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RESEARCH

Enhancement in the Tribological and Mechanical Properties of Electroless Nickel-Nanodiamond Coatings Plated on Iron

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A B S T R A C T

A technology to improve the tribological and mechanical surface properties of iron alloys is developed based on the electroless nickel plating. The technology combines sol-gel and electroless deposition technique. Novel nanocomposite coatings are obtained consisting of Nickel-phosphorus-nanodiamond (Ni-P-ND). The ND sol is added directly to the electroless Ni-P solution. A suitable surfactant is added to achieve well-dispersed ND particles in the electroless solution to facilitate their embodiment and equal distribution in the coating. Substrates of steel 17CrNiMo6 and spheroidal graphite cast irons are used for the manufacture of the iron alloys specimens. The surface morphology and microstructure observation performed by scanning electron microscopy (SEM) and optical metallography confirms the influence of ND particles on the coating structure. The structural phase investigation by X Ray analysis indicates a transformation of the amorphous phase to a crystalline one such as Ni, Ni_3P after coatings' heat treatment. The microhardness investigation by Knoop Method and wear resistance measurement in accordance with the Polish Standard PN-83/H-04302 of Ni-P and Ni-P-ND composite coatings are evaluated and compared with each other. The increase in the value of hardness and wear resistance of Ni-P composite coatings in the presence of ND particles and after heat treatment is obtained.

1. INTRODUCTION

The modification of the materials surface by deposition of thin layers is a wide used method to obtain materials with superior properties, suitable for use in a broad range of industrial applications. A comparative study is conducted in [1] to evaluate the performances against wear and corrosion of CrN, CrMoN, CrZrN, CrVN single layer thin films. The different electrochemical behaviors are observed due to different surface defect densities of the coatings. CrN coating presents the lowest coefficient of friction and a higher wear resistance relatively to the ternary nitride coatings. A comparison between nanocrystalline diamond (NCD) and microcrystalline diamond (MCD) coatings deposited on two cemented tungsten carbide (WC-Co) substrates using HFCVD technique shows that COF of diamond coated-WC-Co substrate decreases with the increase in magnitude of load. Here, the NCD coating has shown the lowest value of COF; however MCD coating has shown the higher value of COF initially, but becomes comparable to that of NCD coating after 20 min of sliding time. Therefore, maintaining an appropriate level of normal load and appropriate type of diamond coating, friction may be kept to some lower value to improve mechanical processes [2].

There are many studies proving the materials properties improvement in the presence of additives as hard micro and nanosized particles. Electroless method for nickel based composite coating deposition is especially important seeing the expectation to replace the toxic Cr-containing coatings [3].

Additionally, it has been demonstrated the benefits of the electroless nickel plating over the electrolytic processes. One of the most important is that the obtained matrix by electroless method is nickel alloy, while the pure nickel is produced by electrolytic process [4]. The as plated nickel alloy matrix is harder than the pure nickel (HK0,02≈450÷550), and yields to hardness increase (HK0,02≈950÷1450) after low temperature treatment (~290 °C, 6h). The chemical process mechanism ensures uniform, density coatings with fine crystalline or X-Ray amorphous structure, which is the answer for high corrosion resistance, increased wear resistance and good adhesion to the coated surface [5,6].

The enhanced tribological properties compared to the conventional binary alloys are achieved in electroless Ni-P-W coating [7]. Hence, electroless Ni-W-P, which is a ternary alloy, is synthesized on mild steel substrates. The coatings' heat treatment at 400°C for 1 hr leads to a higher hardness, which is beneficial for selection of this coating in applications requiring the reduction of friction and wear of mating surfaces working under non – lubricated environment. The authors in [8] analyze the influence of two kinds of particles, SiC and Si3N4 on the codeposition process and on the electroless Ni-P composite coatings properties. The result shows there is no influence of the particles type on the incorporation mechanism for the micron sized particles, while the type of particles is very important for nanosized condition. Moreover, the nanoparticles modify the metallic matrix growth mechanism much more than the micron-sized ones.

