparent granules of recycled PET (Sava and Bujoreanu, 2021).

Moreover, knowing that the reprocessing of PET accentuates the crystallisation phenomenon due to elongation and shear stresses to which the melt is subjected during processing (Wu *et al*., 2019) it can be seen that crystallization releases a substantial amount of energy (28.66 J/g) comparable with the energy absorbed during melting.

The DSC thermogram of a fragment of filament made by transparent granules of PET is shown in Fig. 7.

In this case the phenomenon mentioned in Fig. 6 are present also here but the values are for the absorbed and releases energy during transformation are smaller. It has to be remarked that by comparison with the granules from which they were produced the filaments showed similar melting temperatures, the phenomenon starting at 220°C and finishing completely around 270°C.

The occurrence of the crystallization phenomenon at the filament level is consistent with the studies made by Wan et al. who argued that the complex demands during PET processing induce short molecular chains that crystalize at temperatures around 125°C (Wu *et al*., 2019).

4. Conclusions

There were conducted experimental studies concerning the recycling of PET in view of producing filaments for 3D printing using a filament extrusion line.

The conclusions drown are the following:

– by DSC test it was established the temperature necessary for heating the recycled PET granules at the value of 220°C;

– the extrusion line is functional and obtains filaments from recycled PET using the temperatures obtained from the thermograms at the programming process;

– the extruded filament keeps the phenomena of glass transition and the melting point at values similar to those obtained on granules of recyclable PET from which the filament was produced;

– at the extruded filament it occurred in addition one crystallization phenomenon that was attributed to the fragmentation of molecular chained during extrusion.

All of the above demonstrated the ability of PET to be recycled as a filament for use in 3D printing.

The values obtained on the thermograms for the filament material can be used as input data for the programming of the printing head of the 3D printer to obtain products from recycled PET.

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STUDIU PRIVIND OBȚINEREA FILAMENTULUI PENTRU IMPRIMANTE 3D DIN GRANULE DE POLIETILEN TEREFTALAT

(Rezumat)

În contextul creșterii nevoii de diminuare a poluării la nivel planetar, trecerea la industrii nepoluante este încă un deziderat. Un pas important în această direcție este

implementarea unor procedee, care au o amprentă ecologică pronunțată de exemplu cele care folosesc materiale reciclate. Această lucrare prezintă o posibilă utilizarea a unui material reciclabil binecunoscut, anume polietilen tereftalatul (PET) pentru obținerea de diferite produse prin "tehnologia de printare 3D". Utilizarea acestui material plastic pentru imprimarea 3D necesită filamente, iar posibilitatea fabricării acestora din materiale reciclate este investigată aici. După prezentarea la început a principalelor proprietăți ale materialului și istoricului său, lucrarea prezintă o schiță a tehnologiei de obținere a filamentelor, destinate pentru printarea 3D, utilizând ca materie primă polietilen tereftalat reciclat (PET). Principalii pași ai procesului de reciclare a PET-ului sunt de asemeni arătați pe scurt. Sunt trecute în revistă fenomenele implicate în general în printarea 3D și de asemeni cele implicate direct în cazul utilizării de filament din PET. Au fost determinate, folosind date din literatura de specialitate, proprietățile termice importante ale PET-ului, pe baza cărora materialul poate fi folosit ca filament pentru imprimarea 3D. Lucrarea descrie de asemeni pe scurt echipamentul folosit pentru obținerea de filamente din materiale termoplastice. Pentru determinarea prorietăților materialului, după obținerea de filamente din PET reciclat în condiții diverse, au fost făcute teste pe probe de granule din PET reciclat și pe probe din filament din PET reciclat prin calorimetrie cu scanare diferențială (DSC) și au fost comparate. Rezultatele confirmă păstrarea proprietăților PET-ului după reciclare și după obținerea filamentului pentru printare 3D deci implicit posibilitatea utilizării acestuia pentru obținerea de produse prin tehnologia de printarea 3D.

BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
Publicat de
Universitatea Tehnică „Gheorghe Asachi” din Iaşi
Volumul 67 (71), Numărul 3-4, 2021
Secţia
ŞTIINŢA ŞI INGINERIA MATERIALELOR

NANOTECHNOLOGIES AND NANOMATERIALS USED IN HERITAGE CONSERVATION AND RESTORATION: FROM RED IRON RUST TO BLACK MAGNETITE DUST

BY

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Received: October 4, 2021
Accepted for publication: December 9, 2021

Abstract. In this study is investigated the state of the art in the field of nanotechnology application and the use of nanomaterials in the conservation and restoration of cultural heritage. The use of nanomaterials in this area is not recent, considering that the first gold plating experiment by electrodeposition has ever been recorded since the beginning of the XIX -th century, immediately after the invention of the Volta battery. Among the first nanomaterials used it can mention colloidal gold or metallic pigments used in painting. Among the most recent concerns in the field are those under the aegis of ICROM, promoting technologies and using nanoproducts that are already used in the restoration of objects from materials such as paper, wood, glass, stone, ceramic, marble.

