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MODIFICATION OF SURFACE PROPERTIES BY LASER CLADDING WITH Ni–Cr–B–Fe–Al ALLOY

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ABSTRACT

The paper is focused on modification of surfaces properties by laser cladding. To follow the corrosion behavior in different media of laser cladding layers made of nickel based alloy Ni - Cr - B - Fe - Al. It was studied using the potentiodynamic method. Elasto – plastic behavior of the assembly base material - deposited layer was monitored by using sliding indentation, in dry friction conditions. It was determined the bearing capacity of surfaces.

KEYWORDS: laser cladding, microstructure, potentiodynamic method, sliding indentation

1. Introduction

Laser cladding is predominantly used to obtain highly resistant layers to wear and corrosion Laser cladding was defined as a process used to melt, with a laser beam on a substrate, a material having different physical and mechanical properties. In order to maintain the original properties of the material deposited, only a very thin layer of the substrate must be melted to obtain the minimum dilution (0.5 - 3%) of the metallurgical bond of the additional material with the substrate.

Both structure and properties depend on the melting temperatures of the support and the material deposited, the chemical composition and they may vary by applying various thermal regimes and granulation of the powder added [1, 2].

Thus it was found that by altering the power density, duration of laser action, feed speed, powder feed speed, granulation and powder density, the complex of physical – mechanical properties within the superficial layers of preset size. Also a good quality of the layers deposited implies lack of cracks, of porosity, good bond with the substrate and a low dilution of the material covering the substrate and minimum roughness.

Corrosion is a real calamity for facilities and equipment in all industry sectors, causing premature removal from service, interruptions, damaging for the production processes and especially the loss of huge amounts of metal.

Thus, in parallel with the development of industry there is concern for the study of corrosion processes and the development of new methods of corrosion protection.

To provide a complete characterization of the laser claddind layers with Ni alloys, corrosion behavior was studied using the potentiodynamic method (polarization curves plotting) for determining the corrosion potential (E_{cor}), maximum corrosion current intensity (I_{cor}) and polarization resistance (R_p).

The potentiodynamic tests aim to plot the polarization curves by varying the current density according to the potential. Proportionality between potential and current density arises from the overlap of the two cathodic and anodic processes, both obeying the logarithmic laws. In a corrosion process, the two reactions occur on the same metal surface, equipotential so that the experimental measurements will give values that correspond to the potential and anodic and cathodic current densities, i.e. mixed values. Mixed potential and corresponding current intensity are also called corrosion potential, and corrosion current density, respectively.

The potentiodynamic method implies modification of the electrode potential continuously at a preset scanning speed. The sliding indentation test is today widely used, esspecially by the coating industry and by coating development laboratories, as well as in research for evaluating the tribological properties of coatings and other hard surfaces. In the sliding indentation test, an indentor (in this case a ball bearing) is pressed by a normal force on the workpiece surface, while being pushed by a force tangential to it.

A material behaviour within an elasto-plastic range depends on: construction parameters (shape, dimensions) and operating parameters (kinematics, energy, environmental) of the contact; the surface layer parameters - microgeometry, metallurgical characteristics (chemical composition, purity, microstructure) and mechanical parameters (hardness, tension) [6].

It was found [7, 8, 9, 10, 11] that the value of the hertzian stress at which plastic deformation occurs in contact increases with the surface hardness. Also, the larger the frictional forces, the lower the plastic deformation where the seizing tendency occurs.

The choice of surface hardening processes, suitable to a certain material, is an important way to increase the bearing capacity of the contacting surface and reduce the tendency of seizing. Thus laser cladding with alloy Ni - Cr - B - Fe - Al constitutes an effective way to increase the surface hardness that directly affects their behavior to plastic deformation.

Characterization of the surface layers can be highlighted by an installation with a point contact sphere-plane which provides a sliding indentation in dry friction conditions. The evolution of the plastic deformation of the material tested when applying various normal forces led to the determination of the bearing capacity.

According to the literature [1, 2, 3, 4] with the surface hardened materials transition from elastic to plastic deformation is continuous, so that the strain at the beginning of the plastic deformation (δ_p= 0.1 to 10 μm) can be expressed with an acceptable approximation by Hertz's equations.

For the point contact sphere-plane, the features are:

- Hertzian pressure:

$$P_{max} = \left(\frac{6F \cdot E^{*2}}{\pi^3 \cdot R^2} \right)^{1/3} \tag{1}$$

where: F – normal force, E^* - reduced elasticity module, R – indentor radius, P_{max} max pressure at Hertzian contact

$$E^* = \frac{10^5}{0.85}, \quad \frac{1}{E^*} = \frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2} \tag{2}$$

where: ν_1 , ν_2 - Poisson coefficients, E_1, E_2, elasticity modules of the indentor and surface being tested.