The discovery of ultra-dispersed diamonds (nanodiamonds) in the 1960s opened new prospects for unique materials exploration in this area. Many authors prove the improved coatings properties in the presence of nanodiamond in the bath solution [9÷13]. 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 [14]. These authors prove the Ni-B coatings' mechanical properties improvement because of residual pores filling. The nanodiamond particles addition to the solution for Ni-B plating bath leads to a dendrite structure refinement which is supposed to be the reason of hardness increase and tribological properties improvement. It is ascertained that the coatings' thermal processing affects only the hardness of the diamond-less sample, increasing it. There is no influence on the coating hardness, produced from diamond containing plating bath. It is assumed the nanodiamond additives facilitate amorphous structure formation due to the inhibition of the grain formation.

Deposition of nickel–phosphorus alloy and composite nickel coatings on low alloy cast iron surfaces using electroless deposition method improves its surface characteristics [15]. The evaluation and comparison of the wear properties of composite nickel coatings (Ni+SiC) with those of cast iron, nickel coatings (Ni), phosphate coating, and chromium plating indicate that not only the hardness of the Ni–P/SiC composite coating is high, but its wear resistance is better than that of the Ni–P coating, chromium plating, cast iron substrate, and the phosphatising coating. Under the given experimental conditions, the wear volume of the Ni–P/SiC composite coating is the lowest.

Authors [16] prove that the graphite presence in the samples is of great importance for the electroless nickel plating strength on cast iron. Evaluating the strength of the plating film by bending tests it is found that the film cracks on cast iron are initiated by the graphite existing at the interface between the plating film and the substrate and it depends on the amount increase of graphite than on the graphite shape.

The aim of the present work is to investigate the microstructure and physical and mechanical properties of electroless nickel coatings with strengthening particles of detonation nanosized diamond ND, plated on the 17CrNiMo6 steel samples and spheroidal graphite cast iron. It is supposed the ND shape and particles size (4÷6 nm), as their specific nature and high surface activity ensure higher density and others functional qualities.

2. MATERIALS AND INVESTIGATION METHODS

On the 17CrNiMo6 steel samples and spheroidal graphite iron samples monolayer of nickel coatings are plated as double layer, consists of first nickel layer Ni and second layer of nickel with integrated particles of detonation nanosized diamond ND (Ni/Ni+ND). The EFTTOM-NICKEL technology for elctroless nickel plating developed in TU-Sofia is applied [17]. Detonation nanosized diamond with particles'' size of 4÷6 nm is used as a strengthening material. Nanosized diamond is produced by explosive method, developed in SRTI-BAS [18]. The coating composition is shown in Table 1 and Table 2.

Prior to plating process the samples are undergone trough normalization (Table 1). The iron spheroidal graphite samples are copper alloyed composition: Fe-3,63C-2,59Si-0,30Mn-0,010S-0,034P-0,53Cu wt%. The spheroidal graphite cast irons and austempered iron samples ADI are used (Table 2). Austempering is performed under a regime: heating at 900 °C 1 h and austempering at 290 °C, 2 h in salt bath.

Two kinds of coatings are produced: electroless nickel coating (Ni) and composite nickel - nanodiamond coating (Ni/Ni+ND).

The process of electroless nickel plating is held on one stage for the electroless nickel coating (Ni) and in two stages for the composite nickel - nanodiamond coating Ni/Ni+ND using developed "EFTTOM-NICKEL" Method:

Electroless Nickel layer formation process is performed at the following working conditions:

- pH = 4.6 ÷ 4.7
- T = (92 ÷ 95) °C
- Coating time = 15 min (in one stage process; 10 min (in a two stage process).
- Optimal uses of the solution 7 ÷ 8 times per hour.

Chemical process of nickelization is:

$$3NaH_2PO_2 + 3H_2O + NiSO_4 \rightarrow 3NaH2PO3 + H_2SO_4 + 2H_2 + Ni$$

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 coating.

Composite nanostructured Ni layer is formed by nickelization in an electroless nickel solution with addition of super hard particles. The work is carried out under the conditions, performed in the first stage of the plating process with particles concentration of: 2 ÷ 5 g/l, determined in [19].

