PULSED LASER DEPOSITION OF NI THIN FILMS ON METALLIC SUBSTRATE

Anca LARGEANU[1], G. O. POMPILIAN[2], D. G. GALUSCA[3], Maricel AGOP[4], Silviu GURLUI[5]

Filme subțiri de nichel au fost obținute pe substraturi metalice prin tehnica de depunere prin pulsații laser (PLD). Depunerea a avut loc pentru două condiții diferite ce privesc temperatura substratului (la temperature camerei şi la o temperatură de 400 °C a substratului). A patra armonică (λ = 266 nm) a unei raze pulsatorii laser produse cu un echipament Nd:YAG la 10 ns (Continuum Surelite) a fost utilizată în depuneri. Punctul de impact al laserului este sub formă eliptică (cu o incidență la 45°). Studiile indică un efect al procesului de încălzire a substratului asupra compactității şi rugozității stratului nanometric depus. Câteva proprietăți de strat au fost analizate cu ajutorul microscopului cu scanare de electroni (SEM) dotat cu un sistem de micro-analiză QUANTAX Bruker AXS.

Thin films of nickel on metallic substrates have been obtained by means of pulsed laser deposition (PLD) technique. Deposition was made in two different conditions regarding the substrate temperature (room temperature and 400 °C heated substrate). The fourth harmonic (λ = 266 nm) of a 10 ns Nd:YAG pulsed laser beam (Continuum Surelite) has been used. The laser impact spot is elliptical (45° incidence). Studies indicated an effect of heating process on smoothness and compacticity of deposited nanoscale layer. Few layer properties have been investigated by means of a VEGA-TESCAN Scanning Electron Microscope (SEM) equipped with the QUANTAX Bruker AXS Microanalysis system.

Keywords: thin Ni films, pulsed laser deposition, EDAX, SEM.

1. Introduction

Surface coating of materials to produce novel nanostructured thin films is currently an active area of research, because of newly obtained physical and chemical properties and their wide applications in optics, photonics, catalysis and biochemistry. As a consequence, many preparation methods of thin films are well

[1] “Gh. Asachi” Technical University, Faculty of Materials Science and Engineering, Iasi, ROMANIA
[2] Laboratoire de Physique des Lasers, Atomes et Molécules (UMR CNRS 8523), Université Lille 1 Sciences & Technologies, 59655 Villeneuve d’Ascq, France
[3] Gh. Asachi” Technical University, Faculty of Materials Science and Engineering, Iasi, ROMANIA
[4] Prof., “Gh. Asachi” Technical University, Department of Physics, Iasi, ROMANIA
[5] “Al. I. Cuza” University of Iasi, Faculty of Physics, Iasi, ROMANIA

developed. These methods are divided in two main groups: physical methods, such as Pulsed Laser Deposition (PLD) and laser cladding [1] or Sputtering and plasma spraying [2], and chemical methods, such as sol–gel and electrophoresis [3].

In order to increase the thermal and electrical conductivity of different metallic substrates a process of coating with nickel may be apply using various well known technologies (i.e. thermal evaporation, magnetron sputtering, electroless deposition and pulsed laser deposition).