The present study is focused on the corrosion behavior in different media of laser cladding layers made of nickel based alloy Ni - Cr - B - Fe - Al, and of the elasto – plastic behavior of some laser cladded samples with alloys of Ni - Cr - B - Fe - Al (code A and B) and the base material (code Mb) made from steel improved 1C45, SR EN 10083-1: 2007.

There were determined the pressures where the elasto – plastic transition is initiated for the three samples analyzed.

2. Experimental conditions

„Alliages Speciaux 7569 Alliajes Frittes, France” powder, with the following chemical composition 8.9%Cr; 4.5%Fe; 5.1%B; 2.4%Al; 0.6%Cu; rest Ni [5, 6], was used for cladding.

Grain fractions in the 80-90μm range were screened separately in order to be used as addition material. The powder had a spherical shape which provided a fluid flow of addition material through the injection system. Before the addition material feeding into the system tank, the power was dried at 110^{o}C temperature for 15 minutes.

Cladding was performed on a 1C45, SR EN 10083-1:1994 steel sample in refined conditions.

Lab experiments were performed by a Laser GT 1400W (Romania) type CO_2 continuous wave installation with x-y-z coordinate running table and computer programmed running, provided by powder injection system on the laser melt surface, which exists at S.C. UZINSIDER ENGINEERING Galaţi.

For laser cladding a 1.8 mm diameter laser beam was used, with 1150 W power, 7.5 mm/s sweeping speed, which cladded parallel overlapped stripes with 1.5 mm cross travel pass. Addition material flow was 105 mg/s. Final thickness of the cladding layer was 2.07 mm resulted by 4 layers overlapping.

Determining susceptibility to corrosion was achieved at room temperature (24°C) using a Voltalab 21 system connected to a computer using a VoltaMaster 4 software for exprimental data processing.

The potentiostate is connected to the electrochemical cell by three electrodes: reference electrode, auxiliary electrode and working electrode. In the experimental determinations, as reference electrode was used a saturated calomel electrode Hg/Hg_2Cl_2/saturated K_2SO_4, (SCE=+241 mV/EHS), and as auxiliary electrode (counterelectrod) a platinum electrode.

The working electrode, that is the laser cladding samples on nickel base has been previously prepared, polished, made shiny and degreased in accordance with ASTM G1 standard. To study only the behavior of the laser deposited layers non treated areas were covered with a protective lacquer. Also, the surface submerged into solution was measured and data were entered in the program.

Thus the polarization curves were obtained by means of which the corrosion behavior of Ni based alloy by laser cladding was assessed. Elasto – plastic behavior of the assembly base material - deposited layer was monitored by using sliding indentation, in dry friction conditions. There were determined the pressures where the elasto – plastic transition is initiated for the three samples analyzed.

3. Experimental results and discussions

Corrosion testing of each sample began with monitoring the corrosion potential (open potential circuit - OCP) after immersing samples in the test solution until it reached a stationary value.

Table 1 shows the results of corrosion of the laser deposited layers on Ni alloy base.

Table 1. *Results of corrosion of the laser deposited layers on Ni alloy base.*

Corrosion environ-ment	**Parameters achieved**							
	E (i=0)	**R_p**	**I_{cor}**	**B_a**	**B_c**	**Corossion**	**Initial mass**	**Final mass**
	[mV]	[Ω.cm^2]	[mA/cm^2]	[mV/dec.]		[mm/year]	[g]	
NaOH, 1N	-342.3	245.66	0.03821	34.9	- 56.8	0.01304	2.7709	2.7687
NaCl, 3%	-965.7	315.55	0.22932	438	- 269	0.07826	2.9564	2.9527
HCl, 1N	-505.3	24.65	0.45619	55.70	- 48.4	0.15569	2.8068	2.8016
H_2SO_4 1N	-472.8	6.18	2.066408	82.5	- 45.7	0.70525	2.7687	2.7417

Note: E – corrosion potential; Rp – polarization rezistance; Icor – intensity of corrosion current; Ba, Bc – correspond to constants Tafel for anodic and cathodic reaction.

