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NANOSTRUCTURE FORMATION IN THE NICKEL-CHROME COATING AFTER DUPLEX TREATMENT

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New results of research of the structure and phase state and mechanical properties of the coatings made of industrial composite powders based on Ni-Cr are presented and analyzed. Coatings were deposited by the plasma detonation method on the stainless steel substrate, and then they were exposed to the electron irradiation or plasma-jet melting. TEM metallography, scanning electron microscopy, X-ray photoelectron spectroscopy, X-ray spectral analysis, X-ray structural phase analysis, determination of the microhardness and the corrosion resistance are chosen as the main research methods. It is established experimentally that before irradiation PG-19N-01 coating consists of the nanocrystalline γ phase based on Ni and the microcrystalline CrNi_3 phase. Regions of nanograins with various crystallographic lattice orientations are found in the nanocrystalline phase. The nanograin and microcrystallite sizes, the type and parameters of their lattices are defined. Deposition of the powder PG-10N-01, PG-19N-01 and PGAN-33 coatings by the plasma detonation method with subsequent surface melting leads to the formation of multiphase dense coatings with the intermetallic strengthening compounds, oxides and carbides. The irradiated coatings possess high microhardness, which is about 5 GPa, and corrosion resistance in sea-water.

Keywords: PLASMA JET, NANOCRYSTALLINE γ -PHASE, NANOGRAINS, PROPERTIES AND STRUCTURE OF Ni-Cr.

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1. INTRODUCTION

Technologies of coating deposition and surface modification by the action of high-speed plasma jets are widely used in industry now. These technologies allow to obtain particular structural and phase states in the treated materials and control some properties of solids. In particular, equipment and methods of the plasma surface treatment were widely represented in the International exhibition of nanotechnologies “Nano-Tech’09” (February 2009, Tokyo, Japan).

A number of works devoted to the investigation of coatings deposited by the plasma methods [1-5] defines structure of the given coatings in some cases as nanocomposite one, which consists of two separate phases with nanocrystalline or amorphous structures. The authors of publications [1-4] consider

the unique physical properties of nanocomposite coatings, study dependence between their structure and mechanical properties.

It is well-known [6] that high-energy effect on the substance can provide its amorphization. Formation of sufficiently thick coatings (the thickness is 100-200 μm) is the feature of the plasma detonation method of deposition of powder coatings in contrast to the PVD, CVD, and PED methods, when thin films are formed on the substrate. The one of the main problems of coatings deposited by plasma jet is their porosity, inadequate uniformity due to poor sintering of powder particles, low adhesion to the substrate. The consequence of these disadvantages is poor corrosion and wear resistance of the given coatings. In the work [7], which is devoted to the determination of corrosion resistance of metal and metaloceramic coatings on AISI 304L steel deposited by the plasma spraying method, the coatings of the thickness from 150 to 500 μm are described, and it is noted that excess porosity of the coating is the main reason of its low corrosion resistance.

To remove these disadvantages the irradiation of coatings by an electron beam in the vacuum or rerunning of plasma jet without coating powder over the coating surface in the air is used. In both cases, melting of the treated material on the coating thickness is achieved, and in the most cases substrate melting on 1-2, sometimes 3, coating depths as well. After such combined treatment coatings become smooth. As noted in the work [8], it is possible to achieve a high finish of the coating with polycrystalline structure of grains with the size from 0,1 to 1,0 μm depending on the chosen regime of electron irradiation: current density at the sample, beam energy, number of pulses. Correspondingly, the wear resistance of the coating rises. Coating is alloyed with the substrate, coating particles with each other, and coating becomes structurally uniform, without pores. As the result, the corrosion resistance increases.

Experience of practical use of combined technologies of the powder coating deposition by the plasma detonation method with further modification by the electron irradiation or plasma allows to affirm that mechanical properties of the coatings made of metals and alloys (micro- and nanohardness, wear and corrosion resistance) are extremely good [9-12].