This paper aims to identify whether the synthesis of magnetite (and especially the synthesis of magnetite from precursors such as rust) is already used in the preservation and restoration of archaeological iron, and to what extent. Iron green rust, the one that contains divalent ions (Fe^{2+}) is already studied as a precursor in the synthesis of magnetite. The synthesis of magnetite by simultaneously heating (frying) the mixture of siderite and hematite is also studied and reported in different publications. However, applications of these studies in the field of heritage conservation and restoration are unknown.

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State of the art clearly showed that iron corrosion products are investigated using the latest methods for a variety of purposes. These are chemically stabilized, impregnated, or removed as appropriate. It seems, however, that it is not yet the subject of some applications of nanotechnologies that convert them from vulgar (not necessarily harmful) patina to noble patina. There are mentioned cases where, after removing the vulgar patina, a patina (of magnetite) is restored, by anodizing, but which uses the metallic iron of the object and not the corrosion products already existing.

Keywords: nanotechnologies; nanomaterials; magnetite; conservation; restoration; cultural heritage.

1. Introduction

Restoration of metal objects also involves certain chemical cleaning operations that aim to remove all or part of the corrosion products. Sometimes, however, the total removal leads to unsatisfactory results because what remains of the object does not resemble the original object. Its integrity is lost and much of the historical message that the object should convey is lost (Fig. 1).

Fig. 1 – Chemical treatment with orthophosphoric acid.

What is the role of magnetite in restoration? First, in some cases of chemical cleaning (for objects made of Fe-C alloys of archaeological origin), what remains on the surface of the object is magnetite. About how it appeared, the subject remains open. Being hundreds of years old, it is very chemically

resistant and very adherent to the surface of the object. It cannot be removed by ordinary chemical processes. In some cases, its expulsion is observed, but due to the chemical attack of the surrounding alloy. It can be removed by mechanical sandblasting with hard particles.

But is it necessary to completely remove magnetite? After so much time lying in the ground, its presence on the surface of objects draws our attention to its chemical stability. A possible vintage accident (fire) led to the production of magnetite. It is a harmful or useful product depending on the thickness affected. But, if the mechanical properties are not too important, it can have beneficial properties on the object. It can protect him. As a protective film or as a depolarizer (through the iron ions it contains).

Browning, as a protective and aesthetic film is already known. But it is not the browning itself that is the subject of this study, but the preservation of the already existing magnetite and the transformation of the other corrosion products of iron into magnetite.

The purpose of this work can be defined as the identification of a protocol for the conservation and restoration of archaeological iron objects, through which all corrosion products are transformed into magnetite, while preserving the original shape of the object and efficient removal of chlorides.

2. History

How did the modern era of nanotechnology begin? The ideas and concepts behind nanoscience and nanotechnology began with a discussion entitled "There's Plenty of Room at the Bottom" by physicist Richard Feynman at a meeting of the American Physical Society at the California Institute of Technology (CalTech) on December 29, 1959, with long before the term nanotechnology was used. In his speech, Feynman described a process in which scientists will be able to manipulate and control individual atoms and molecules. Later, a decade later, in his research into ultra-precision processing, Professor Norio Taniguchi coined the term nanotechnology. It was not until 1981, with the development of the scanning tunneling microscope that could "see" individual atoms, and so, modern nanotechnology began.

Historically, nano-sized particles are neither new in nature nor in science. The first electrodeposition gold plating experiment was recorded at the turn of the XIX-th century, immediately after the invention of the Volta battery. Colloidal gold was used much earlier. In the work Lycurgus cup (Freestone *et al*., 2007), an early model of nanostructured material is presented, based on empirical understanding and manipulation of materials by time craftsmen. Another example of the early use of colloidal gold is presented in China's Ancient Gold Drugs (Zhao and Ning, 2001).

In 2000, US President Bill Clinton launched the National Nanotechnology Initiative (NNI) to coordinate federal research and development efforts and promote US competitiveness in nanotechnology.

In Romania, the issue of nanotechnology was publicly discussed for the first time during the scientific seminar "Micro and nanostructures. Possibilities and perspectives", organized by the Romanian Academy together with the National Agency for Science, Technology and Innovation (ANSTI), on February 4, 2000, in the Hall of the Romanian Academy and which was later considered the First National Seminar of Nanoscience and Nanotechnology. Thus, the year 2000 can be considered the year in which Nanotechnology was framed as an independent science and received a legal framework.

Globally, the most well-known institutions and centers involved in nanoscience and nanotechnology research are those such as Center for Nanotechnology and Biomaterials, University of Queensland, Australia; National Institute of Nanotechnology, University of Alberta, Edmonton, Canada; Science et Inginérie Supramoléculaire (ISIS), Université Strasbourg, France; Institut Charles Sadron, Strasbourg, France; Max Planck Institute of Colloids and Interfaces, Potsdam, Germany; Fraunhofer Institute Golm, Germany; Department of Physics and Nanotechnology, Aalborgy University, Denmark; Interdisciplinary Research Institute for Nanotechnology and Nanoscience, Tel Aviv University, Israel; National Nanotechnology Laboratory, University of Lecce, Italy; Nanotechnology Research Institute AIST Tsukuba, Japan; Research Institute of Nanomaterials, Nanjing University of Aeronautics and Astronautics, P.R. China; Nanotechnology Centre, Institute of Physics London, UK; The National Nanotechnology Initiative (NNI), Washington DC, USA; Nanoscience and Technology Institute (NSTI), Cambridge Ma, USA, etc.