From Table 1 it may be noted that laser cladding layer based on Ni alloy is corrosion resistant in environment 1N NaOH and H_2SO_4 1N presents the lowest resistance therefore it causes the highest corrosion rate. The corrosion caused by Cl^- ions is weaker than that caused by SO_4^{2} ions therefore in these cases a lower rate of corrosion is reported. Polarization resistance R_p is representative for the degree of protection of layer deposited on the the steel surface. The higher the polarization resistance, the more resistant the alloy and lower the I_{cor}. Thus we can see that the polarization resistance is higher in NaOH and NaCl environments and I_{cor} is lower which indicates that coating with Ni based alloy resists corrosion in these environments, a fact also visible from the values of the corrosion rate.

Corrosion potential and corrosion current intensity characterize the general corrosion resistance. The more electropositive corrosion potential values and the lower the I_{cor} values of the corrosion current intensity, the higher the overall corrosion resistance. We can therefore conclude that the deposit features good behavior in NaOH environment.

The polarization curves provide additional information on the corrosion behavior of these laser deposited layers.

Fig. 1 shows the Tafel curve resulting from corrosion in NaOH 1N.

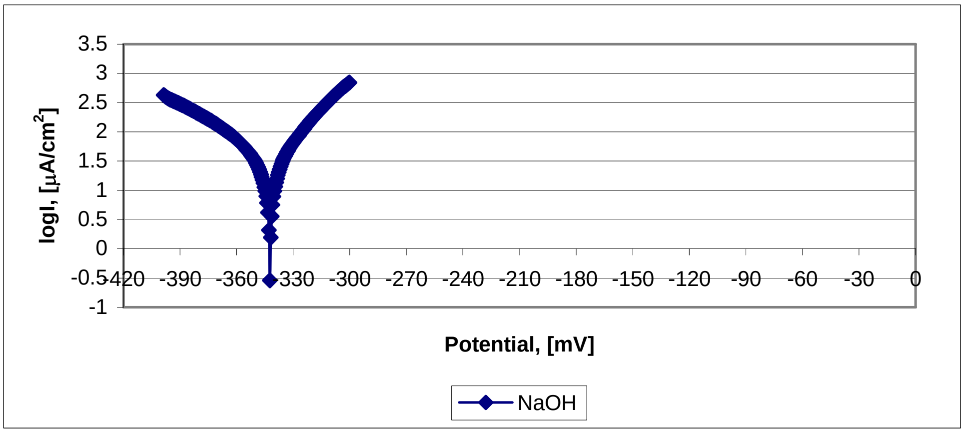


Fig. 1. *The Tafel curve - NaOH, 1N environment*

Analyzing Fig. 1 we can see that in this solution a general corrosion may occur. On the alloy surface no protective passive layer is formed.

Fig. 2 shows the Tafel curve resulting from corrosion in NaCl 3%. Fig. 2 shows that the nickel based deposition resists corrosion on a wide range of potential. This may undergo localized corrosion (pitting) caused by the chloride ions.

Fig. 3 illustrates the Tafel curve resulting from corrosion in HCl 1N. Looking at Fig. 3 it can be noticed the presence of widespread high-speed corrosion can be noticed.

Fig. 4 illustrates the Tafel curve resulting from corrosion in H_2SO_4 1N. Fig. 4 reveals a general corrosion. Analyzing Figures. 1, 2, 3, 4 it may be noticed that the laser cladding with Ni-alloy layer is corrosion resistant in environment 1N NaOH and in H_2SO_4 1N environment features the lowest resistance.