Coatings based on Ni deposited by the plasma detonation method are not superhard, but the value of their microhardness is not less than 4 GPa [11, 12] that allows to suggest the formation of nanostructures in such coatings. Moreover, it is known that superhard coatings deposited by the PVD and CVD methods can lose their properties during some hours after the coating formation. Coatings deposited by the plasma detonation method do not possess this disadvantage, and the conditions of their deposition, namely, the temperature of plasma jet which is about some thousands $^{\circ}\text{C}$, high particle velocities of metal coating (from 600 to 1000 m/s [9]) in plasma jet, small time of the jet action (about 3 ms), are such that the assumptions about the formation of amorphous regions or nanostructures in the coatings are quite reasonable. It is known that especially effectively amorphous or nanostructured states are achieved at high heating velocities, pressure and small time of the high temperatures action [6]. The authors of publications [8, 13] devoted to the study of the coating structure and properties deposited by plasma jet after electron irradiation note the formation of nanostructures in these coatings.

However, using the combined treatments a number of problem questions still remains. First of all, to obtain coatings with the desired properties one should take a clear view of the structure and phase state of the coating not

only after irradiation, but before it. There is not enough published TEM data about the structure and phase state of the coatings deposited by the plasma detonation method. Secondly, due to the relatively large thickness of such coatings it is impossible to identify their properties and structure with those for coatings similar in the chemical composition but obtained using other methods. Thirdly, it is necessary to substantiate the choice of the regimes of combined treatment: beam energy and current density, irradiation duration, etc. Substantiation can be carried out within the certain model, which takes into account the coating structure before irradiation. Knowledge of these parameters allows to conserve energy and automate irradiation treatment of the coatings.

Both the new experimental results and investigation of the properties and structure and phase states of the coatings made of industrial composite powders PG-10N-01, PG-19N-01, and PGAN-33 (the Russian Industrial Standard) deposited by plasma jet on the steel substrate are presented and analyzed in the given review.

The aim of the work is following: to establish experimentally the structure and phase state of the coatings based on Ni after their deposition by the plasma detonation method on the stainless steel substrate and after electron irradiation; to check the assumptions about the formation of nanostructures in the given coatings; based on the analysis of experimental data, to propose the model of coating structure before irradiation in order to substantiate in the sequel the choice of the irradiation regimes; to give recommendations of use of the given coatings based on the investigation of their microhardness and corrosion resistance in sea water.

2. EXPERIMENTAL DETAILS

Protecting coatings of the thickness from 80 to 300 μm were formed from powder alloys in the plasma detonation device "Impul's-6" on the stainless steel 3 substrate (Fe is the base, C – 0,25%, Mn – 0,8%, Si – 0,37%, and P < 0,045%). Powders based on Ni-Cr, namely, PGAN-33 (Ni is the base, Cr – 2-24%, Mo – 4%, B – 2%, Si – 2%, and W – 1%), PG-10N-01 (Ni is the base, Cr – 14-20%, B – 3,5%, Si – 4,3%, Fe – 7%, and C – 0,8%), and PG-19N-01 (Ni is the base, Cr – 8-14%, B – 2,3%, Si – 1,2-3,2%, Fe – 5%, and C – 0,5%) were used for coating deposition. Powder with the fraction size from 56 to 260 μm was used for sputtering. As the substrate material we have taken the steel samples of the size $20 \times 30 \times 2 \text{ mm}^3$, which surface was beforehand exposed by the sand-blasting treatment.

Powder coatings were deposited in the air at the following regimes of the pulse-plasma deposition: the distance from the sample to the nozzle section of plasmatron is 60 mm, the sample velocity is 360 mm/min, the pulse repetition frequency is more than 4 Hz, the powder consumption is 21,6 g/min, the capacitor battery capacity is 800 μF , the pulse duration is 0,6 ms. Propane, oxygen, and air were used as combustible and orifice gases. Mo was chosen as the material of eroded electrode of plasmatron.

Irradiation of the samples from the side of the coatings was realized in the vacuum by high-current electron beam in the source "U-212" with accelerating potential of 30 kV in continuous operation. Coating deposition was carried out in the Sumy Institute for Surface Modification (Sumy, Ukraine) and their melting by an electron beam was performed in the Paton Electric Welding Institute of NAS of Ukraine (Kiev, Ukraine).

