Enhancement of surface properties of steel samples using new technique for electroless nickel plating

Verbesserung der Oberflächeneigenschaften von Stahlproben durch neue Technik für stromlose Vernickelung

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***Abstract* —** This study is focused on the investigation of the possibilities for materials surface properties enhancement by electrolees nickel plating method. Substrates of steel 17CrNiMo6 are used for the manufacture of the specimens. Electroless method EFTTOM-NICKEL is applied for the development of an innovative technology for production of as plated nickel and composite Nickel coatings. Detonation nanodiamond particles (ND) are used as a strengthening material for production of composite nickel coatings. Suspension of ND is added directly to the electroless bath using a suitable surfactant to achieve well-dispersed particles in the bath and to facilitate their embodiment and equal distribution in the coating. The influence of ND particles on the coatings mechanical and physical properties is confirmed by the results achieved carrying out as morphology and microstructure observations by optical metallography and scanning electron microscopy (SEM) and also wear and nano indentation tests. The influence of the thermal treatment of the obtained coatings on the above mentioned properties is examined.

***Zusammenfassung* —** Die vorgestellte Arbeit untersucht die Möglichkeiten zur Verbesserung der Oberflächeneigenschaften der Materialien mittels der Methode der stromlosen Vernickelung. Die Testproben sind aus Stahl 17CrNiMo6 gefertigt. Eine innovative Technologie zur Herstellung von Nickel- und Verbund-Nickel-Beschichtungen ist mit der EFTTOM-NICKEL-Methode entwickelt. Nano-Diamantpartikel (ND), die durch das Detonationsverfahren erhalten werden, sind als Verstärkungsmaterial für die Herstellung von Verbund-Nickel-Beschichtungen verwendet. ND-Salzgel wird direkt zu der Beschichtungslösung unter Verwendung eines geeigneten Tensids zugemischt, um die Partikel in der Wanne besser zu dispergieren und ihre Infiltrierung und gleichmäßige Verteilung in der Beschichtung zu erleichtern. Der Einfluss von ND-Partikeln auf die mechanischen und physikalischen Eigenschaften der Beschichtungen wird von den erhaltenen Ergebnissen bei der Beobachtung der Morphologie und der Mikrostruktur der Beschichtungen durch optische Metallographie und Rasterelektronen-mikroskopie (SEM), sowie von den durchgeführten Verschleiß- und Nanoindentationsversuchen, bestätigt. Ebenfalls ist auch der Einfluss der thermischen Behandlung der erhaltenen Beschichtungen auf die vorgenannten Eigenschaften untersucht.

I. Introduction

Surface finishing of the materials is an opportunity for obtaining new improved properties by surface modification. One preferred, simple and ecologically friendly method is electroless plating of different materials. Many advantages between all of these methods possess electroless nickel plating. Electroless nickel plating is a form of alloy treatment designed to produce consistent, even thickness across component surfaces with zero or compressive stress without an electrical current during the process, characterized by increase resistance and hardness in a metal or plastic, superior corrosion resistance and solder ability [1]. Incorporation of distinct strengthening particles into the deposit to impart a specific property in the electroless nickel coatings (EN) forms composite coatings. Theoretically, almost any type of particle could be co-deposited, as long as it could withstand the conditions within an EN bath, and if it is of the appropriate size [2]. Electroless nanometer composite coatings where nano-particulates used as reinforcing phase are important due to their excellent performance. The incorporation of nano-sized particles within Ni–P autocatalytic coatings greatly improved their properties and added entirely new features to the coatings performance, which enhance their applicability in different industries such as electronic components and computers, general mechanics, automobile, paper mills, textile and food [3]. Many authors prove the improved coatings properties in the presence of nanodiamond in the bath [4 – 8]. But the opinions about the action mechanism of nanoparticles are controversial. Some of the researches believe the properties improvement is due to the nanodiamond incorporation into the Ni-P matrix, while others attribute this improvement to the change of the reaction conditions, which results in the coatings morphology [9].