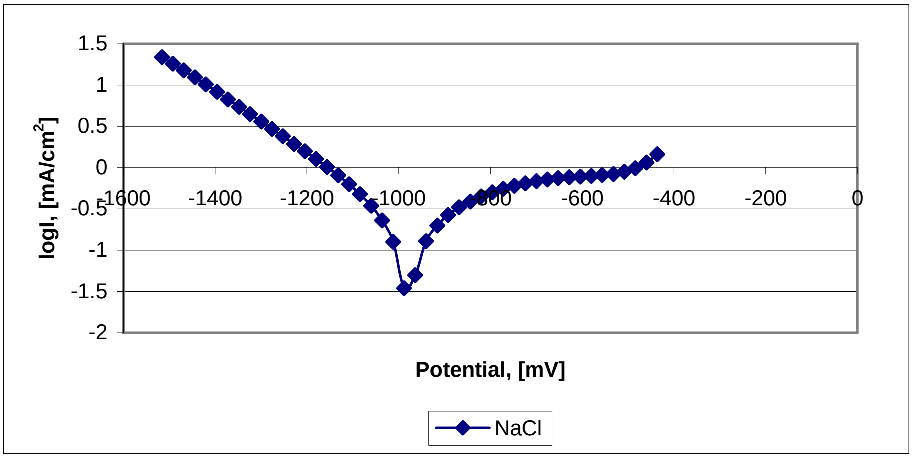


Fig. 2. *Tafel curve - NaCl, 3% environment*

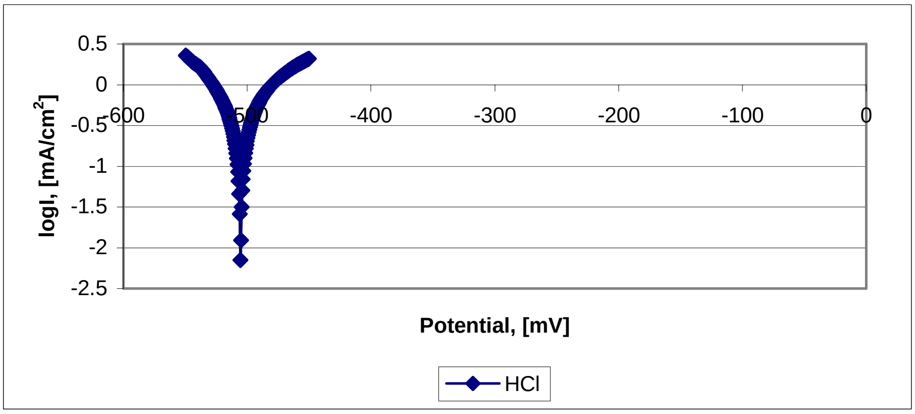


Fig. 3. *Tafel curve - HCl, 1N environment*

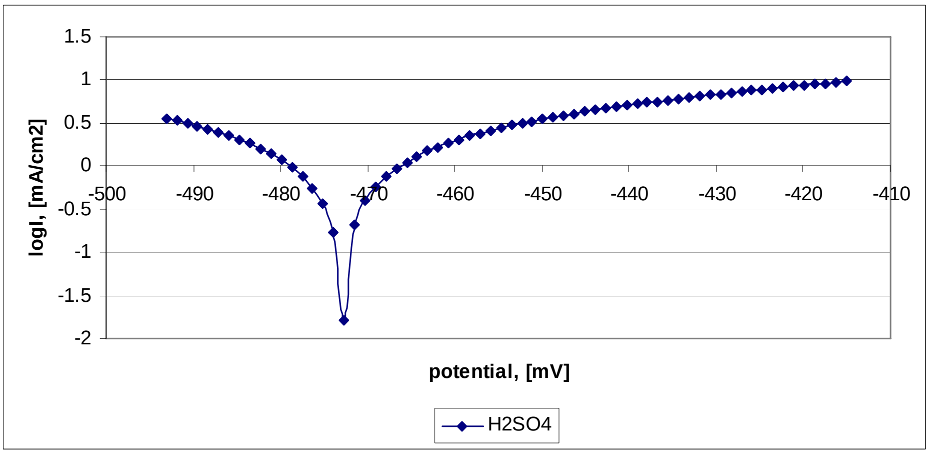


Fig. 4. *Tafel curve - H_2SO_4, 1N environment*

Porosity and inclusions may play an important role on the corrosion behavior when they are frequent and high enough. Inclusions facilitate formation of micro-corrosion cells on the surface of the sample which worsens its resistance to corrosion. If inclusions are high enough local corrosion will occur. Influence of porosity on the layer corrosion resistance consists of a long process and their effect at the beginning of corrosion is not important until porosities are not penetrating. The presence of porosity can weaken the cohesion forces within the layer, resulting in a greater mass loss under the action of the electrolyte. In principle, the lower the number of defects on the surface, the greater its resistance to corrosion. Data presented in the literature [3, 4, 5] indicate that corrosion of the Ni-base alloy coating occurs first around the particles that were not melted during deposition and around defects such as pores, inclusions and micro cracks, being followed by its propagation along the paths formed by pores, micro cracks or lamellar structure, further causing exfoliation.

Adjusting the coating parameters to reduce the electrochemical non uniformities or the pore coating may increase the layer resistance to corrosion.

Microstructures of the mark sample and the layers subject to corrosion layers are presented in Figures 5, 6, 7, 8, 9.

Fig. 5, 6, 7, 8, 9 indicate the presence of a columnar dendritic fine structures of the deposit containing nickel-based solid solution and Eutectic colonies of borides (NiB, Ni_2B, CrB, Cr_3B_4 and FeB), the main hardening phase being CrB.

The presence of corrosion at the boundary of the grain could also be observed in some areas.