Plasma jet treatment in the melting regime for the investigation of the surface structure and morphology was carried out by the scanning electron microscopy methods using JSM-6390LV ("JEOL", Japan) with the add-on INCA ENERGY ("Oxford Instruments", Great Britain) for the energy dispersion analysis. To determine the elemental composition of the coating and the substrate we applied the X-ray fluorescence spectral analysis using X-ray spectrometer JSX-3100RII ("JEOL", Japan). Change in the chemical composition of the coatings in depth was studied by the X-ray photoelectron spectroscopy method using JPS-9010MC ("JEOL", Japan); coating was exposed to 12 nm etching in the vacuum by Ar ions. To investigate the structure and phase state of the coatings the X-ray diffractometer X'Pert PRO ("PANalytical", Netherlands) was used. The surface topography was studied using the atomic-force microscope JSPM-5200 ("JEOL", Japan).

Metallographic study of the substrate was carried out with the inverted photomicroscope of reflected light Neophot-21 ("Carl Zeiss", Germany). To reveal the grain boundaries we used electrochemical etching in electrolyte of the following composition: 270 ml of glacial acetic acid (12%) and 30 ml of chlorine acid (10%) at the voltage of 15 V (the etching time is 1 sec).

Microhardness tests were performed using PMT-3 (LOMO, Russia) with indenter loads of 2, 5, 10 N. To carry out the corrosion tests we used the potentiostatic method estimating the corrosion rate in sea water. Polarization curves were obtained using potentiostat PI-50.1.1. Area of the samples was chosen to be equal to the area of auxiliary electrode, i.e., 1 cm². During the experiment we used three-electrode electrolytic cell of the volume of 120 ml. NaCl 0,5H (3%) solution was taken to imitate sea water. Potentiostatic control was realized using the silver-chlorine comparison electrode.

For the more detailed analysis of the PG-19N-01 coating deposited by the plasma detonation method, it was mechanically cut off from the substrate surface, and then its structure and composition were studied from two sides (from the side of the surface and the side of the substrate). Investigation by the TEM methods was realized using JEM-2100 ("JEOL", Japan). Coating separated from the surface is cut with difficulty due to high hardness. This conditioned difficulties of foil preparation for TEM. We studied foils made of the coatings, which were beforehand mechanically thinned and etched by argon beams in the vacuum till the formation of through hole, in the plant PIPS ("Gatan", Japan) with the beam energy of 5 keV. Since the coating thickness is large, to investigate the structures formed in different coating layers, we used the following etching procedure: a part of foils was etched during 12 hours till the formation of through hole from the surface side; a part – from the opposite side adjoining to the substrate. A part of foils was turned over in 6 hours of etching, and then another side was etched in order to obtain the through hole in the middle of the foil thickness.

3. EXPERIMENTAL RESULTS

Topographic analysis of the surface of PG-19N-01 coating before its melting by an electron beam is represented in Fig. 1. Measurements of the roughness height show that height of some peaks is 656 μm from the substrate, while of other peaks is 86 μm , at the mean coating thickness of 150 μm . The microhardness analysis of the coatings is difficult due to their strong roughness.