The mechanical properties mainly depend on the phosphorus/boron content in the deposit. The coatings normally have high strength, limited ductility, and high modulus of elasticity. The ultimate tensile strength of commercial coatings exceeds 700 MPa and allows the coatings to withstand loading without damage [10]. The structural changes during heat treatment at temperatures above 220° C cause a volumetric shrinkage of electroless nickel deposits of up to 6%. This increases tensile stress and reduces compressive stress in the coating. High levels of internal stress also reduce the ductility of the coating [11]. However, heat treatment has little effect on the ductility [12].

The aim of the present work is to investigate the influence of nano additives of ND to the plating bath and the heat treatment of the obtained coatings on the microstructure and physical and mechanical properties of electroless nickel coatings, plated on the 17CrNiMo6 steel samples. It is supposed the ND shape and particles size (4÷6 nm), as their specific nature and high surface activity ensure higher density of the coatings and others functional qualities.

II. Materials and Investigation Methods

17CrNiMo6 is used for a production of the samples. The composition of the 17CrNiMo6 steel is shown in Table 1. The form of the samples is consistent with the requirement of the respective test method.

Nano sized diamond particles (ND) obtained by detonation method are used as strengthening particles. ND production is performed by an optimized technology in order to achieve high quality product, suitable for use in the electroless deposition of composite coatings [13].

The physical properties of ND are shown in Table 2.

The coatings are produced by advanced technology based on EFTTOM-NICKEL method [14], developed at SRTI-BAS. The strengthening particles are used in a suspension. The formation of the particles aggregates is avoided by a deactivation of the particles surface. The suspension preparation is performed in an environment of suitable surfactants as follows: to 10 ml distilled water the proper quantity of the nano sized powder is added and mixed for 20 minutes with 0,02g of surfactant (in this case sodium lauryl sulphate) before the plating process. The plating process is performed in an electroless nickel plating bath without and with addition of strengthening particles. Two types of coatings are made:

- Electroless nickel coating (Ni)
- Composite nickel with nanodiamond coating (Ni/Ni+ND) in the following technological mode:
  - pH = 4.6 ÷ 4.7
  - T = (92 ÷ 95) ºC
  - Coating time = 15 min (for Ni coating); 10 min (for Ni+ND coating)
  - Optimal uses of the solution 7 ÷ 8 times per hour
  - Concentration of the strengthening particles - 5 g/l .

The preparation of nickel coating takes place through a one-step process, whereas the composite coatings of Ni/Ni+ND are obtained by a two-stage process in which two layers are formed:

- Electroless nickel layer, obtained in a plating bath by "EFTTOM-NICKEL" Method
- Composite nanostructured layer Ni with strengthening particles, obtained in the same bath with nano sized additives concentration of 5 g/l.

Chemical process of nickelization is:

$$3NaH_2PO_2+3H_2O+NiSO4 \rightarrow 3NaH_2PO_3+H_2SO_4+2H_2+Ni$$

The coating composition is shown in Table 3.

TABLE I. Chemical composition of 17CrNiMo6 steel

Composition	C	Si	Mn	Cr	Mo	V	Ni
(%)	0,18	0,20	0,70	1,65	0,30	-	1,55

TABLE II. Physical properties of ND

Strengthening particles	Average size	Specific surface area (m²/g)
ND	2-4 nm	330-400

TABLE III. Composition, heat treatment, thickness and wear of the coatings

Number of the sample	Coating		Thick-ness, δ (µm)	Wear (g)
	Composition	*Heat treatment*		
1	Ni	-	8.7	7.5
2	Ni	290^{o}C,6h	8.7	5.8
3	Ni/Ni+ND	-	9.3	8.0
4	Ni/Ni+ND	290^{o}C,6h	7.3	4.8

Part of the sodium hypophosphite is undergone to reduction process with phosphorous formation:

$$NaH_2PO_2+H \rightarrow H_2O+NaOH+P$$

Hereby the coating obtained is amorphous alloy consists of nickel and phosphorous.

This layer works as a snubber in a two stage process, enhancing the coating ability to take a contact load and improves the adhesion between the sample base and the coating.

After plating the coatings 2 and 4 are undergone to a heat treatment at 290^{o}C for 6 hours (Table 3) for the coatings' adhesion enhancement and hardness increase.

The below described methods are used to characterize the coatings.