CSGI (Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase, Research Center for Colloids and Nanoscience, Italia), is a world leader in the development of innovative systems and nanostructured formulations for the conservation and restoration of cultural heritage (stone objects, wooden objects, frescoes, paintings, canvas, paper). The latest results in this field can be seen in the paper Nanotechnologies and Nanomaterials for Diagnostic, Conservation and Restoration of Cultural Heritage. Topics covered include: Advanced microscopy techniques for nanoscale diagnosis of cultural heritage (Khramchenkova *et al*., 2018); Neutron tomography (Bernardini *et al*., 2018); Synchrotron radiation imaging (Kardjilov *et al*., 2018; Festa *et al*., 2018); Thermal analysis and analytical methods of analysis (Tiné and Duce, 2018); Raman spectroscopy and imaging (Cappa *et al*., 2018); Multispectral and fluorescent imaging; Dendrochronological dating (Bernabei *et al*., 2018); Nanoparticles for paper and wood artefacts (Cavallaro *et al*., 2018); Smart nanomaterials for cleaning (Baglioni *et al.*, 2018); Parchments and canvas (Bukreeva *et al*., 2018), From the structure of proteins to the preservation of works of art (Giordano *et al*., 2018); Enzymes and microorganisms for cleaning;

Case studies from archeological sites and museums (Serafini and Ciccola, 2018). Conclusions, perspectives for nanotechnologies and nanomaterials in the diagnosis, conservation and restoration of cultural heritage (Tiňo *et al*., 2018), (Secco *et al*., 2018). The book is a collection of previously published works individually and is aimed at scientists, from university professors to professional conservators and restorers, who are involved in the conservation and restoration of movable and immovable cultural heritage, as well as those who want to learn how nanotechnology can increase the efficiency of conservation and protection techniques.

3. Current State of Methods of Conservation and Restauration for Iron Artifacts of Archaelogical Provenance

The methods used in the conservation and restoration of archaeological iron parts, in order to stabilize and / or convert unstable corrosion products into more stable products can be classified into: chemical methods; electrochemical methods; classical thermal methods (thermal reduction); plasma treatment; use of ion exchange resins.

The stabilization and conversion of these corrosion products comes from the need to keep them on the surface of objects so that they can keep their original shape and image. This is the case of metal parts (made of Fe and Fe-C alloys) with a high degree of mineralization, with a shapeless metal core that no longer resembles the original shape, or completely mineralized.

Chemical methods refer to those chemical treatments that aim to eliminate chlorides (alkaline solutions with sodium sulphite, sodium hydroxide, etc.); these are long-term treatments (from a few months to years). Chemical methods also refer to the conversion of corrosion products, to the passivation of metal surfaces by using rust convertors.

In the works (North and Pearson, 1978a; North and Pearson, 1978b), (ICOM Committee for Conservation 5th Triennial Meeting Zagreb, 1978), "methods of treating sea iron" are briefly described. Some of these methods, considered old since then, are also described in works such as (Schmidt-Ott, 2006; Schmidt-Ott, 2017), or (Watkinson and Rimmer, 2013; Watkinson *et al*., 2019) without too many technical details, being considered established. In a recent article, the same authors (Thunberg *et al*., 2021) they shall also consider preventive measures, in particular those relating to the moisture content of the storage medium, as additional measures for the long-term stabilization of objects.

The alkaline sulphite method for archaeological iron was proposed by N.A. North and C. Pearson (1978a, 1978b) for seawater desalination. They reported that the final product of treatment was double iron oxide, Fe_3O_4, magnetite. However, they did not describe the thermodynamics of the process.

Later, M. Gilberg and N.J. Seeley (Gilberg and Seeley, 1981), revealed that the formation of magnetite is a more complicated process than described by previous authors. An experiment presented in the paper (Eggert, 2010), (Some New Advances in Alkaline Sulphite Treatment of Archaeological Iron, Svetlana Burshneva, Natalia Smirnova), proposed a two-stage mechanism of ferro-ferric oxide formation.

The evolution of the chemical stabilization process with alkaline solutions, a process that leads to the formation of magnetite, can also be observed from communications and projects launched and reported in BROMEC (Bulletin of Research on Metal Conservation).