The comparative experimental study of the coatings' wear is carried out. The wear resistance tests of the coatings plated on spheroidal graphite cast iron and austempered ductile cast iron substrates are performed in fixed grinder conditions on TABER – ABRASER test machine by developed by authors method [20]. While the wear of the coatings plated on the samples of 17CrNiMo6 steel are tested by friction wear tests performed under 50MPa loading conditions – in accordance with the Polish Standard PN-83/H-04302.

Table 1. Properties of Ni and Ni-ND coatings on CrNiMo6 steel samples.

Number of the sample	Sample material	Heat treatment	Coating		Microhardness HK0,02	Thickness δ, μm	Wear, g
			Composition	Heat treatment			
1	steel 17CrNiMo6	Normalization	Ni	-	494	8,7	7,5
2			Ni	290 °C, 6 h	1452	8,7	5,8
3			Ni /Ni + ND	-	712	9,3	8,0
4			Ni /Ni + ND	290 °C, 6 h	1112	7,3	4,8

Table 2. Properties of Ni and Ni-ND coatings on ductile cast iron and ADI samples.

Number of the sample	Sample material	Coating				Wear resistance *I*
		Composition	Heat treatment	Microhardness HK0,02	Thickness δ, μm	
1	ductile cast iron	Ni	-	430	10	$0,27 \cdot 10^7$
2		Ni	290 °C, 6 h	878	9	$0,31 \cdot 10^7$
3		Ni /Ni + ND	-	466	8	$0,30 \cdot 10^7$
4		Ni /Ni + ND	290 °C, 6 h	950	8	$0,47 \cdot 10^7$
5	ADI	Ni	-	538	9	$0,37 \cdot 10^7$
6		Ni	290 °C, 6 h	850	8	$0,31 \cdot 10^7$
7		Ni /Ni + ND	-	588	8	$0,44 \cdot 10^7$
8		Ni /Ni + ND	290 °C, 6 h	1112	7	$0,49 \cdot 10^7$

The samples surface microstructure before and after tribological test is investigated by scanning electron microscope РЭММА 101-А at magnification x1000.

3. RESULTS AND ANALYSIS

3.1 Electroless composite nickel coatings on 17CrNiMo6 steel samples

Figure 1 represent the coating view and the microstructure of the steel base (17CrNiMo6 steel), obtained in an as-plated condition (Figs. 1a and 1b) and after thermal processing at 290°C, 6h (Figs. 1c and 1d). The coating appears as a white strip, following the surface topography and filling defects as micro pores and micro cracks. The samples are put to normalization before plating. The base material microstructure consists of ferrite and granular, sorbite shaped pearlite (Figs 1a-1d).

The coatings thickness δ is 8, 7 μm for Ni-coating and in the range of 7,3 ÷ 9,3 μm for Ni/Ni + ND coating.

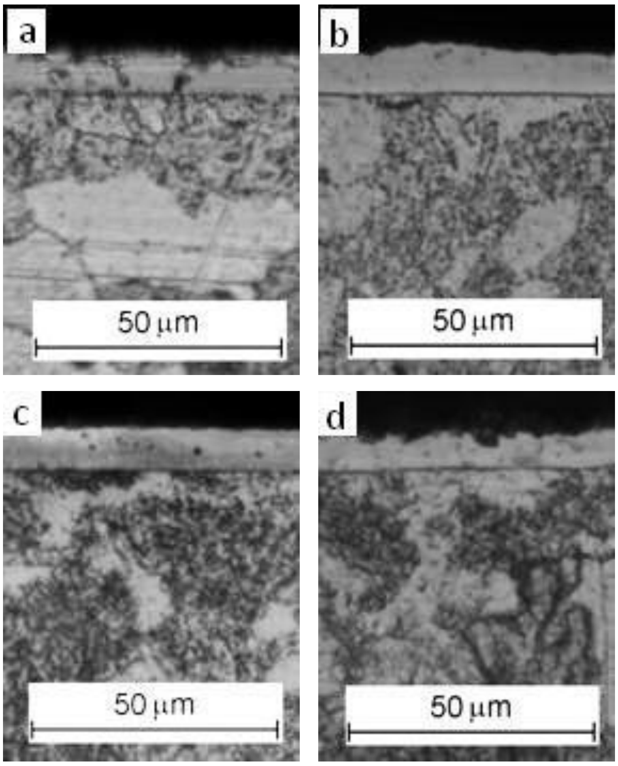

Fig. 1. Microstructure of Ni (a, c) and Ni/Ni+ND (b, d) coatings on 17CrNiMo6 steel samples; a, b – coatings in as-plated condition; c, d –thermal treated coatings at 290 °C, 6h.