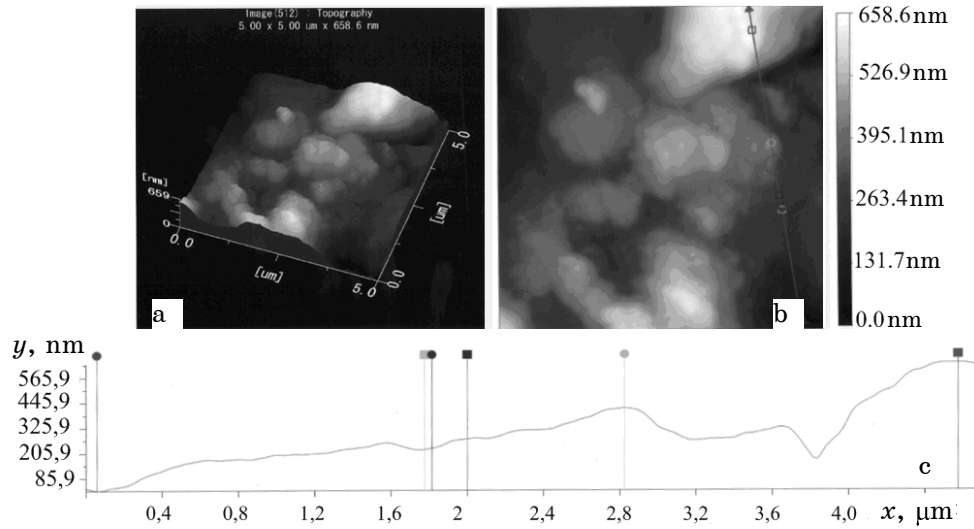


Fig. 1 – Surface topography of PG-19N-01 coating deposited by the plasma detonation method (before its melting by an electron beam)

To profile variations of the chemical composition of PG-19N-01 coating in depth, the microanalysis of the coating surface before and after its 12 nm etching by argon ions was performed by the X-ray photoelectron spectroscopy method. After ultrasonic cleaning in ethanol solution we determined such elements as C, O, Cr, and Ni and established the presence of Cr_2O_3 and Al_2O_3 oxides (Fig. 2).

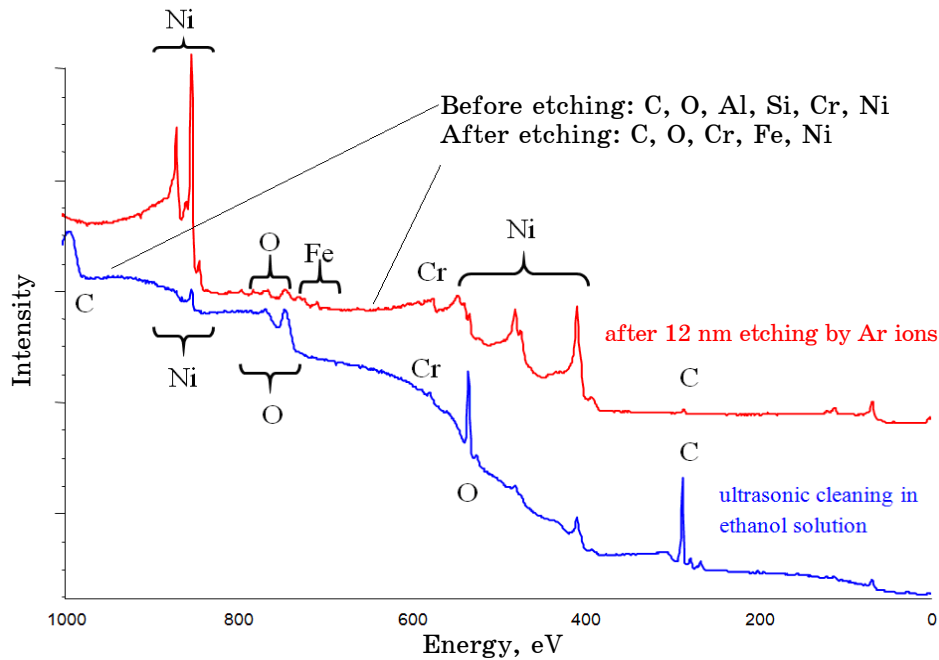


Fig. 2 – Results of the qualitative microanalysis of PG-19N-01 coating

Using data of the X-ray photoelectron spectroscopy it was established that at the depth of 12 nm from the surface the C content decreases from 69,41 at.% to 15,54 at.%, the O content from 23,48 at.% to 15,54 at.%. On the contrary, the Cr content increases with depth from 1,26 at.% to 7,27 at.%, the Fe content from 0,07 at.% to 1,47 at.%, the Ni content from 1,24 at.% to 53,25 at.%, and the Al content from 2,33 at.% to 7,32 at.% (see Fig. 3).