Thus, in BROMEC 5, (Degrigny, 2003a), page 4, a new concept for the desalination of iron artifacts in neutral solutions is presented. BROMEC 7, (Degrigny, 2003b), highlights another important feature of alkaline sulphite treatment: the possibility of mass treatment of archaeological iron artifacts. BROMEC 16, (Degrigny and Crawford, 2005), page. 12, also mentioned the use of the alkaline sulphite treatment method for the preservation of large quantities of iron, archaeological objects. In BROMEC 18, (Degrigny and Crawford, 2007a; Wiesner *et al*., 2007) a study is presented in a doctoral project (SABKS: State Academy of Art & Design Stuttgart), on the effectiveness of desalination with hydroxylamine as an alternative to alkaline sulphite treatment. BROMEC 21, (Degrigny and Crawford, 2007b; Schmidt-Ott, 2006) presents an interesting work: "Alkaline sulphite desalination- tips and tricks", from Swiss National Museum The experiences gained over twelve years have led to a number of changes in the conservation process that make the application easier, more efficient over time and more economical. The same method is described in the paper (Jacot-Guillarmod *et al.*, 2019), where the main purpose is to quantify the remaining chlorides by tomography.

In BROMEC 22, (Crawford, 2007), the official takeover of the Hunley project is announced by Clemson Conservation Center de la School of Materials Science and Engineering of Clemson University. Iron (dry) samples obtained from the submarine H.L. Hunley (1864) have been treated in subcritical conditions (at 180°C and 52 barr using a 0.5% NaOH solution in water).

In all these works presented above, the stabilization treatments of iron archeological artifacts are usually considered to be effective, although the extraction mechanisms are not yet well understood.

For rust convertors, the success of a rust conversion treatment depends on the nature and properties of both the rust layer (total resistant rust, rust film thickness, rust structure and composition, etc.) and the rust compound, rust transformation (structure, concentration, solubility, pH, etc. ability to chelate with ferrous ions).

The most widely used rust convertor recipes are based on phosphoric acid, tannic acid and lignin. The first uses of tannin in the preservation of artifacts of archaeological origin are mentioned in (Plenderleith and Werner,

1971; Plenderleith, 1987; Oddy, 2010). It seems that tannin fails to stabilize this category of objects in the long run (Figs. 2-5). Phosphating is applied in the chemical passivation procedures of archaeological pieces, but commercial formulations are not used, but laboratory reproducible recipes, of controlled and verified composition. It is a surface process, which fails to chemically modify the chlorides located at the interface between the metal core and corrosion products (especially magnetite).

Tannin-treated and monomer-impregnated part (after about 20 years)

Fig. 2 – Post-treatment cracks and swellings.

Swelling due to post-excavation crystallization of chlorides

Fig. 3 – Object undergoing re-restoration treatment (previously treated with tannin and impregnated).

Migration of chlorides to the surface

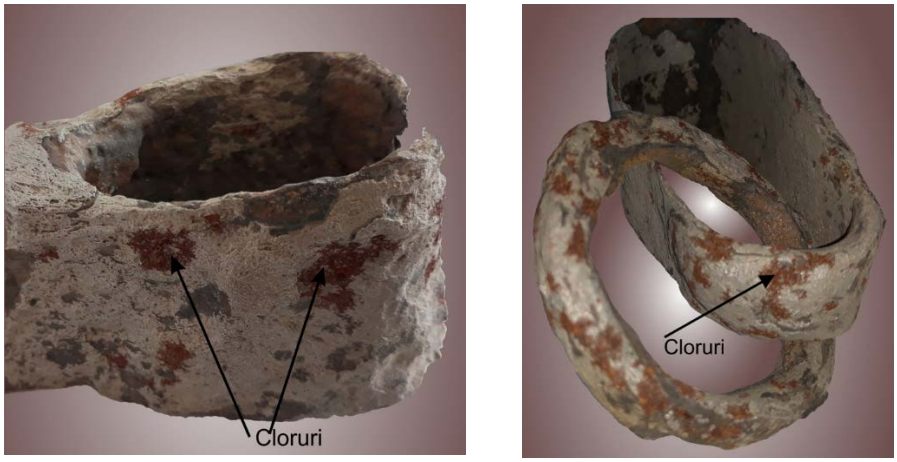

Fig. 4 – Post-treatment, (after about 1 year).

Expulsions of the oxide layer treated with tannin and impregnated

Fig. 5 – Approximately 10 years after the first treatment.

The latest studies on rust convertors are presented in (Saji, 2019).

Electrochemical methods are more laborious, require specially designed facilities and spaces and can also be divided into two groups: with and without external direct current source. The hydrogen that is released at the cathode can produce reduction phenomena, but also oxide dislocations, achieving both reduction and cleaning. The first basic information about these two processes can be found in (Plenderleith and Werner, 1971), Wihr (Wihr, 1975) and North (Wihr, 1975) which provides detailed discussions on the electrolytic reduction of iron corrosion products. In March 1976, museum curators, archaeologists, curators, museum scientists, researchers and engineers in the field of metal corrosion, metallurgists, met in Gaithersburg, Maryland, United States at a meeting entitled: “Corrosion and Metal Artifacts: A Dialogue Between Museum Conservators and Archaeologists and Corrosion Scientist”. The success of this meeting was due to the presence of Professor Marcel Pourbaix from Centre Beige d’Etude de la Corrosion (CEBELCOR), which through his work, entitled

"Electrochemical Corrosion and Reduction", sets the standards for future studies in this field.