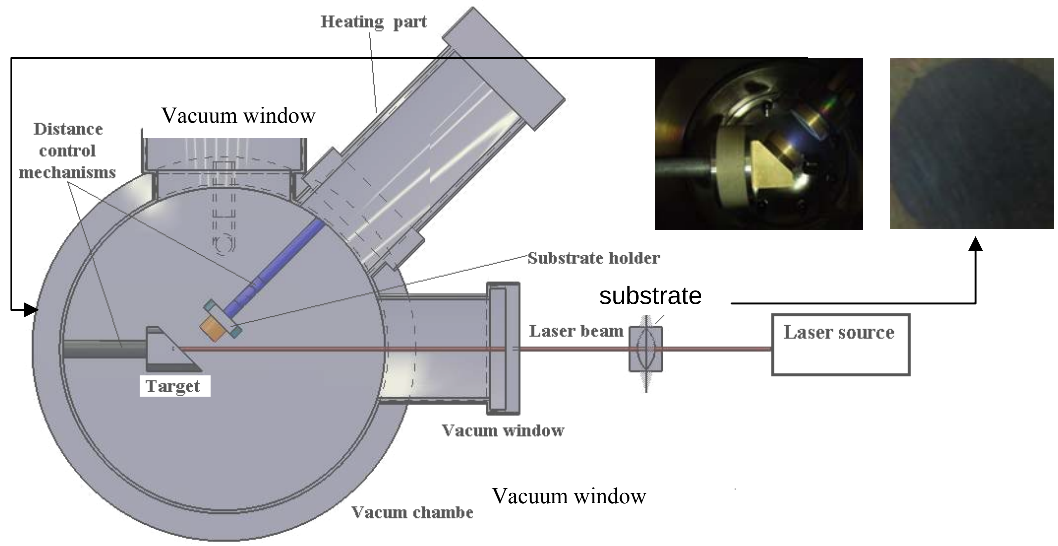
Pulsed laser deposition (PLD) is a versatile technique. This method is used mainly because of the stoichiometric transfer between the target and deposition film and thus good controllability of the film composition. It is a fast and effective growth method and intensive research on different kinds of polymers, oxides, nitrides, carbides and metallic systems have been reported [4,5]. Process parameters (gas pressure, substrate temperature, pulse frequency, number of pulses and the laser fluence) for the PLD technique influence the surface morphology of the grown thin films [6]. Optimization of these parameters is therefore needed for the growth of ideal thin films as demanded by the application. PLD produce a layer of high-pressure vapour species near the surface of the target, which is called the plume.

Employed in specific conditions to ensure the stoichiometry transfer from target to substrate, it allows the deposition of a large variety of materials. Moreover, in UHV, implantation and intermixing effects, originating in the deposition of energetic particles, lead to the formation of metastable phases, nanocrystalline highly supersaturated solid solutions and amorphous alloys. The preparation in inert gas atmosphere of Ni thin films makes it possible even to tune the film properties (stress, texture, optical and magnetic properties, etc) by varying the pulse laser energy.

In the present paper, nickel films deposited by PLD on a steel substrate ($42CrMo_4$) are investigated.

2. Experimental details

A schematic view of the experimental set-up for pulsed laser deposition 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 rotated high purity nickel target placed in a vacuum chamber (evacuated to 10^{-2} Torr) [7,8]. 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 40–50 mJ/pulse, which leads to a typical laser intensity of 1 GW/cm2.



Vacuum chamber

Fig. 1. Experimental set-up.

The material used for deposition is pure nickel 99.8 %, the substrate is 42CrMo$_4$ steel. The substrate was first mechanically prepared by gridding and polish was heated from room temperature to 400 °C; the distance between target and substrate was 2.5 cm and the deposition time was 60 minutes at a 10 Hz frequency.

3. Results and discussion

In figure 2, the scanning electron microscopy is presented: Samples a) and b) are recorded for films deposited at room temperature and samples c)-d) for the substrate heated at 400 °C. The images are obtained with a secondary electrons detector, at 16 mm from target, for 100x and 10000x power amplification. These results are in good agreement with those presented in [9].

The layer deposition limit can be easily identified in figure 2 a); the sample preparation before pulsed laser deposition influences the aspect, orientation and quality of the layer.