Figures 2 and 3 show the X-ray diffraction (XRD) patterns of the tested samples. As Ni - coating and Ni/Ni+ND coating (samples 1 and 3) show amorphous structure in an as-plated condition (Fig. 2). The peaks of the diffraction patterns angles at 44,6° (2θ) and 64,8° (2θ) are due to the iron (Fe), containing in the substrate (steel 17CrNiMo 6). The coatings' structure (as Ni and Ni/Ni+ND) becomes crystalline after thermal processing at 290 °C, 6 h (Fig. 3). The diffraction patterns of the samples 2 and 4 prove the presence of Ni3P and Ni phases in the coatings' structure.

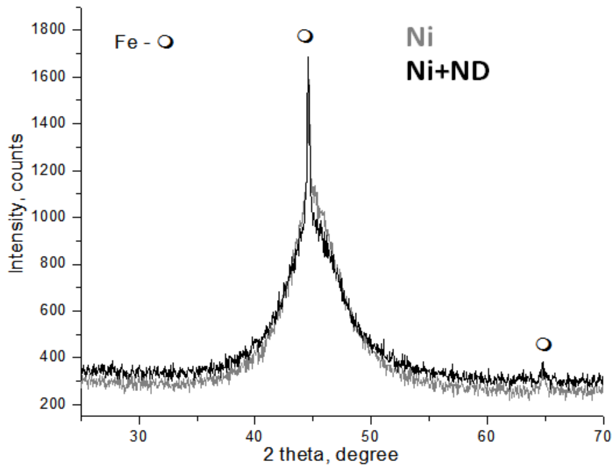

Fig. 2. X– ray diffraction pattern of samples 1 (Ni coating) and 3 (Ni/Ni+ ND coating) in an as-plated condition.

The coatings microhardness in an as-plated condition and after thermal processing is shown in Table 1 and Fig. 4a. The thermal processing of the coatings at 290 °C, 6 h results in about threefold microhardness increase (from 494 HK0,02 to 1452 HK0,02) for Ni coating and about one and a half increase (from 712 HK0,02 to 1112 HK0,02) for Ni/Ni + ND coating.

Coating microhardness increase after annealing at 290 °C, 6 h is related to dispersion strengthening by a reason of dispersive crystal phase formation of Ni_3P. The higher microhardness of the 2 and 4 samples after heat treatment at 290 °C, 6 h explains their higher wear resistance (Fig. 4b).

3.2. Electroless composite nickel coatings on spheroidal graphite cast iron samples

The results for microshardness HK0,02 testing of different coatings are presented in Table 2 and Fig. 5.

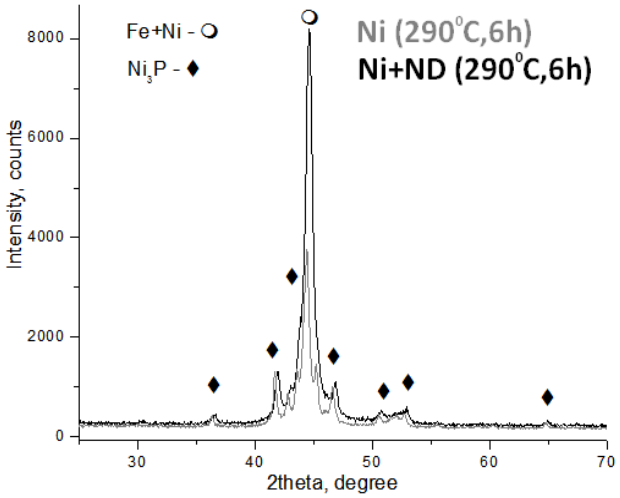

Fig. 3. X– ray diffraction pattern of samples 2 (Ni coating) and 4 (Ni/Ni + ND coating) after thermal processing at 290 °C, 6 h.