The same electrochemical or electrolytic reduction techniques are described in the paper (Mourey, 1987), (published in Romanian in 1998), structured as a textbook, and which is especially useful for all those who want to study the restoration and conservation of metal objects.

A recent study analyzing the transformation of ferrhydride into goethite and magnetite, by electrochemical methods, is presented in the paper (Aeppli *et al*., 2019).

Thermal reduction is a classic method of reducing oxides, less commonly used in conservation and restoration because it is considered that the internal structures of the alloy undergo phase transformations and thus the original structure of the metal is not preserved, and historical information is lost (sometimes the term falsification of historical truth is used). But most of the time, the objects reached the ground as a result of events that also involved arson; mineralization is very advanced or even complete, and there is no question of keeping any proof of time technology. One of the first processes of thermal reduction of oxides used in the case of archeological pieces of iron, is described by North and Pearson, (North and Pearson, 1978a; North and Pearson, 1978b), where the reduction of oxides takes place in a pure, dry hydrogen stream at 400°C (Rosenberg method). There is also a modified Rosenberg method, which uses carbon instead of hydrogen.

The thermodynamics of the reduction of iron oxides with hydrogen is also presented in the review paper (Spreitzer and Schenk, 2019). In general, the reduction of α-Fe_2O_3 (hematite) does not occur directly in the iron. If the reduction temperature is lower than 570°C, the reduction to Fe takes place gradually from Fe_2O_3 to F_3O_4, magnetite, and continues to Fe. The intermediate oxide, wüstite, Fe(1-x)O, is not stable at temperatures below 570°C. At reduction temperatures above 570°C, wüstite must also be taken into account in the progress of the reduction. In this case, the reduction takes place from Fe_2O_3 through F_3O_4 to Fe (1-x) O and then continues to Fe.

Plasma treatment is a particular case of thermal reduction with hydrogen, as a result of which corrosion products are transformed into magnetite, considered inert to storage or display conditions in museums. The first to use this technique were researchers at the British Museum, then this process was developed especially in Switzerland, in Zurich, and in Denmark, in Copenhagen. It requires expensive equipment, specially designed spaces and staff specialized in plasma physics. The process itself is by far the most effective in solving the problems raised by the metal of archaeological origin and the archaeological iron in particular. Plasma used in the conservation and restoration of heritage objects falls into the category of cold (or non-thermal) plasmas, identical to the plasma found in neon fluorescent lighting tubes. The electric discharge can be supported by an alternating electric current (1.6 kV, 50 Hz) or in

a radio frequency field. Depending on the purpose, the gas used can be O_2/Ar or H_2/Ar mixtures, in various proportions, where argon is used to reduce the risk of explosion.

Since their first application to metal artefacts in 1979, gas plasmas have been the subject of conservation research. The Swiss National Museum has been involved in the development of this treatment for iron artifacts since 1984 and has purchased its own device since 1990. Hydrogen plasma used at the Swiss National Museum (Schmidt-Ott and Boissonnas, 2002), is produced by an electric discharge in a radio frequency (RF) field. The highly reactive plasma, with its partially ionized molecules and atoms, will react easily with iron corrosion products. Thus, oxides and chlorides are reduced. The technology consists of a partial reduction of corrosion products, which is preferable to a complete reduction, because it gives better results and there is no risk of advanced embrittlement. With a partial reduction, the surface layers increase their porosity, implicitly the fragility and will be able to be removed mechanically later more easily. In addition, the microcracks formed will improve the subsequent removal of chlorides.

Ion exchange resins are known from water softening and demineralization processes. It is a process that mainly removes carbonates and thus avoids the use of chemical baths that can affect the base metal or other corrosion products. It can be considered more of a preliminary treatment, decalcification, descaling; by removing the limescale, the oxide film becomes porous and therefore more permeable for subsequent treatments.

4. Objectives Regarding the Use of Nanotechnologies and Synthetic Magnetite in Heritage Restoration and Conservation

Fig. 6 summarizes the main stages of a classical restoration-conservation technological flow for archaeological iron artifacts, and some ways in which synthetic magnetite could be used as alternative methods.

In this flow, CHLORIDE TESTING, occupies the central position. It is not possible to test the amount of chlorides remaining in the part, by non-destructive methods, but only the amount of chlorides extracted. A complete dechlorination by classical chemical methods is not possible, therefore an attempt is made to reduce them to certain limits (*e.g.* 70 ppm in the treatment bath). A piece dechlorinated within conventional limits is considered stable, and the (active) preservation in this case can be considered completed. Its monitoring (passive preservation) is sufficient.

Thin arrows of various colors represent the classic technological flow. Thick blue arrows represent the possibilities of implementing nanotechnologies and the use of synthetic magnetite. In general, any treatment involving substances (hydrochloric acid, NaCL, KCl, etc.) that bring chlorine to the part is avoided.