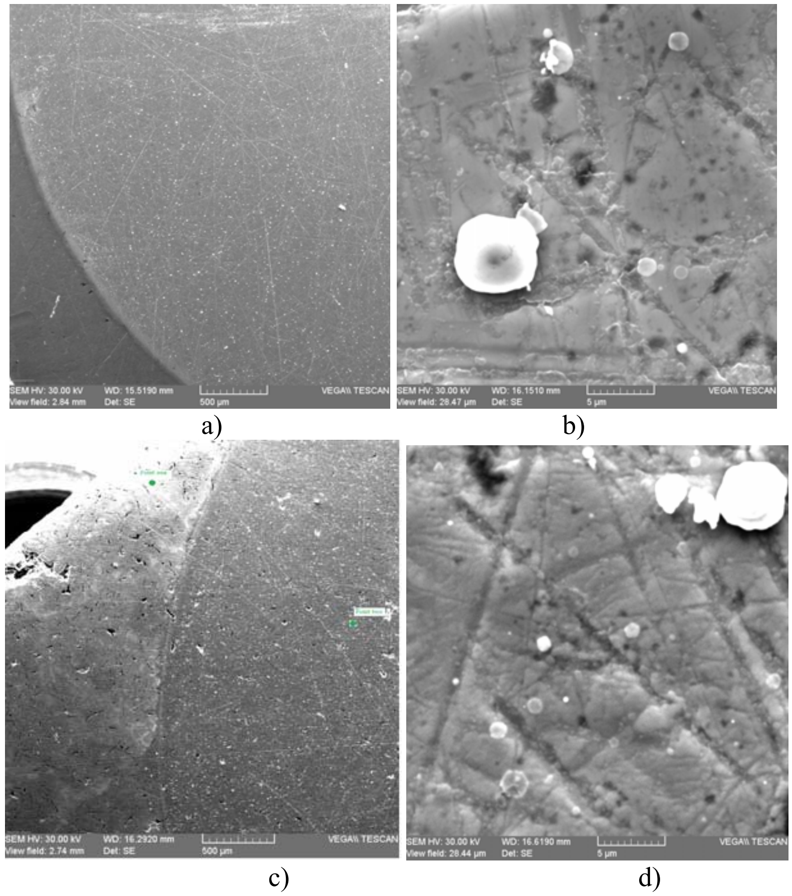


Fig. 2. SEM images of a nickel layer deposited by PLD on a 42CrMo4 steel substrate at room temperature: a) 100x, b) 10000x, and heated at 400°C: c) 100x and d) 10000x

As indicated in figure 2 a) and c), the substrate weakly alloyed steel $42CrMo_4$ suffers modification under thermal effect by heating at 400°C with carbon concentrations appearance all over the material surface. Preliminary results show that the Ni- PLD thin films with heated substrate show smoothness and compactness compared to the one obtained without heating.

These considerations are based on dependence of diffusion coefficient to activation energy (implicit temperature) lead to a higher diffusion activity on heated substrate comparing to samples at room temperature.

Under our deposition conditions, both some spherical droplets with sizes in the range of 0.1–0.2 μm and also a few large round well contoured droplets with dimensions of 0.3–0.5 μm have been obtained. In most cases, the formation of large droplets can be influenced by the physical properties of the bulk material (density and smooth surface of the material) [9,10] but may be depending on the plasma plume particles charge type and velocity, too. The ablation of smaller droplets originating from the fast heating and cooling processes of the target, which is due to the pulsed laser irradiation, cannot completely be avoided and further spectral and electrical plasma plume diagnosis [7] must be taken into account.

In figure 2 c) two reduced areas are selected, around 90 nm, named “point one”, on the substrate, and “point two”, on the thin film, for chemical composition investigation, with the results presented in table 1 as mass and atomic percentages. The analysis was made using energy dispersive X-ray spectroscopy microanalysis (EDAX) equipment.

“Point two” evidences the nickel layer presence on the steel $42CrMo_4$ surface and because of its reduced thickness, the substrate signal is very strong giving a 55 at% of iron, 27 at% of oxygen, carbon, silica, manganese and 5 at% of nickel.

The “point one” was selected on the uncovered area of the substrate and the Ni element being totally deficient; the iron element increasing as mass and atomic values to 88 respectively 69 %.

Table 1

Chemical composition of substrate (point 1) and of the thin film PLD layer (point 2) areas represented in figure 2 c).