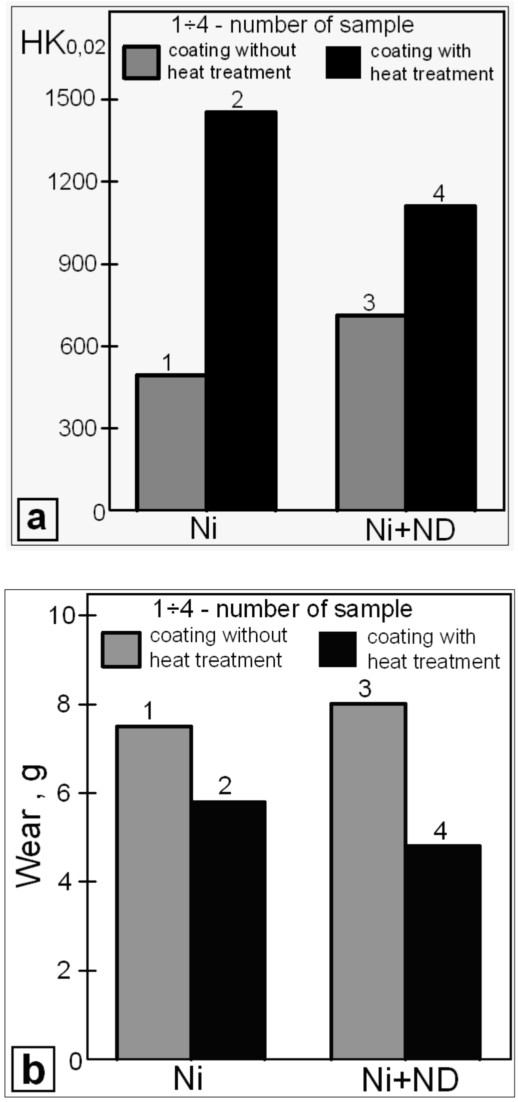

Fig. 4. Microhardness HK 0,02 (a) and wear (b) of Ni and Ni/Ni+ND coatings plated on steel 17CrNiMo6 samples (Table 1).

Thermal treating after plating – hardening at 290 °C for 6 hours increases the microhardness about 2 times. Highest microhardness is achieved in the coatings with nanosized diamond, deposited on cast iron (950 HK 0,02) and austempered cast iron ADI (1112 HK 0,02) after thermal processing at 290 °C for 6 hours.

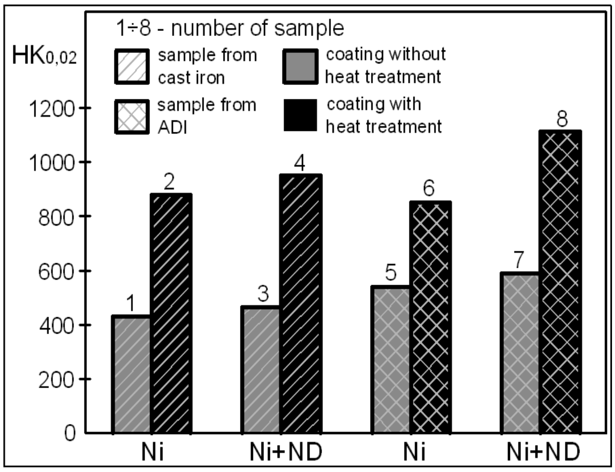

Fig. 5. Microhardness HK 0,02 of Ni, Ni/Ni + ND coatings , deposited on ductile cast iron (samples № 1÷4) and austempered cast iron ADI (samples № 5÷8) (Table 2).