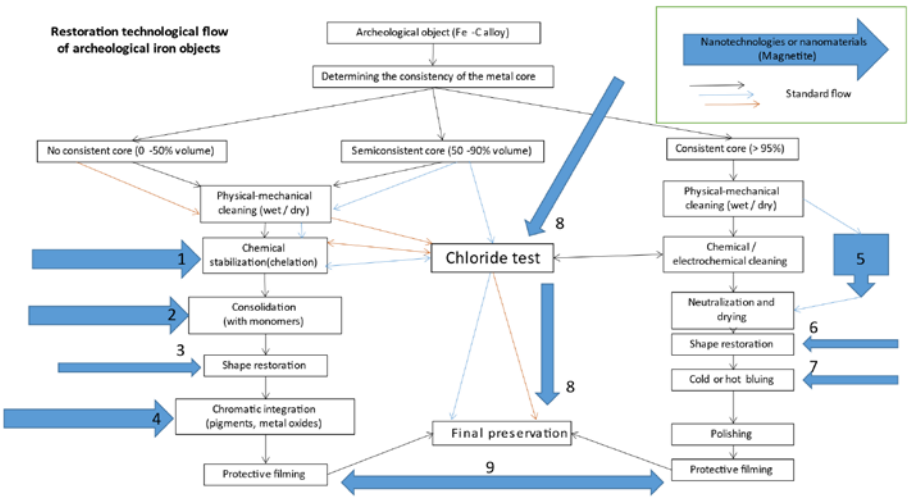

Fig. 6 – Technological flow of restoration of archaeological iron objects.

1) *Chemical stabilization* (thick blue arrow numbered 1) - the transformation of chlorides (which is usually done with sodium sulphite, with partial conversion to magnetite) can be replaced by the synthesis of magnetite, using existing chlorides as precursors. Instead of obtaining a chelate, we obtain an oxide (spinel), chemically inert. A comparative study will prove effective.

2) *Consolidation* - Instead of using a monomer (varnish) for impregnation, magnetite nanoparticles are used, possibly synthesized right in the pores of the object (part). In the case of fully mineralized parts, the use of "fossilizing" precursor combinations containing both magnetite and SiO_2 precursors (TEOS-tetraethoxyorthosilicates) may be considered.

3) *Form filling* - The use of composite materials in which one of the components is magnetite in the form of nanoparticles or the use of xerogels, to fill small gap areas.

4) *Chromatic integration - Use of nano magnetite as a pigment.*

5) *Chemical cleaning* - Synthesis of magnetite, using corrosion products as precursors, having the advantage of lower losses of basic metal material. (A conventional chemical cleaning removes both corrosion products and the base metal material, whether or not a corrosion inhibitor is used).

6) *Completion of the form* (in the case of objects with a consistent metal core, is identical to Objective 3, but on a smaller scale, and involves the use of magnetite in the form of composite, gels, to remedy cracks, small gaps, exfoliation, or other defects which does not significantly affect the mechanical strength of the object.

7) *Patination* - Replacement of the chemical patina (bluing), which involves treating the whole part, with a thin layer of magnetite obtained by synthesis from precursors, deposition (sol-gel method) or anodic (last two already known, but not used in restoration), by local application techniques.

8) *Conversion of the chlorides* brought by the piece from the excavation into magnetite and final preservation. A method that respects the principle of minimum intervention, and that is usable in the case of objects without exhibition value, which do not financially justify a full flow of restoration, but are still recorded as assets. (This category of objects also has the largest share, in number, in collections).

9) *Protective film* - varnishes, protective waxes containing magnetite nanoparticles as pigment (various compositions for various shades of gray - black).

An important tool for establishing the conservation / restoration protocol by converting corrosion products to magnetite is given in the image shown in Fig. 7.

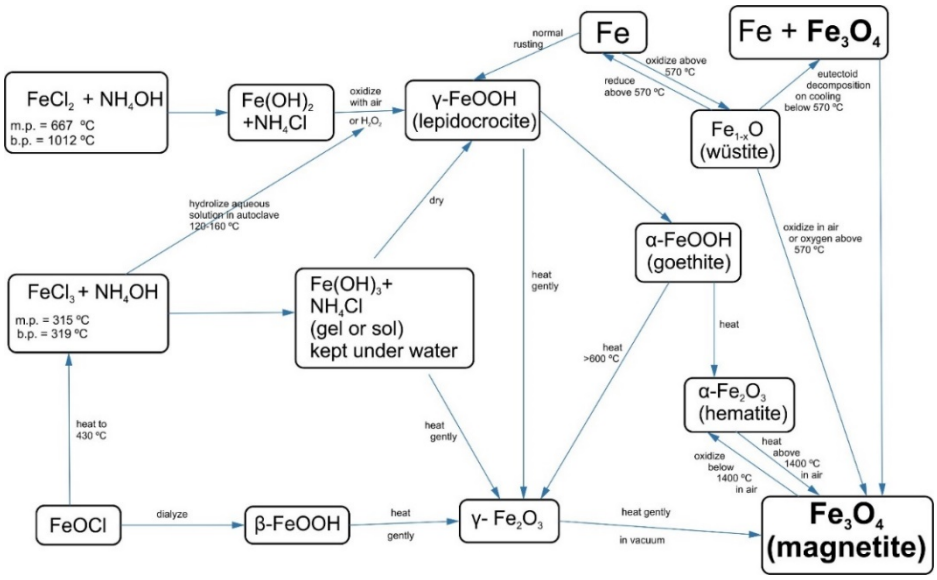

Fig. 7 – Relations among some iron componds (adapted from A.F.Wells).