Chemical element/	Point 1 (substrate)		Point 2 (layer)	
	wt [%]	at [%]	wt [%]	at [%]
Fe	88	69	76	55
O	6	15	11	27
Ni	-	-	7	5
Si	2.5	4	3	4
C	3	10	3	9
Mn	1	0.8	1	0.7

From table 1 can be observe that the oxygen element percentage increase on the thin layer comparing with the substrate but only based on big iron signal decrease (because of the formation of the thin layer occur). In figure 3 Edax analyses spectra on Ni thin layer deposited by PLD technique and on a Ni (of high purity 99.4 %) material are presented to highlight the Ni energy peaks, which are at similar keV energies, fact that shows the presence of the Ni on the thin film obtained through PLD method.

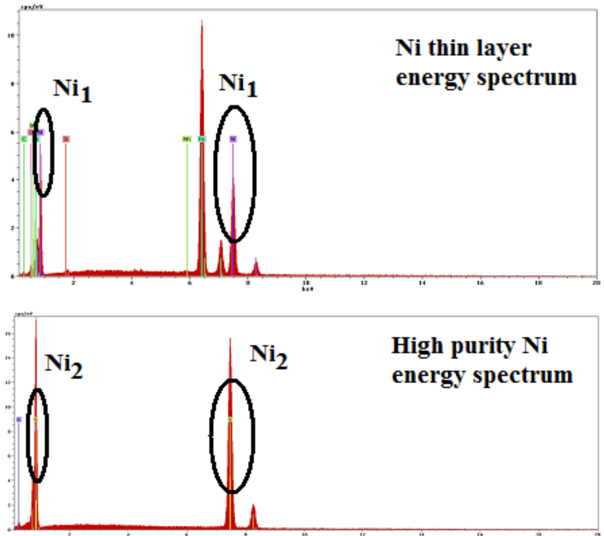


Fig. 3. Chemical elements energy spectra of a thin Ni layer and a high purity Ni bulk

Mapping analysis both of nickel, iron and carbon, most important chemical elements on PLD thin film selected areas have been investigated. Thus, in Fig. 4, the diagram distribution of iron, carbon and nickel elements have been shown over the selected thin films sample area (sample part images represented in the bottom part of the image; the Ni-PLD thin films were obtained at room temperature). As it can see from Fig. 4, the thin Ni-PLD film layer is almost homogenous and has a uniform distribution over the all region selected area. This region has 200 nm in thickness and is quite smooth and the iron signal is reduced from 95 to 75% even if the entire surface is covered with nickel.

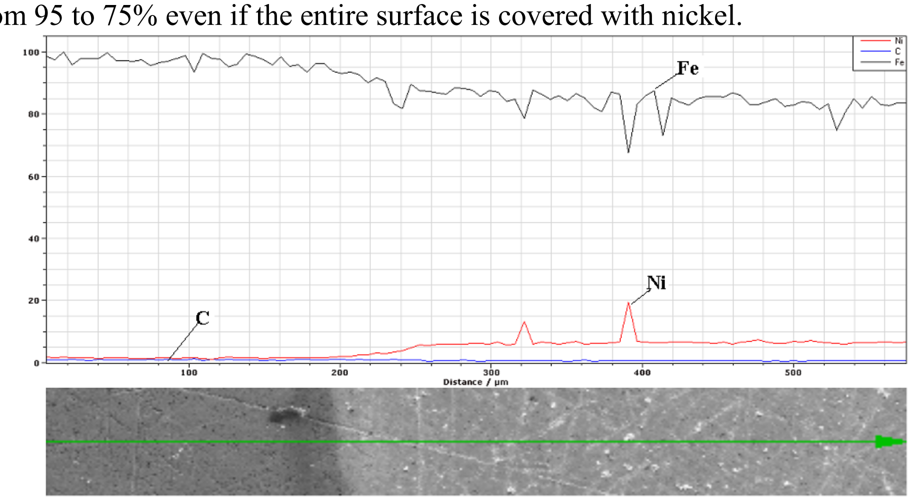


Fig. 4. Iron, carbon and nickel distribution on a selected area from deposited steel with nickel in the cold substrate case

Analyzing that 250 µm area selected on the right part of the Fig. 4, the side with the nickel layer deposited, one can observe from the Ni variation that there is a very smooth layer - chemically speaking – which presents variation only in nickel bigger formations from the surface, the dimension of the layer in thickness is under 200 nm; this fact reduces the iron signal from 95 to 75% even if the entire surface is covered with nickel.

