Preliminary Results on Pulsed Laser Deposition of PMMA on Nitinol Substrate

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Shape memory alloys are often used in applications where corrosion resistance property is very important. We can obtain a thin polymer layer using pulsed laser deposition on a nitinol wire with many applications in medical field. The polymer and the shape memory element with a non-metallic thin layer on the surface were analyzed by structural and chemical point of view using scanning electrons microscopy and X-ray dispersive energy analyze. Thermal insights were realized using a differential scanning calorimeter to analyze the polymer behaviour before and after deposition process. Preliminary results on the deposition set-up and the physico-chemical properties of the thin layer are presented and discussed below.

Keywords: Shape memory alloys, thin polymer layer, pulsed laser deposition, PMMA

Corrosion includes a series of processes, chemical and electro-chemical reactions through all the metals, generally speaking, passes from the initial to a modified status. This transformation is possible because in nature the metals can be found in complex forms: oxides, phosphates, carbonates, nitrate compounds or hydroxides whose free energy is lower than of the metal in initial state giving a justification for the tendency of the metals to pass to a lower energy form. The goal of the work paper is to improve the resistance of corrosion of a metallic intelligent material, nitinol alloy, through superficial deposition by laser ablation of polymeric materials. Approximately one third of the metal production in the world is affected by corrosion and 10 % of the production is completely lost because of the corrosion destructions [1-3]. The shape memory alloys NiTi have a very good resistance at corrosion but the presence of Ni in the chemical composition of alloy cause reserves in the applications with long periods of time of this material. Being known the toxical and cancerous character of Ni it is very important to prevent the access in the human body. The raw materials used in industry can suffer a direct chemical attack while the electro-chemical attack appears only in metals due to the possession of free electrons. The synthetic materials are exposed to destruction only through chemical attack because they do not have free electrons [4-6].

In order to obtain a superficial cover PMMA (Poly(methyl methacrylate)) is a resistant and a light material ($\rho=1.17...1,20$ g/cm^3) with the chemical formula of $(C_5O_2H_8)_n$ and the melting point 200 °C. It has an impact resistance higher than that of a glass or polyester but lower than polycarbonate or other polymers used in engineering. PMMA is flammable at 460 °C and burns forming, CO_2, water, CO and compound with low molecular weight including formaldehyde. The PMMA material is dissolved in organic solvents and has a low resistance at many chemical substances. Due to the groups of esters it can be easily hydrolyzed. Nevertheless the stability at the environment action is superior to many plastic materials as polystyrene and polyethylene and PMMA is usually recommended for outdoors applications [7].

PMMA has the maximum rate of water absorption of 0.3-0.4 % from its weight and a relatively high thermal dilatation coefficient of $(5...10) \cdot 10^{-5}$ K^{-1} [8,9]. PMMA has a high degree of compatibility with the human tissue and it is used for making intraocular artificial lenses when those natural were removed through the treatment of cataract. The dental prosthesis made by PMMA has the advantage of the same color with the teeth and the gingival tissue. In the cosmetic surgery the microspheres of PMMA in suspension in biological fluids are infected under skin in order to reduce the wrinkles or permanent scars. Most of the white filling dental materials (eg the dental composites like Z250 or XT from Filtek) have PMMA in their composition [10]. In the biomedical research PMMA material is used to create micro-fluidic lab-on-a-chip devices with reduce dimensions of micrometric sizes (~100 μm).

In order to obtain both high corrosion resistance and to improve the biocompatibility, to obtain a good compactness, uniform, pure and dense layer surface, but also to keep the chemical composition (stoichiometric) of the bulk material, pulse laser deposition technology (PLD) is mostly used [11-12]. Moreover, the Pulsed Laser Deposition (PLD) is stirring interest due to its versatility and controllability. PLD is a thin film deposition technique where a high-power pulsed laser beam is focused inside a vacuum chamber to strike a target of material that is to be deposited, in our paper- a bulk PMMA material. This material is vaporized from the target (in a plasma plume) which deposits as a thin film on a substrate (such as a Ni-Ti shape memory alloy under wire round form). This process can occur in ultra high vacuum or in the presence of a