The microstructure is observed by means of an optical metallographic microscope Neophot 32. The samples are treated with 3 % HNO_3 - C_2H_5OH solution before testing. The data for the coatings thickness are also received (Table 3).

The wear of the coatings are tested by friction wear tests performed under 50MPa loading conditions – in accordance with the Polish Standard PN-83/H-04302 (Table 3).

Investigation of the hardness and elasticity modulus of the produced coatings and of the substrate is performed by nanotester FISCHERSCOPE® H100 (Table 4). The data presented for each of the samples are received by defining of the average value of 5 measurements with 95% convergence. The tests are carried out under loading of F=50mN (the penetrating of the indenters is less than 10% of the coating thickness to avoid the substrate influence on the results. The steel substrate is measured under loading F=1000mN.

The results for HU universal hardness (the indenter is in the maximum loaded position taking into account the elastic and plastic deformation at the measuring location (Table 4).

H_{plast}. – plastic hardness (indenter is in the final unloaded position taking into account the residual plastic deformation);

h – maximum depth of penetration of the indenter top under maximum loading during test;

E* – approximate module of elasticity (Jung module). The real E is evaluated by the formula E*= E/(1-v2),

where v is a sliding coefficient (v=0,30, for the steel substrate, but for Ni coatings - 0,29);

W_{total} – total energy spent for an elastic and plastic deformation of the coating during indenter penetration;

W_{total}l = Wr + We , where Wr % – plastic part of W total ; We % – elastic part of W_{total};

HV - recalculated plastic hardness H_{plast}. into Vickers hardness.

TABLE IV. MECHANICAL CHARACTERISTICS OF THE COATINGS

Number of the sample	HU (MPa)	H_{plast}. (MPa)	h (µm)	E* (GPa)	E (GPa)	W_{total} (nJ)	W_r (%)	HV (kg/mm^2)
Coatings data, Load F = 50 mN								
1	6625	7814	0.534	146	134	10.80	66.18	738
2	10267	13117	0.429	185	169	8.90	54.00	1238
3	6670	7968	0.533	143	131	10.80	66.00	752
4	11253	14453	0.410	198	181	8.31	53.59	1364
Substrate data F = 1000 mN								
8	4479	6159	2.478	170	155	10.45	77.25	581

III. RESULTS AND DISCUSSIONS

Steel 17CrNiMo6 samples are normalized before plating. Optical microscope observations reveal all of the tested samples as a white strip, following surface relief and filling the defects such as micro pores and micro cracks (Fig. 1, 2). Samples 2 and 4 are undergone to heat treatment at 290^{o}C for 6 hours after plating. No changes in the substrate microstructure are found. The coatings thickness measurement shows results in the range of 5, 3 ÷ 9, 3 µm (Table 3).

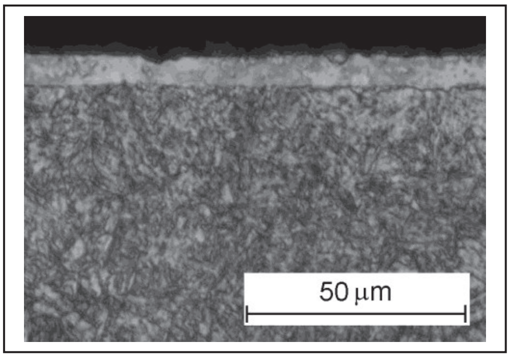

Fig. 1. Ni- coating microstructure after heat treatment at 290^{o}C, 6h (sample 2)

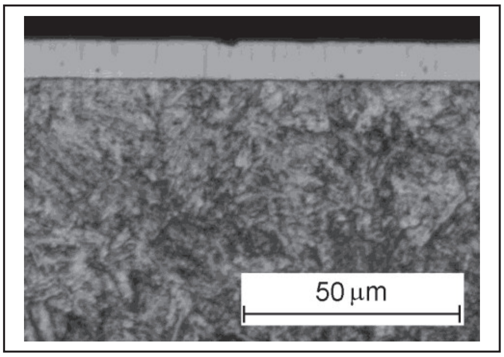

Fig. 2. Ni/Ni+ND coating microstructure after heat treatment at 290^{o}C, 6h (sample 4)