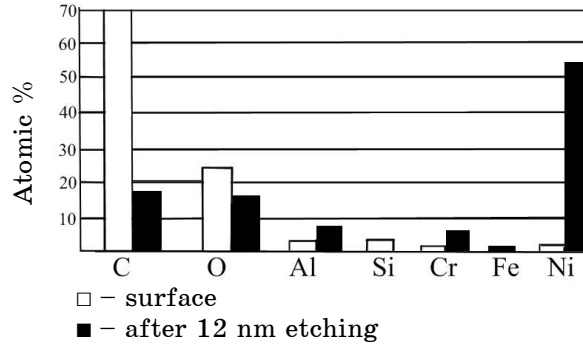


Fig. 3 – Results of the quantitative analysis of the composition of PG-19N-01 coating (□ – surface, ■ – at the depth of 12 nm from the surface, after argon etching)

However, chromium-enriched layers are located sufficiently near to the surface, since the X-ray structural analysis of the reverse side of PG-19N-01 coating has determined the existence of only γ -phase of Ni with the fcc-lattice and α -phase of Fe with the bcc-lattice in the layer where coating of the thickness of 150 μm adjoins to the steel substrate (Table 1).

Table 1 – Experimental results of the X-ray structural phase analysis of the composition of PG-19N-01, PGAN-33, and PG-10N-01 coatings

Coating	Phase composition, lattice type and parameters (Å) of the coating phases before electron irradiation	Phase composition, lattice type and parameters (Å) of the coating phases after electron irradiation
PG-19N-01 (surface)	FeNi ₃ : primitive cubic, $a = 3,5450$; Cr ₂ Ni ₃ : fcc, $a = 3,5400$; FeS: orthorhombic, $a = 5,7000$, $b = 3,3510$, $c = 5,7570$;	CrO ₂ : tetragonal, $a = 4,4210$, $b = 4,4210$, $c = 2,9160$; CrNi ₃ : fcc, $a = 3,5520$; Cr ₃ Si: bcc, $a = 4,5640$; Fe ₇ Ni ₃ : bcc, $a = 2,8610$;
PG-19N-01 150 μm thickness (from the side of the substrate)	Ni: fcc, $a = 3,5250$; Fe: bcc, $a = 2,8662$;	Analysis has not performed
PG-10N-01 (surface)	Ni: fcc, $a = 3,5260$; Fe: bcc, $a = 2,8707$;	Cr-Ni-Fe-C: fcc, $a = 3,60$; Fe: bcc, $a = 2,8860$; Fe-Cr ₂ O ₃ : fcc, $a = 8,344$;
PGAN-33 (surface)	Ni: fcc, $a = 3,5350$; Fe: bcc, $a = 2,8670$;	Ni: fcc, $a = 3,5350$; Fe: bcc, $a = 2,8664$; Mo ₂ C: hexagonal, $a = 3,0029$, $b = 3,0029$, $c = 4,7290$; Fe _{0.9646} O: fcc, $a = 4,3007$.

After melting by an electron beam all coatings become multiphase (Table 1). Chrome oxides, intermetallic compounds (CrNi_3 and Fe_7Ni_3), and Cr-Ni-Fe-C compound are formed in PG-19N-01 and PG-10N-01 coatings (Table 1). In PGAN-33 coating the fine-dispersed phases of molybdenum carbide Mo_2C and ferric oxide $\text{Fe}_{0.9646}\text{O}$ are formed.