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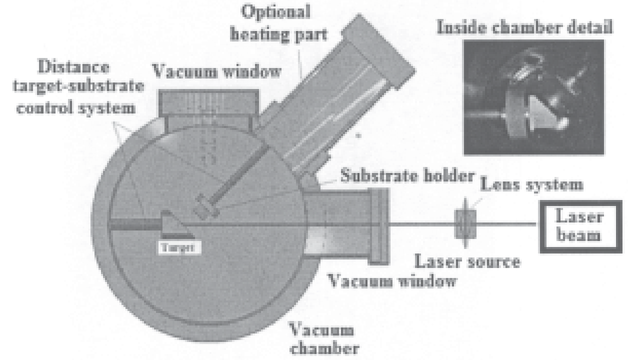


Fig. 1. Experimental set-up of deposing equipment

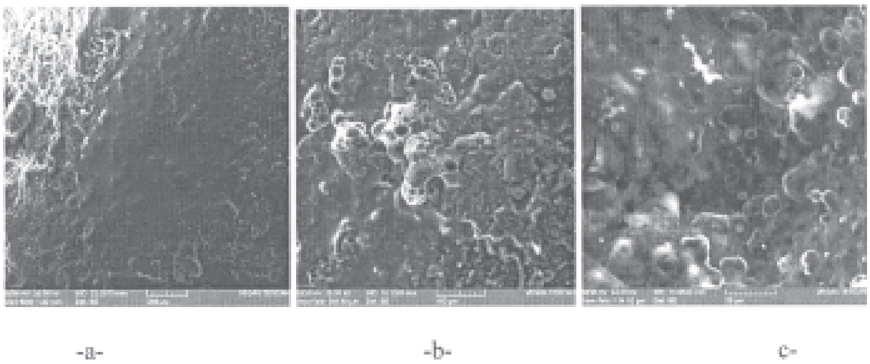


Fig. 2. SEM images of the PMMA material at different powers of amplifications a- 100x, b-500x and c- 1000x

background gas, such as oxygen which is commonly used when depositing oxides to fully oxygenate the grown films.

While the basic-setup is simple relative to many other deposition techniques, the physical phenomena of laser-target interaction and film growth are quite complex. Under the laser-matter interaction, the ejected plasma plume into the surrounding vacuum contains many energetic species including atoms, molecules, electrons, ions, clusters, particulates and molten droplets, before depositing on the substrate. A thorough investigation of the complex laser–sample interaction seems necessary, in terms of ejected products, nature of the desorption process itself, and/or the specific response to different parameters involved, like pulse energy or wavelength [12] of the exciting laser beam. To obtain a shape memory complex material some preliminary studies in a new PLD-experimental set-up will be discussed.

Experimental part

A schematic view of the experimental set-up is given in figure 1. The fourth harmonic (λ = 266 nm) of a 10 ns Nd:YAG pulsed laser beam (Continuum Surelite) has been focused by a f = 25 cm lens onto a polymer target placed in a vacuum chamber (evacuated to 10^{-2} Torr) [7]. The laser impact spot is elliptical (45° incidence) with an estimated area of ~0.4 mm^2. The laser beam energy has been continuously monitored by an OPHIR joulemeter. The energy usually employed was 25-30 mJ/pulse, which leads to a typical laser intensity of ~1 GW/cm^2.

The alloy used as substrate in this study is manufactured by Saes Getters Group, USA, and it is a shape memory material as a 700 μm diameter wire. The deposited thin layer was obtained by PLD process from a bulk sample of PMMA (Lactel Biodegradable Polymers, Birmingham U.S.A.) having the density of 1.18 g/cm^3. Deposition parameters, used to obtain the polymer thin film, were: ablation time of 1200 seconds, at 23°C temperature and a $3 \cdot 10^{-2}$Torr pressure with 50 mJ energy of the laser.

The polymer target is moved in XY plane by a micrometric manipulator in order to expose a fresh area to the laser beam. The unheated substrate is kept fixed and is parallel to the target surface. The target-substrate distance is 20 mm and the deposition time is 20 min.

To characterize the deposited thin films, a VEGA-TESCAN Scanning Electron Microscope equipped with the QUANTAX Bruker AXS Microanalysis (EDAX) system has been used. The microscopy was realized with a Secondary Electron detector for different scales to present the surface wires using 10 (for polymer material) to 30 (for metallic material) kV voltage supply of electron gun tungsten filament. Also 2D and 3D insights were taken to characterize the thin deposited layer surface state [13]. The images were taken at 10 mm distance to samples, for SEM imagery and at 15.5 mm distance between samples and EDAX detector for chemical analysis in automatic, element list and Line mode.