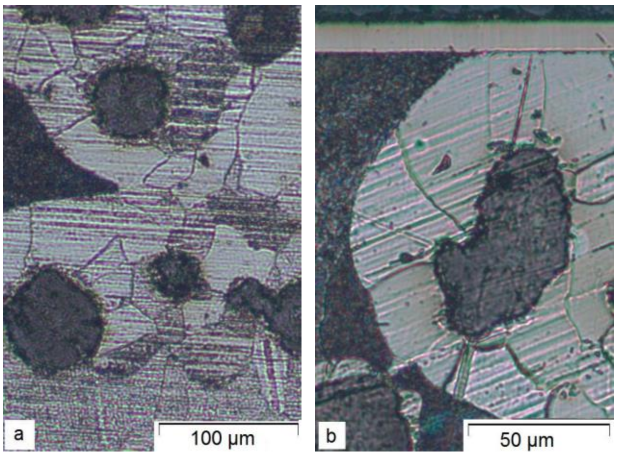

Fig. 6. Microstructure of ductile cast iron samples without coating (a) and with Ni (b) coating with thermal processing at 290 °C, 6 h.

The microstructures of the padding and coatings are presented in Figs. 6 and 7. The cast iron structure consists of ferrite, pearlite and graphite after casting (Fig. 6a), while after austempering at 290 °C, 2 h – of lower bainite and graphite (Fig. 7a). The coatings appear as a white strip, following the sample surface relief (Figs. 6b and 7b). The coating thickness is in the range 7÷10 µm (Table 2).

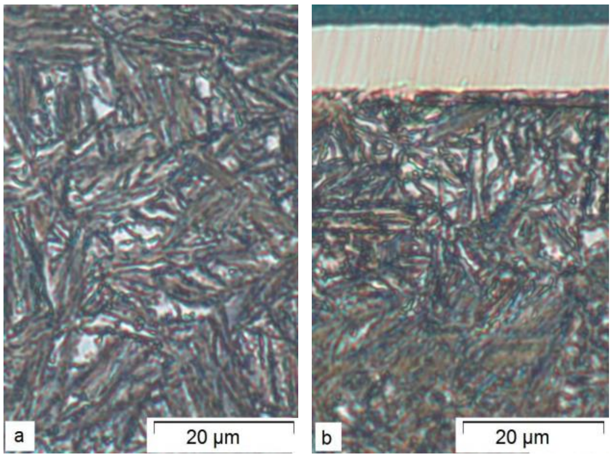

Fig. 7. Microstructure of austempered cast iron samples ADI without coating (a) and with Ni/Ni+ND (b) coatings with thermal processing at 290 °C, 6 h.

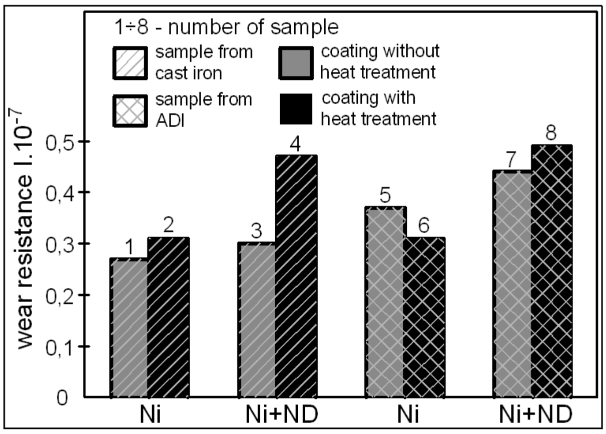

Fig. 8. Wear resistance of cast iron samples (№ 1÷4) and austempered cast iron samples ADI (№ 5÷8) with Ni, Ni/Ni+ND coatings (Table 2).

The following could be concluded analyzing the received results of the wear testing (Table 2 and Fig. 8). The composite nickel coatings with nanosized diamond Ni/Ni+ND show higher wear resistance compared to this one of the samples coated with nickel. The measured higher microhardness (Fig. 5) of the thermal processed coatings (samples № 2,4,6,8 in Table 2) compared to this one of the coatings without thermal processing (samples № 1,3,5,7 in Table 2) corresponds to higher wear resistance (Fig. 8).The lack of a correlation between the coatings microhardness and wear resistance of the sample 6, probably due to the low adhesion of the coating to the iron for the graphite presence in the iron structure. Maximum wear resistance (I = 0,49 .10^7) possesses sample № 8 with coating Ni/Ni+ND after thermal processing at 290 °C, 6 hours, which correlates with the maximum coating microhardness 1112 HK0,02.