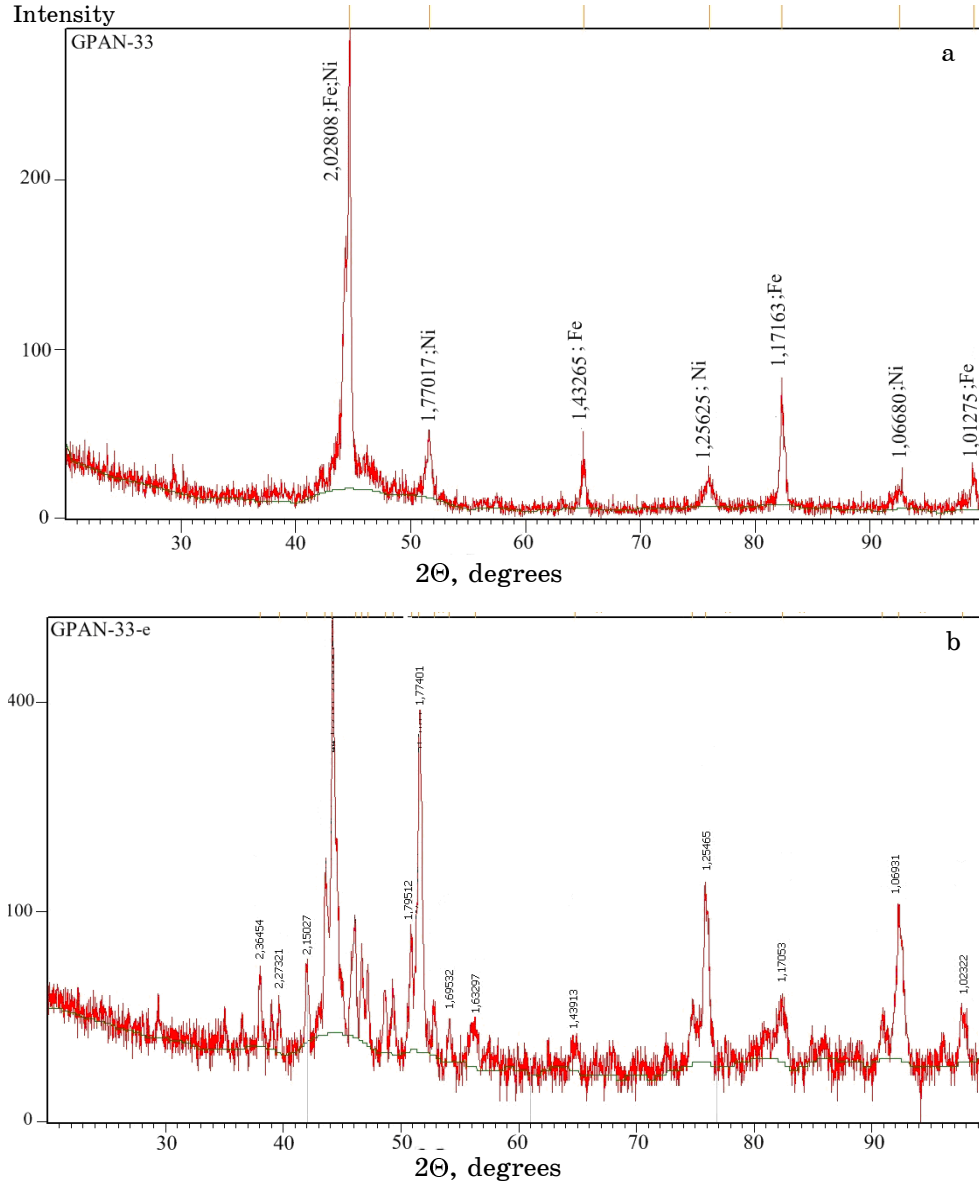


Fig. 4 – X-ray diffraction patterns of PGAN-33 coating after deposition by the plasma detonation method (a) and after modification by the electron irradiation (b)

A great number of low-intensity and hardly identifiable peaks are observed on the X-ray diffraction pattern of the melted by an electron beam PGAN-33 coating (Fig. 4). Slight rise of background in the region of small angles and minor spreading of the peak in the region of 2Θ from 40° to 50° implies about the possibility of formation of the regions with crystallographically disoriented nanograins or about the amorphization of a part of material (Fig. 4a). After irradiation such structure is also possible judging by the diffraction pattern (Fig. 4b). Broadening of all peaks, which is typical for the transition of a part of material to the nanophase or to the amorphous state, is observed.

Coating surface after melting essentially differs; rough edges melt (see Fig. 5a). Boundary of the coating and indentations of the hardness meter indenter are observed in Fig. 5b. It is seen that the area of indentations is less on the coating, and its microhardness higher than of the steel substrate.