To determine the bearing capacity were made series of marks on each specimen. For this type of testing, the mobile tribo-element (ball) is subject to two forces: one normal on the fixed tribo-element and one tangential to its surface. Initially the normal force is applied, the ball making a plastic deformation, and then the tangential one resulting a trace in the form of an elongated groove.

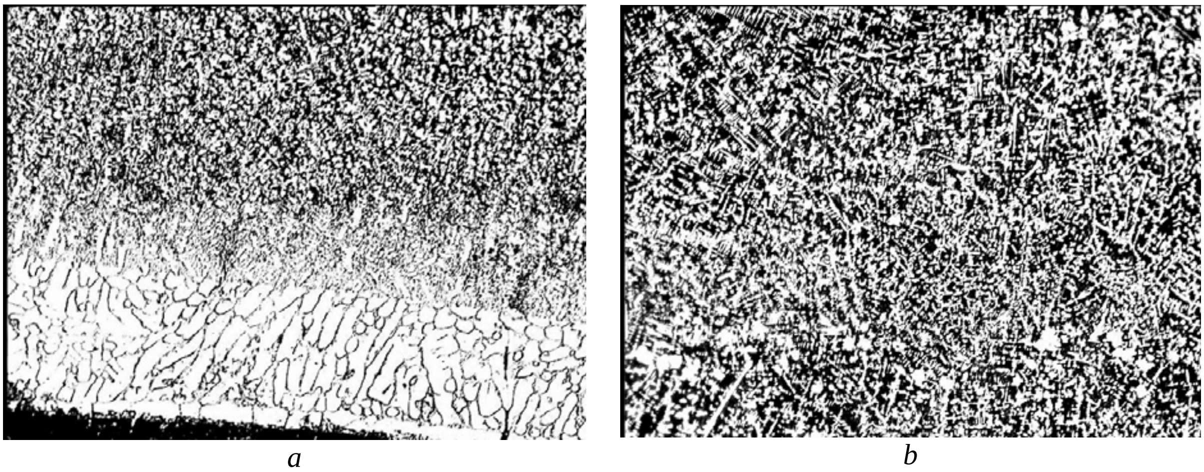

a *b*

Fig. 5. *Microstructure of the laser cladding layer on Ni based alloy, mark sample; a- layer base, b-layer cross section (x500). Electrolyte attack, solution 50%* HNO_3