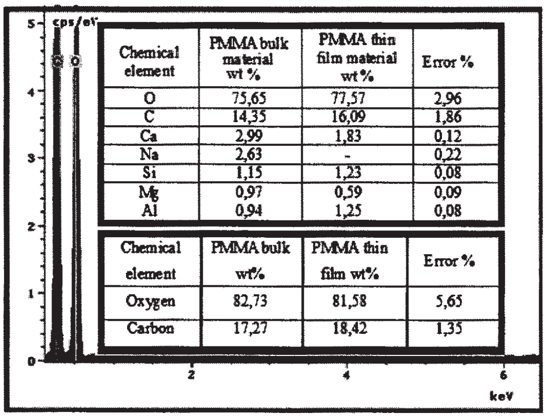
Results and discussions

In figure 2a is presented the general aspect of the surface of the polymer PMMA and in b and c few details of the microstructure. There were used different power amplification value for micro and macroscopic analyses at 100x and 1000x noticing instability of the material in vacuum chamber and under the influence of primary electrons fascicle.

In figure 3 is presented the spectrum of characteristic energies for PMMA where we can notice two main energies for C and O compounds around 0.5 KeV.

The chemical analysis of PMMA bulk was made on a surface of 2 mm^2 and the results are presented in the table from figure 3. The main elements found are oxygen and carbon in a approximate report of 4:1 atomic percentage but also a high number of other elements which occur in small proportions and appear on the polymer from different reasons like obtaining procedures and processing to different contamination reasons [14].

Pure poly(methyl methacrylate) homopolymer is rarely sold as a final product, since it is not optimized for most applications. In fact modified formulations with varying amounts of other comonomers, additives, and fillers are created for uses where specific properties are required. For example a small amount of acrylate comonomers are



Chemical element	PMMA bulk material wt %	PMMA thin film material wt %	Error %
O	75,65	77,57	2,96
C	14,35	16,09	1,86
Ca	2,99	1,83	0,12
Na	2,63	-	0,22
Si	1,15	1,23	0,08
Mg	0,97	0,59	0,09
Al	0,94	1,25	0,08

Chemical element	PMMA bulk wt%	PMMA thin film wt%	Error %
Oxygen	82,73	81,58	5,65
Carbon	17,27	18,42	1,35

Fig. 3. Energies spectrum of PMMA polymer and as details chemical compositions, full elements and particular case for C and O, for bulk material and as thin film material

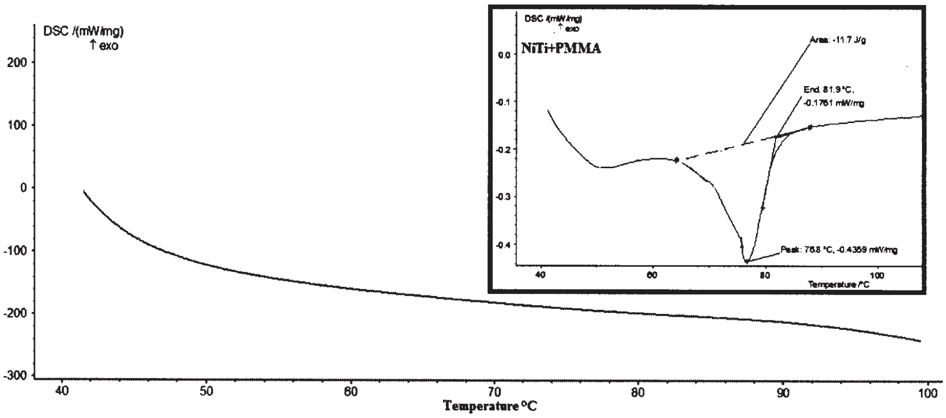


Fig. 4. Differential scanning calorimetry of PMMA polymer and in detail the calorimetric response of the nitinol alloy improved with the superficial layer

routinely used in PMMA grades destined for heat processing, since this stabilizes the polymer to depolymerization (“unzipping”). During processing also comonomers such as butyl acrylate are often added to improve impact strength and comonomers such as methacrylic acid can be added to increase the glass transition temperature of the polymer for higher temperature use such as in lighting applications [12,15].

In the second table – presented in detail in figure 3 is presented the chemical composition of PMMA only regarding the main elements C and O, obtained from the main spectrum and using the Element List analysis mode. A report of 1 to 3.6 at. percentages is observed between C and O.