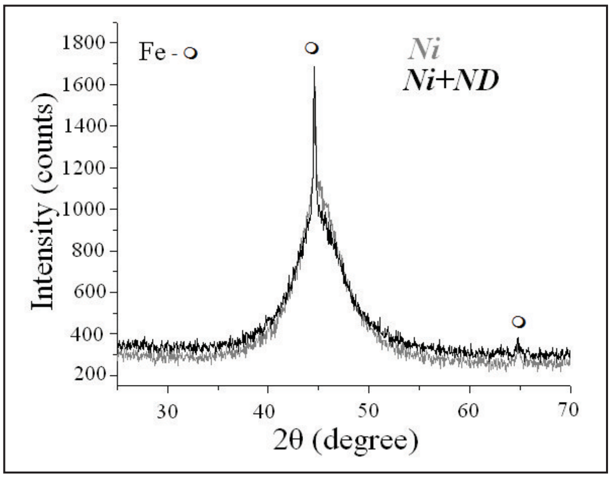

Fig. 3. X– ray diffraction pattern of samples 1 (Ni coating) and 3 (Ni/Ni+ ND coating) in an as-plated condition.

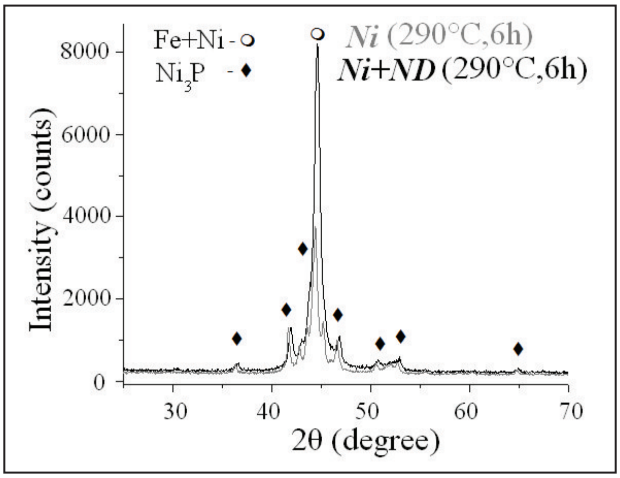

Fig. 4. X– ray diffraction pattern of samples 2 (Ni coating) and 4 (Ni/Ni + ND coating) after heat treatment at 290°C, 6h.

X-Ray analysis shows an amorphous structure for Ni and Ni/Ni+ND coatings in as-plated condition (samples 1 and 3). Heat treatment at 290^{o}C, 6h of the coated samples (samples 2 and 4) initiates a crystallization process in the coating and the qualitative X-Ray analysis of the last mentioned samples proves the presence of the crystalline phase of Ni_3P and Ni in the coatings' structure (Fig. 3, 4) [15].

The tests performed by nano tester FISCHERSCOPE H100 allow receiving data for the hardness and elasticity module of the substrate and of the coatings (Table 4).

The increase of the universal hardness HU from 6625 for nickel coatings to 6670 MPa for composite nickel coatings is received.

The heat treatment of the coatings at 290^{o}C, 6h leads to the increase of the universal hardness HU to 10267 MPa for Ni coatings and to 11253 MPa for composite Ni/Ni+ND coatings (Fig. 5).

H_{plast}. defined on the base of the residual plastic deformation shows higher value for the composite coatings with addition of ND respectively 7968 compared to the Ni coatings (namely 7814). The heat treatment of the coatings at290^{o}C, 6h leads to the increase of the H_{plast}. to 13117 for Ni coatings and to 14453 for composite Ni/Ni+ND coatings.

The higher universal and H_{plast} hardness achieved after heat treatment at 290^{o}C, 6h could be explained with the structure change and with the dispersed crystalline phase formation of Ni_3P [15].