The majority component of rust will determine the type of protocol to be adopted.

Thus, if the rust is composed mainly of γFeOOH (lepidocrocite), it is possible (theoretically) to adopt two methods:

Protocol 1 (via maghemite) (Iacob *et al.*, 2019; Cornell, no date)
γ-FeOOH(lepidocrocite) → γ-Fe_2O_3 (maghemite) → ***Fe_3O_4*** *(magnetite)*

Protocol 2 (via goethite-hematite) (Khan *et al.*, 2015; Bohra *et al.*, 2019; Zhang *et al.*, 2019)
γ-FeOOH (lepidocrocite) → α-FeOOH (goethite) → α- Fe_2O_3 (hematite) → ***Fe_3O_4*** *(magnetite)*

Protocol 3 (via lepidocrocite-maghemite) is carried out in most cases of synthesis of nanoparticulate synthetic magnetite (Schwaminger *et al*., 2020; de Viviés *et al*., 2007).
$FeCl_3$ +/ ($FeCl_2$) + NH_4OH → γ-FeOOH (lepidocrocite) → γ-Fe_2O_3 (maghemite) → ***Fe_3O_4***

Protocol 4 is possible in the case of objects with a high chloride content (hydroxichloride, β-FeOOH (akaganeite) (Watkinson and Emmerson, 2017; Thickett, 2012; Rémazeilles and Refait, 2007).
β-FeOOH-Cl (akaganeite) → γ-Fe_2O_3 (maghemite) → ***Fe_3O_4***

Protocol 5, in which electrochemical methods were used, presented in the paper (Aeppli *et al.*, 2019), could also target archaeological iron artifacts.
$Fe(OH)_3$ → α-FeOOH (goethite)
$Fe(OH)_3$ → ***Fe_3O_4*** *(magnetite)*

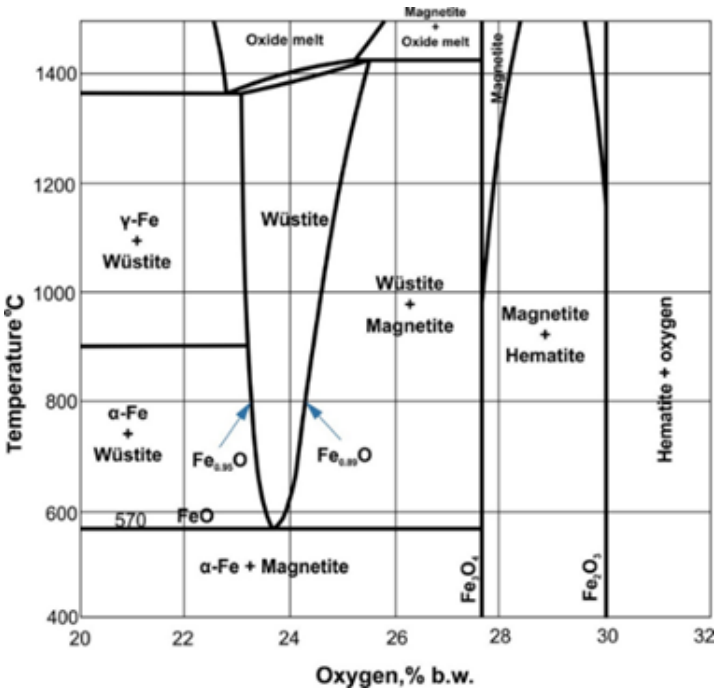

Fig. 8 – Fe-O diagram.

If we want to obtain magnetite starting from metallic Fe we can use one of the routes:

$Fe \rightarrow Fe_{1-x}O$ (wustite) $\rightarrow$ **Fe_3O_4**

$Fe \rightarrow \gamma$-FeOOH (lepidocrocite) $\rightarrow$ γ-Fe_2O_3 (maghemite) $\rightarrow$ **Fe_3O_4**

$Fe \rightarrow \gamma$-FeOOH(lepidocrocite) $\rightarrow$ α-FeOOH(goetithe) $\rightarrow$ αFe_2O_3 (hematite) $\rightarrow$ **Fe_3O_4**

In addition, when using thermal methods, the Fe-O diagram is also another useful tool.

Fe_3O_4 can be obtained by reducing Fe_2O_3 to temperatures above 570°C, or below this temperature. The minimum temperature should be T_{minim}=315°C, corresponding to the decomposition temperature of $FeCl_3$.

5. Conclusions

The aim of this paper is to identify whether magnetite is used in the conservation and restoration of archaeological iron artifacts. "Due to their geographical dispersion and early excavations, the artifacts have been exposed to various conservation interventions. Their nature depended on the approach of the main schools of weather restoration and knowledge development, as well as on the new conservation protocols" (Eggert, 2010).