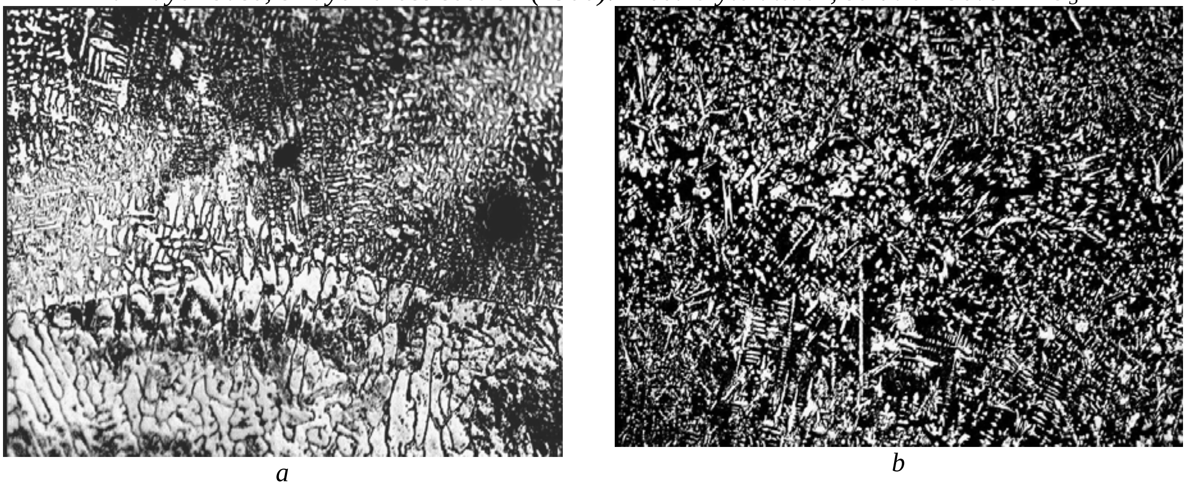
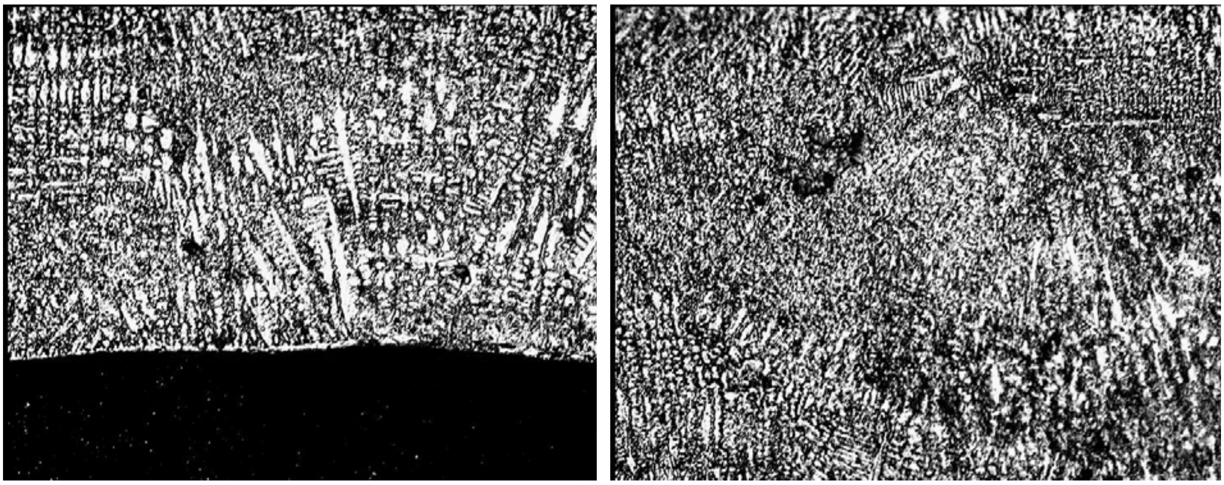
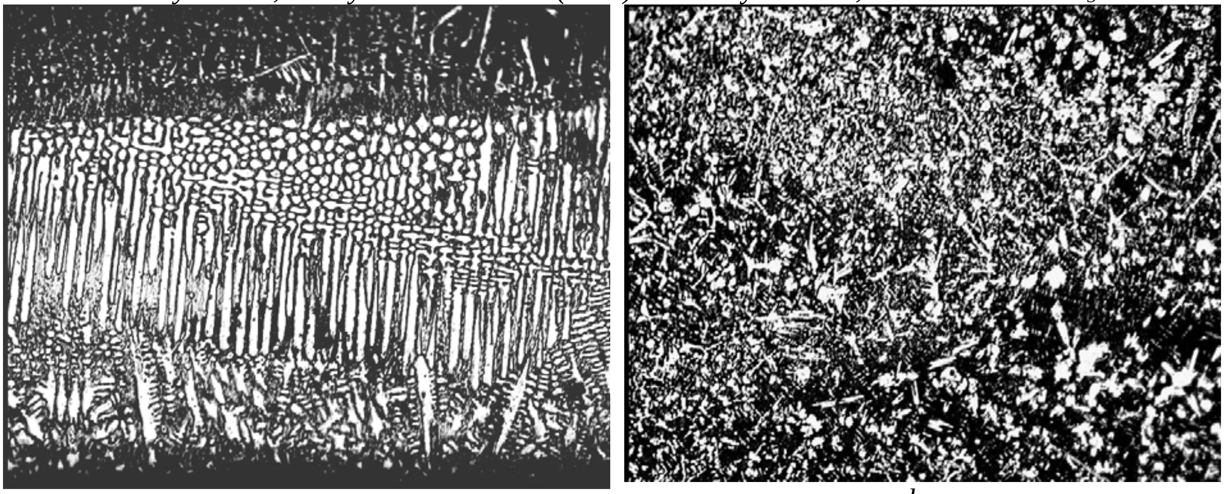

a *b*

Fig. 6. *Microstructure of the laser cladding layer, subjected to corrosion in NaOH, 1N; a - layer base, b - layer cross-section (x500). Electrolyte attack, solution 50%* HNO_3