After realizing the deposition chemical analyses were made and the same chemical elements were observed like in the bulk material. The results obtained present small variations between the two chemical compositions and analyzing the basic elements of the polymeric material, O and C, we notice a report of 1 to 3.3 between C and O. Also it was noticed the lack of Na from the polymer layer composition which can be attributed on the interactions during the deposition process and lack in the vacuum chamber of this element after the interaction of laser fascicle with target.

The calorimetric analyses were made with the equipment DSC Maya Netzsch in the 30-100°C temperature range to determine the behaviour of the polymeric material in the temperature domain of the martensitic transformation characteristic for intelligent metallic material. In figure 4 is presented the result of differential calorimetry of PMMA of the DSC signal, temperature flow depending of the temperature variation.

From the calorimetrical variation of the material to depose it can not be noticed any alteration in the solid state of the polymer in the temperature interval 40 – 100 °C which includes the martensitic transformation range of the smart material. The active intelligent element realizes the phase transition and implicitly the mechanical displacement in the 70-85°C temperature range and taking into consideration the thermal inertia we can reach maximum of 90-100°C temperatures. For these reasons it is important that the polymer use for deposition to be thermally stable in order to maintain his structural integrity. This result favors the appliance of this material, without degradation of the polymer during heating cycles, in the biomedical field where is followed and permanently controlled the contamination of the environment problems. In the detail from figure 4 is presented the calorimetric behavior of the alloy with shape memory effect improved with a superficial layer of PMMA through laser ablation and it is highlighted the M→A transformation temperatures range.

In figure 5 are presented the results of the analysis of the superficial layer PMMA deposited on a circular shape substrate with intelligent behaviour. In figure 5 a-b, are presented the microscopy at 100x and 5000x where are evidenced the macroscopic and the microscopic structural aspects of the thin layer as well the organization of the particles of PMMA ablated with laser and deposited on the metallic substrate. We can observe on the surface the formation of micrometer particles from the ablated target material of PMMA and a high homogeneity of the thin layer deposited on the material exposed to polymer plasma. From figure 5c we notice a small variation of the deposited layer, a good structural homogeneity and from the 3D morphology a smooth surface with the local spotting of the micrometers particles of the material ablated.

The superficial layers deposed through laser ablation depending of the time of deposing and the nature of the ablated material have thicknesses between 100 5000 nanometers and in the case of PMMA the layers thickness of 400-800 nm. Because through the technique of analysis EDAX data are collected from a depth of 5 μm the signal of the substrate will be very powerful in all the types of analysis used.

In figure 6 b is presented the distribution of substrate elements (Ni and Ti) and the main thin layer elements (C

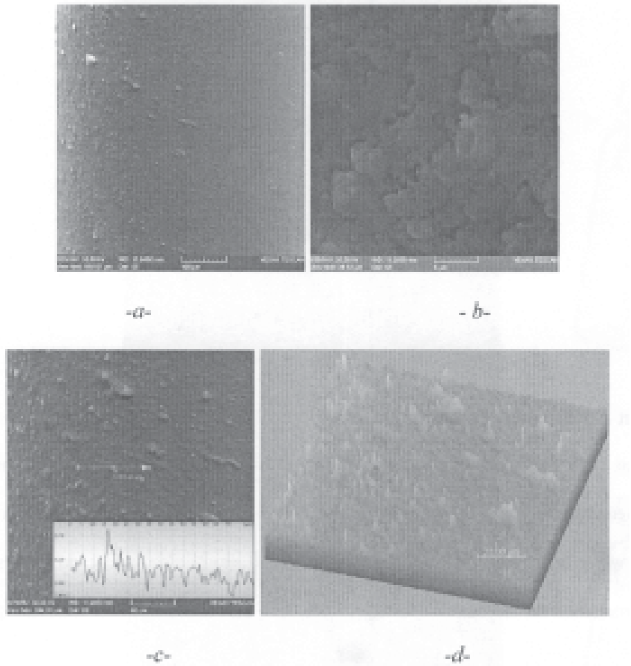


Fig. 5. The surface state of the polymer deposited on metallic substrate through pulsed laser deposition a-100x, b-5000x, c- deposited surface profilometry and d- 3D morphology of deposited surface