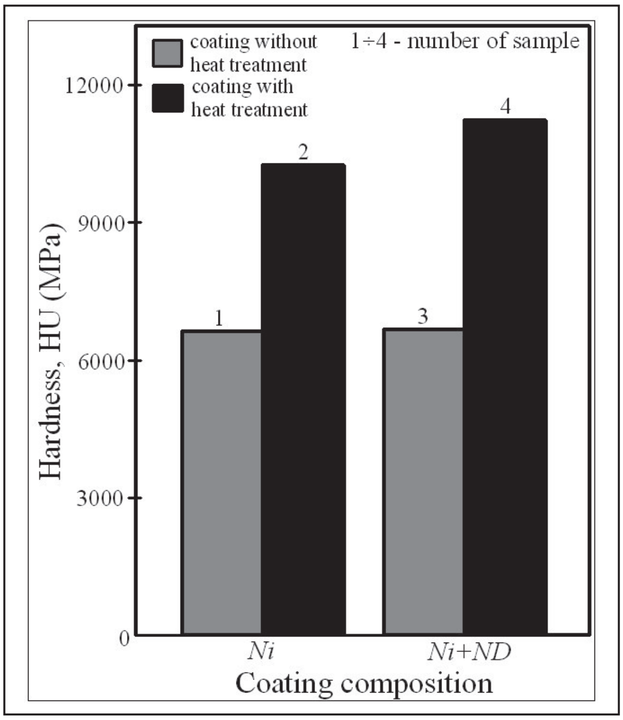

Fig. 5. Universal coatings harness *HU*

The higher hardness of Ni / Ni + ND coating compared to the Ni coating is due to addition of the high hard nano sized particles of ND.

The universal and H_{plast} hardness are higher for all of the coatings compared to this one of the substrates.

The substrate material possess higher approximate module of elasticity E* than this one of the coatings in as plated conditions. While the coatings heat treatment results in higher module values than those of the substrate material.

For the both coatings of Ni and Ni / Ni + ND the heat treatment leads to a significant increase in E*.

The low ductility is due to the amorphous structures of the coatings in as plated condition that essentially precludes plastic deformation. The deformation is therefore mostly elastic until fracture occurs [16].

The W_{total} – total energy spent for an elastic and plastic deformation of the coating during indenter penetration and W_r % – plastic part of W total are in correlation with the results achieved for the approximate module of elasticity E*.

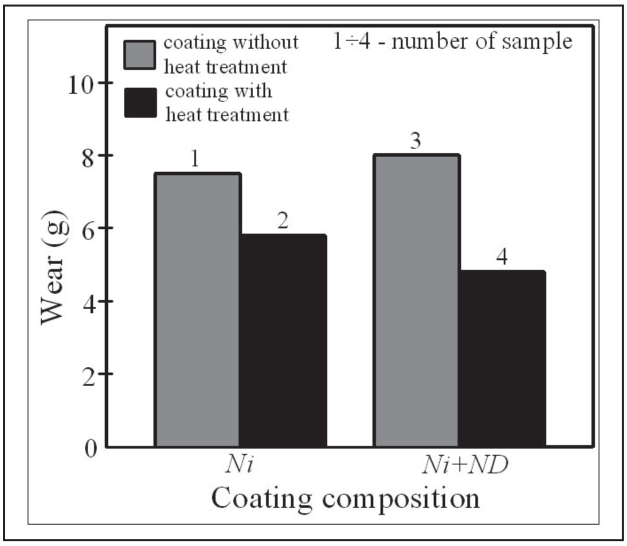

Fig. 6. Wear of the coatings Ni и Ni/Ni+ND

The performed wear test determines the influence of the added particles of nano sized ND on the coatings wear (Table 1, Fig. 6). The correlation between hardness and wear of the samples with coating of Ni and Ni/Ni+ND after heat treatment at 290^{o}C, 6h is established (samples 2 and 4).

IV. Conclusions

Nanosized diamond additions to the plating bath for electroless nickel plating possess a modifying effect on the coatings microstructure, which influences on their physico-mechanical properties. An additional impact has also the coatings heat treatment at 290°C, 6 h:

X-Ray analysis reveals amorphous structure of the coatings in as-plated condition which is converted to a crystalline formation of Ni_3P and Ni phases after heat treatment.

Slight increase in the micro hardness is defined after addition of ND strengthening particles and about 1,7 times increase after heat treatment. Higher hardness of the heat treated samples correlates with the lower wear;

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