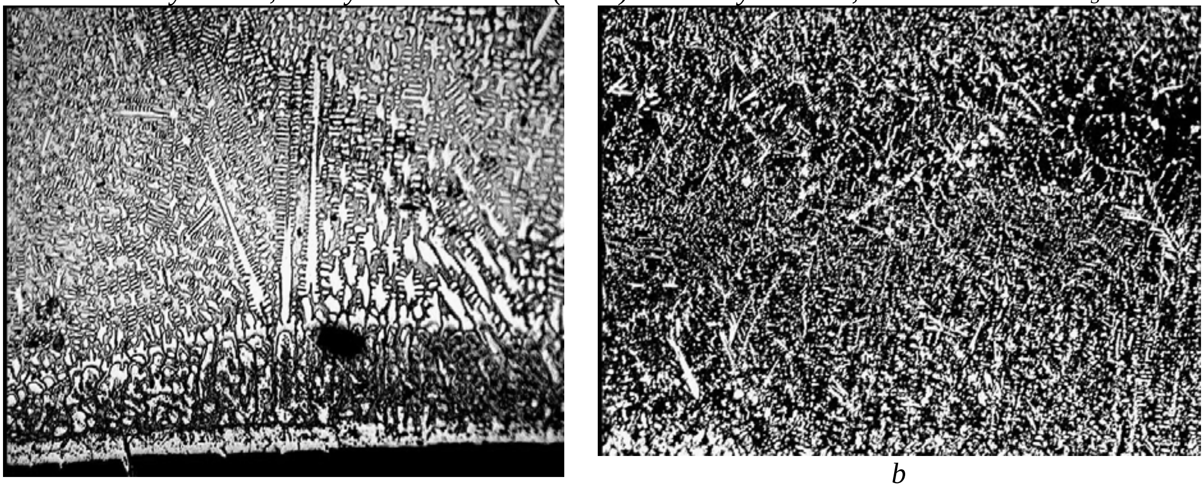
a b

Fig. 7. *Microstructure of the laser cladding layer, subjected to corrosion in NaCl, 3%; a - layer base, b - layer cross-section (x500). Electrolyte attack, solution 50%*HNO_3



a b

Fig. 8. *Microstructure of the laser cladding layer, subjected to corrosion in HCl, 1N; a - layer base, b - layer cross-section (x500). Electrolyte attack, solution 50%* HNO_3



a b

Fig. 9. *Microstructure of the laser cladding layer, subjected to corrosion in* H_2SO_4*, 1N; a - layer base, b - layer cross-section (x500). Electrolyte attack, solution 50%* HNO_3

The indentor speed is 0.2 mm/s, diameter ϕ 12.675mm, is made from Rul 1 (SR EN ISO 683-17:2002), hardened and annealing steel. After each test, the ball bearing has been replaced and degreased. Before carrying out any test, the sample surfaces have been degreased with alcohol, to provide conditions for dry friction. The normal forces F_N, used for indentation were: F_1 = 2.886kN; F_2 = 4.330kN; F_3 = 5.773kN; F_4 = 7.216kN. Roughness Ra, as measured by a roughness gauge Surtronic 3+, is Ra ≈0.210μm for all surfaces. Max. pressures obtained by relation (1) for the normal forces used are given in Table 2. The graphical representation of the variation of plastic deformation of the depth profile depending on Hertzian pressure P_{max} in Figure 10 shows the higher behavior of laser deposited layers to plastic deformation.

For the experimental data obtained, there were determined regression curves showing the dependence of plastic deformation given by the Hertz pressure under dimensionless form on the bearing capacity values for $\delta_p/R < 0.001$, where δ_p is the trace depth, and R the indentor radius.

Table 3 provides the regression coefficients for the materials investigated which allowed for the determination of the max pressure when elasto-plastic transition is initiated.

***Table 2.** Maximum pressure obtained for the normal strains applied*

P_{max}	**Normal force, F_N**
[MPa]	[kN]
5773.529	2.886
6609.550	4.330
7274.611	5.773
7836.247	7.216