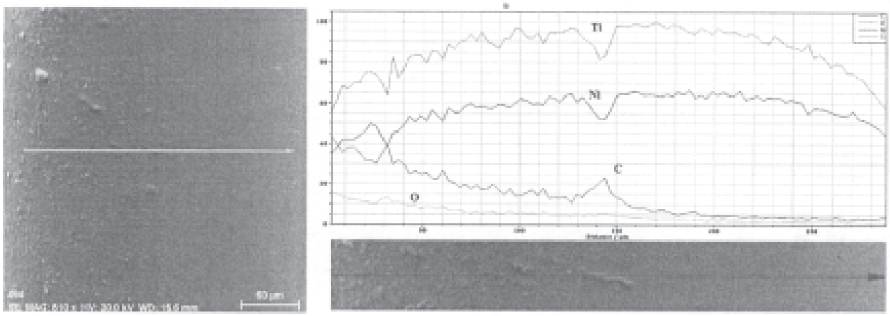


Fig. 6. Distribution of Ti, Ni, C and O in b) on the selected surface in a)

Table 1

CHEMICAL COMPOSITION ON THE SELECTED SURFACES IN FIGURE 7

Chemical element	Point1 wt%	Point2 wt%	Point3 wt%	Error %
Ni	50.82	46.17	6.24	1.32
Ti	45.41	43.77	7.94	1.30
C	3.77	10.05	21.26	0.66
O	-	-	64.57	8.36

and O) on a 300 µm line on the selected area from image 6 a). The line of distribution was selected on two surfaces, one with superficial deposited material in the left part of the image 6 a) and the other on metallic substrate. The metallic wire was covered only on one part by polymer. Also the rounds shape of the surface influence the signals of the chemical elements from its surface being lower on the edges (fig. 6 b).

It can be noticed from the variation of the chemical elements a growth of the signal for C and O elements for identification of the polymer layer on the area with ablated material and especially on areas with big polymer formations characteristics for pulsed laser deposition on nano seconds regime.

The evidence of the polymeric layer obtained through laser ablation as well as its chemical characterization can be made through mass and atomic determinations on the selected zones from figure 7.

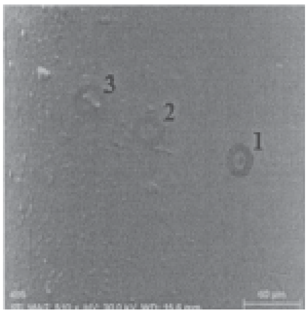


Fig. 7. SEM micrograph with selected areas for chemical analyses

The selected zone from figure 7 point 1 is on the substrate and the selected points 2 and 3 are on the superficial polymer layer. The chemical compositions of the areas selected in figure 7, which were made on surfaces of 1800 nm^2 are presented in table 1. It can be noticed the appearance on the surface of the shape memory alloy substrate of a percent of carbon element after the laser ablation process, table 1, but with a relatively low value. The value of C percentage increases in the case of the analyzed zones on the polymer thin layer by 3 to 7 times bigger than the initial result.

For practical applications in which the intelligent elements are used as final product like springs, stents, and wires or tubes the process of depositing must be enhanced with a rotational system of the substrate for a homogeneous covering of the intelligent active systems. The mechanical processing of the intelligent alloys and in general, of the new classes of materials [16], requires many heating and plastic deformation cycles that will affect the superficial polymer layer in the case when this is deposited in the initial state of the metallic material before education and after pouring.

The last selected area, point 3, was on a large particle of ablated material that has a high percentage of O and also an increase of C corroborated with the decrease of Ni and Ti through the decrease of signal strength of the substrate elements.

Conclusions

Preliminary studies on the physico-chemical properties of PMMA thin films deposited through PLD on NiTi shape memory alloy substrate have been performed using Scanning Electron Microscopy. The polymer thin films are “quasi-uniform” having nanoscale morphology with some micrometric inserted droplets. In order to associate the shape and dimensions of the included droplets with different experimental parameters, further fundamental research has to be considered. For instance, both space- and time-resolved optical and electrical methods can be applied to characterize the transitory plasma plume dynamics between target and substrate. Comparative chemical EDX analysis and elemental Point mode of the PLD deposited films versus bulk polymer have been done. To preserve the bulk material properties, the stoichiometry is an important parameter to be taken into account. Our polymer thin films keep the 1:3 ratio of carbon:oxygen similar to the chemical composition of the bulk polymer.

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