Electron microscopic analysis of the samples surface before and after tribological testing (Fig. 9) shows the following:

In the initial state it is observed elements of a relief due to mechanical treatment of the samples (Figs. 9a and 9c). The coatings copy this sample's relief.

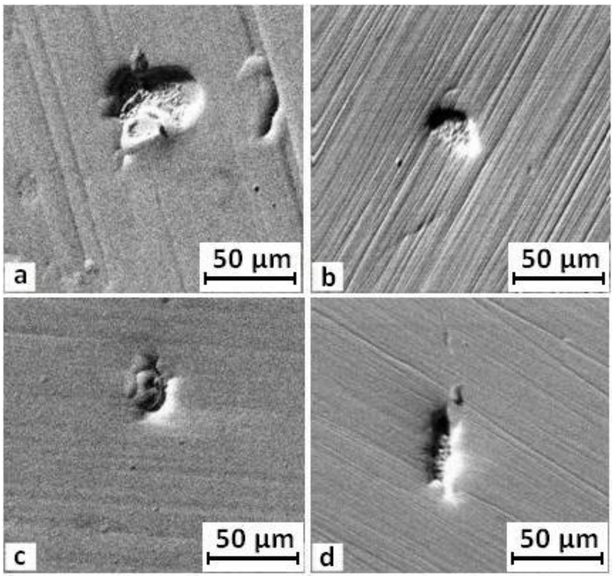

Fig. 9. SEM images of surface structures: coated sample surface without heat treatment before (a) and after (b) wear test; coated sample surface with heat treatment (290 °C, 6 h) before (c) and after (d) wear test.

The sample's surface is changed after wear test. It is observed developed relief with furrows due to surface wear of the sample with coating without thermal processing (b) and single furrows due to surface wear of the coated sample with thermal processing at 290 °C, 6 h (d).

The surface morphology peculiarities of the samples after tribological testing (Fig. 9) correspond with the received results of their wear resistance (Fig. 8).

4. CONCLUSION

The following data are received for the coatings plated on the 17CrNiMo6 steel samples:

- 1.6 to 3 times increase in the microhardness after thermal processing at 290 °C, 6 h. The higher hardness heat treated samples correlates with the higher wear resistance;
- amorphous structure of the coatings in as-plated condition;
- crystal formation of Ni_3P and Ni phases in the coatings' structure after heat treatment at 290 °C, 6 h.

For the coatings plated on spheroidal graphite cast irons and austempered ductile iron (ADI) it is found:

- Two times increase in the microhardness HK0,02 after thermal processing at 290 °C, 6 h;
- 52 % (for ductile cast iron) and 58 % (for ADI) higher wear resistance for nickel coatings with nanosized diamond Ni/Ni+ND compared to this one of the coatings without ND after heat treatment at 290 °C, 6 h.

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REFERENCES

[1] K. Bouzid, N. Beliardouh and C. Nouveau, 'Wear and Corrosion Resistance of CrN-based Coatings Deposited by R.F Magnetron Sputtering', *Tribology in Industry*, vol. 37, no. 1, pp. 60-65, 2015.

[2] K. Najar, N. Sheikh and M. Shah, 'Enhancement in Tribological and Mechanical Properties of Cemented Tungsten Carbide Substrates using CVD-diamond Coatings', *Tribology in Industry*, vol. 39, no. 1, pp. 20-30, 2017.

[3] M. Feldstein, 'The Environmental Benefits of Composite Electroless Nickel Coatings', *Product Finishing*, 01.08.2002.

[4] Electroless Nickel Plating, available at: http://erieplating.com/electroless-nickel, accessed: 29.08.2015.