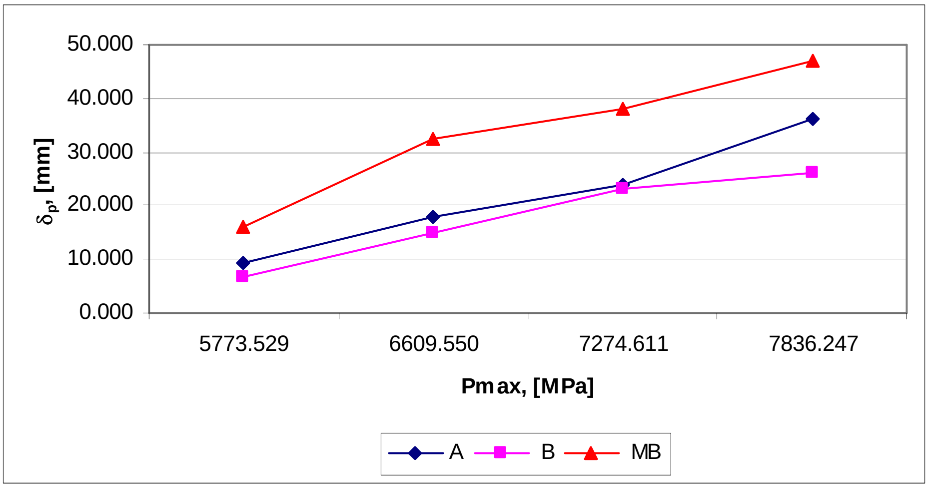


***Fig. 10.** Variation of plastic deformation of the depth profile depending on Hertzian pressure*

***Table 3.** Determination of the max pressure when elasto-plastic transition is initiated*

Sample code	**Function**	**Coefficients**				**P_{max}** [MPa]
		a	**b**	**c**	**d**	
MB	$y=(a+bx)/(1+cx+dx^2)$	185896.2	-73.287	30643.098	3.083	2536.56
A	$y=(a+bx)/(1+cx+dx^2)$	101921.62	-20.880	-5772.622	0.560	4881.09
B	$y=(a+bx)/(1+cx+dx^2)$	1357861.8	-257.846	-29288.481	1.174	5266.16

Thus the graphical representation of the relative plastic deformation variation δ_p/R according to the hertzian pressure P_{max} in Figure 11 shows the maximum bearing capacity of the laser cladded layers.

Analyzing Figure 11 it appears that plastic deformation is initiated at 4881.09MPa maximum pressure for the sample code A, to 5266.16MPa for sample code B (which features higher hardness) and to 2536.56MPa for base material (MB).

Thus the bearing capacity is increased by over 100% in laser cladding. The efficiency of the laser cladding in increasing the bearing capacity and the extension of elasticity range of steel 1C45 becomes obvious.

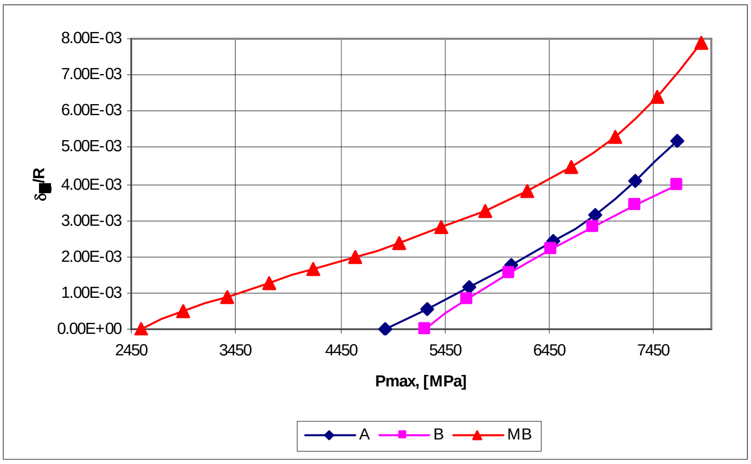


Fig. 11. *Variation of the relative plastic deformation acc.to Hertz pressure for the samples code A, B, MB*

4. Conclusions

By multi-layer deposition with beam laser in continuous wave it can be achieved thick compact layers of nickel alloy resistant to wear and corrosion, from the Ni-Cr-B-Fe-Al system with good adherence to the substrate by a low dilution layer.

The research on the behavior of laser deposited layers with the nickel alloy base in different corrosive environments revealed that the layer is corrosion resistant in environment 1N NaOH, and 3% NaCl, while in H_2SO_4 1N environmental it features the lowest resistance and the highest corrosion rate. The corrosion caused by Cl^- ions is weaker than that caused by $SO4^{2-}$ ions and the rate of corrosion is lower.

It was noted that the presence of porosity and inclusions affect corrosion behavior. Thus adjusting the deposit parameters to reduce or eliminate electrochemical non uniformities or pores may increase the layer corrosion resistance.

Experimental research on sliding indentation test revealed the following conclusions:

- ❖ laser cladding is an efficient way to move the elasto-plastic transition at higher contact pressures;
- ❖ with increased layer hardness and normal force, the friction coefficient decreases, and the material can be used at higher pressures;
- ❖ with increase layer hardness the trace depth is reduced; plastic deformation is initiated at the maximum pressure of 4881.09 MPa with sample code A, to 5266.16 MPa for the sample code B (which has higher hardness) and to 2536.56 MPa for the base material (MB). Thus the bearing capacity is increased by 92.42% at the sample code A and to 107.61% for sample code B, as compared with the sample code MB.

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