In Fig. 5 the same distributions follow, but in the substrate heated case, the main difference that appears is a modification in iron variation based on carbon agglomeration in formations to almost 99 % C, fact that increases the element signal [11].

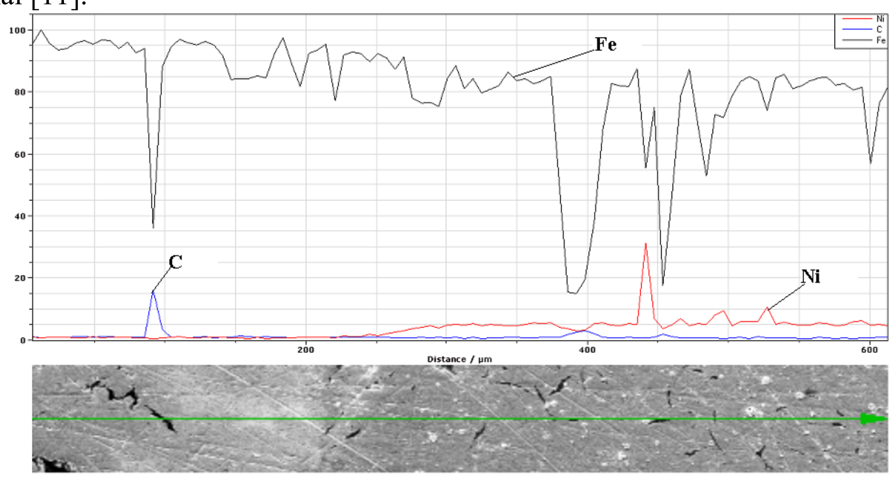
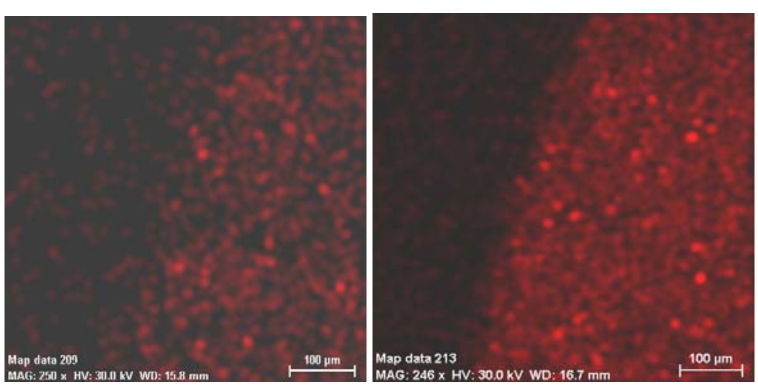


Fig. 5. Fe, C and Ni distributions on the selected target area heated at 400°C temperature.

Fig. 6 presents the Ni concentration mapping in a covered / uncovered border zone on the substrate. One can easily notice the influence of the substrate heating on in a obtaining a more compact, more uniform and better defined deposited layer.



a) b)

Fig. 6. Ni mapping in a covered / uncovered border zone:
a) Substrate at room temperature; b) substrate at 400 °C temperature

4. Conclusions

In this paper we tested the pulsed laser deposition method of nickel on a metallic substrate in vacuum. The deposited layers have been subsequently investigated by SEM and EDAX techniques. These studies indicated a clear effect of the substrate heating in obtaining smoother nanoscale films. However, some spherical droplets with sizes in the range of 0.1–0.2 μm and also a few larger well contoured droplets with dimensions of 0.3–0.5 μm have been obtained. The formation of large droplets can be influenced by the physical properties of the target and substrate, but they may also depend on the plasma plume dynamics between target and substrate. In this frame, further spectral and electrical plasma plume investigations can provide valuable insight [12, 13].

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