[5] Z. Karaguiozova, J. Kaleicheva, V. Mishev, G. Avdeev and S. Stavrev, 'Microstructure and Properties of Electroless Composite Nickel Coatings with Nanodiamond', *Nanoscience & Nanotechnology: Nanostructured materials applications and innovation transfer,* no. 13, pp. 74-77, 2012.

[6] Z. Karaguiozova, S. Stavrev, T. Babul and Al. Ciski, 'Influence of cubic nanostructure additions on the properties of electroless coatings', *International Journal of Nanomanufacturing*, vol.5, no. 1-2, pp. 129-138, 2010.

[7] A. Mukhopadhyay, S. Duari, T.K. Barman and P. Sahoo, 'Evaluation of Tribological Properties and Optimization of Electroless Ni-P-W Coating under Dry Condition using Grey Fuzzy Analysis', *Tribology in Industry,* vol. 39, no. 1, pp. 50-62, 2017.

[8] M. Sarret, C. Müller and A. Amell, 'Electroless NiP micro- and nano-composite coatings', *Surface and Coatings Technology,* vol. 201, pp. 389-395, 2006.

[9] H. Xu, Z. Yang, M.K. Li, Y.L. Shi, Y. Huang and H.L. Li, 'Synthesis and properties of electroless Ni–P–nanometer diamond composite coatings', *Surface and Coatings Technology*, vol. 191, pp. 161-165, 2005.

[10] H. Matsubara, M. Kobayashi, H. Nishiyama, N. Saito, Y. Inoue and M. Mayuzumi, 'Co-deposition Characteristics of Nanodiamond Particles in Electrolessly Plated Nickel Films', *Electrochemistry,* vol. 72, pp. 446-448, 2004.

[11] H. Matsubara, Y. Abe, Y. Chiba, H. Nishiyama, N. Saito, K. Hodouchi and Y. Inoue, 'Co-deposition mechanism of nanodiamond with electrolessly plated nickel films', *Electrochimica Acta*, vol. 52, pp. 3047–3052, 2007.

[12] A. Miteva, 'Functionally graded materials in tribology', *Tribological Journal BULTRIB*, vol. 3, no. 3, pp. 371-375, 2013.

[13] A. Miteva, 'On the Microstructure and Mechanical Properties of Nanocomposites', in *Proceedings of the eighth scientific conference with International Participation S E S 2012,* Sofia, Bulgaria, 2012, pp. 220-225.

[14] A. Gurga, V. Mochalin, D. Pepe, C. Picardi and Y. Gogotsi, 'Nanoindentation Study of the Effect of Nanodiamond Additives on Electroless Deposition Nickel-Boride Coating', *Advances in Technology of Materials and Materials Processing Journal*, vol. 10, no. 1, pp. 47-52, 2008.

[15] Y.C. Wu, G.H. Li and L. Zhang, 'Wear resistance of electroless deposited Ni–P and Ni–P/SiC composite coatings on low alloy cast iron', *Surface Engineering*, vol. 16, no. 6, pp. 506-510, 2000.

[16] T. Yamada, A. Yamamoto, M. Fujiwara and Y. Kunugi, 'Strength evaluation and effect of graphite on strength of electroless nickel plating on cast iron', *Journal of Materials Science,* vol. 28, no. 13, pp. 3513-3518, 1993.

[17] G. Gavrilov and C. Nicolov, *Electroless Nickel and Composite Coatings*. Sofia: Tehnika, 1985.

[18] S. Stavrev, S. Lazarov, K. Stoev, L. Markov and V. Ivanov, 'Method for production of ultradispersed diamond', *US Patent No. 5353708,* 1994.

[19] Plating of composite coatings with nanodiamond powder by EFTTOM-NICKEL Method, *Project BAS-SRTI* 1460-5/1991.

[20] J. Kaleicheva, M. Kandeva, Z. Karaguiozova, V. Mishev and P. Shumnaliev, 'Investigation on wear resistance of ductile cast iron covered with nanostructured composite nickel coatings', in *Proceedings of the 9th Int. Conf. The "A" Coatings in Manufacturing engineering,* 3 – 5.10.2011, Thessaloniki, Greece, 2011, pp. 405-414.