• In all the techniques presented, for all periods, "it is possible, the thermodynamic conditions of magnetite synthesis are produced or fulfilled".

• This magnetite appears as a side effect, in chemical or electrochemical processes when the removal of chlorides is desired; sometimes undesirable (when covering carbon steel anodes of electrolysis cells).

• Magnetite from chemical processes such as washing with lye (NaOH, hydroxylamine, KOH solutions), alkaline sulphite method, alkaline method, is uncontrollable in terms of place or area of formation, duration, substrate on which it is formed and preferential precursors. In the conditions of ensuring the thermodynamic parameters, the formation of magnetite has a semi-natural evolution, in a long time, sometimes "consuming" metallic iron.

• Magnetite appeared in electrochemical conditions is difficult to control in the absence of specialized electrical equipment, which allows discrete control of current-voltage parameters. This magnetite is formed mainly at the interface between the metal core and corrosion products, with the effect of expelling (cleaning) them most of the time. The method cannot be applied to fully mineralized objects.

• The thermal reduction processes manage to simultaneously achieve both the reduction of corrosion products from rust to magnetite and the efficient

removal of chlorides. Carrying out these treatments in high annealing areas can affect the internal structure of the object, which can still hold important information about old manufacturing technologies. Requires thermal heating units at high temperatures and advanced knowledge of extractive metallurgy.

• Non-thermal plasma treatment processes with low pressure hydrogen also manage to reduce all iron corrosion products to Fe_3O_4 but fail to remove chlorides. It is used as a pre-treatment method (in alkaline sulphite methods), which, by increasing the porosity, improves the removal of soluble salts and chlorine from any combination.

• The implementation of nanotechnologies, as complementary methods, presented in Fig. 6 and using the scheme in Fig. 7 as a tool in decision making, could solve some of the shortcomings of classical methods such as the use of high temperatures; long treatment times in the case of the alkaline sulphite method (a method which is still empirical); or the high costs of the necessary equipment (plasma generators, stabilized current or voltage sources, thermal heating units (with predetermined construction dimensions). There is a wide range of methods for the synthesis of magnetite, with a great potential for solving problems, sometimes on a nano scale (Fig. 9) (Co-precipitation, micro / nano emulsions, hydrothermal and solvothermal reactions, sol-gel method, polyol, flow-injection, electrochemical methods, aerosol-vapor, Sonolysis, etc.)

Coat of mail rings

Fig. 9 – Obiective 2, 1, 5 or 8; *Protocol **3***.

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NANOTEHNOLOGII ŞI NANOMATERIALE UTILIZATE ÎN CONSERVAREA ŞI RESTAURAREA PATRIMONIULUI: DE LA RUGINĂ LA MAGNETITA SINTETICĂ

(Rezumat)

În acest studiu este investigat stadiul actual în domeniul aplicării nanotehnologiei și utilizarea nanomaterialelor în conservarea și restaurarea patrimoniului cultural. Utilizarea nanomaterialelor în acest domeniu nu este recentă, având în vedere că, primul experiment de placare cu aur prin electrodepunere care fost înregistrat vreodată, datează de la începutul secolului al XIX-lea, imediat după inventarea bateriei Volta. Printre primele nanomateriale utilizate intenționat se poate menționa aurul coloidal sau pigmenții metalici folosiți în pictură. Cele mai recente preocupări în domeniu se numără cele aflate sub egida ICROM, privind promovarea tehnologiilor și utilizarea nanoproduselor care sunt deja folosite în restaurarea obiectelor din materiale precum hârtie, lemn, sticlă, piatră, ceramică, marmură.

Această lucrare își propune să identifice dacă sinteza magnetitei (și mai ales sinteza magnetitei din precursori precum rugina) este deja utilizată în conservarea și restaurarea fierului arheologic și în ce măsură. "Green rusts" (oxizii verzi), care conțin ioni divalenți de fier (Fe^{2+}) sunt deja studiați ca precursori în sinteza magnetitei. Sinteza magnetitei prin încălzirea (prăjirea) simultană a amestecului de siderit și hematit este, de asemenea, studiată și raportată în diferite publicații. Cu toate acestea, aplicații ale acestor studii în domeniul conservării și restaurării patrimoniului sunt necunoscute.

Stadiul actual realizat, a arătat în mod clar că produsele de coroziune ale fierului sunt investigate folosind cele mai recente metode pentru o varietate de scopuri. Produsele de coroziune sunt astăzi stabilizate chimic, impregnate sau îndepărtate, după caz. Se pare însă, că procedeele nu constitue încă subiectul unor aplicații ale nanotehnologiilor care convertesc din patină vulgară (nu neapărat dăunătoare) în patină nobilă. Sunt mentionate cazuri în care, după îndepărtarea patinei vulgare, se reface o patină (de magnetit), prin anodizare, dar care folosește fierul metalic al obiectului și nu produsele de coroziune deja existente.