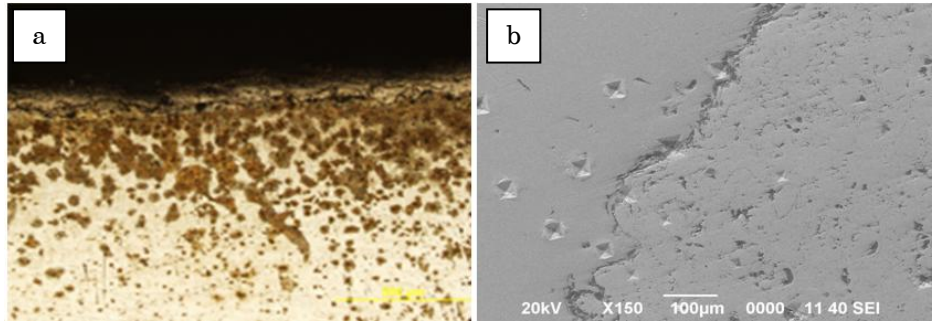


Fig. 5 – View of the PG-19N-01 coating at the boundary with the substrate after melting by an electron beam: optical microscopy (a); cross-section, SEM secondary emission image (b)

Microhardness measurements of the treated by an electron beam coatings carried out on the cross-sections resulted in the following: it is established for the PG-19N-01 coating that there is the two-fold decrease in the microhardness at the depth of $55\ \mu\text{m}$ from the coating surface. Values of the coating microhardness H_μ on the surface take the values $5,50\ \text{GPa}$ (at the H_μ dispersion of $0,16\ \text{GPa}$). Mean value of the microhardness decreases with thickness. Sufficiently large values of the microhardness dispersion are conditioned by the coating multistaging.

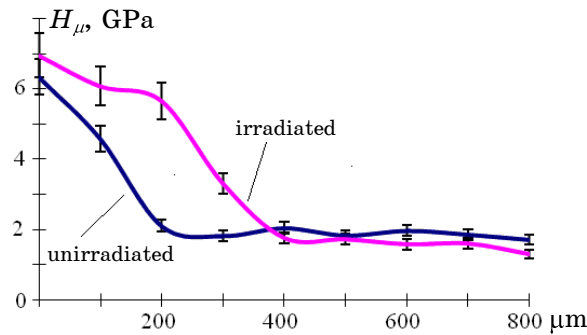


Fig. 6 – Dependence of the PG-19N-01 microhardness on the distance to the surface

As seen from the results of the X-ray structural analysis (Table 1), there are different phases in the coating, therefore the microhardness values depend on the content of these phases in local regions. Results of the microhardness analysis in depth for PG-10N-01 and PGAN-33 coatings are similar to those for PG-19N-01 coating. Average grain size of the coating after melting by an electron beam is about 1 μm (Fig. 7).

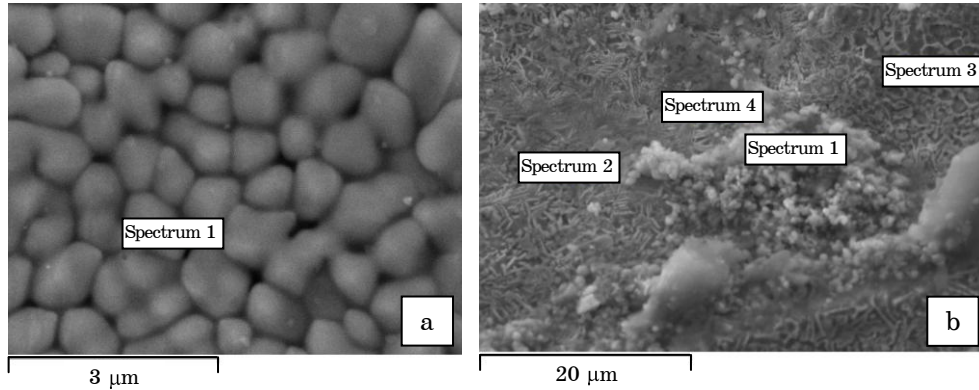


Fig. 7 – SEM secondary emission images of the coating surface after electron irradiation: PGAN-33 (a); PG-10N-01 (b)

Using data of the X-ray fluorescence analysis, appearance of ferric coatings from the substrate in nickel matrix was revealed. Increase in the iron weight fraction in the coatings after electron irradiation is typical for all types of the coatings that is confirmed by the EDS data as well (Fig. 8b). Appearance of iron in the coating material before (Fig. 11 and Tables 1 and 2) and after (Table 1) its melting by an electron beam is the characteristic feature.

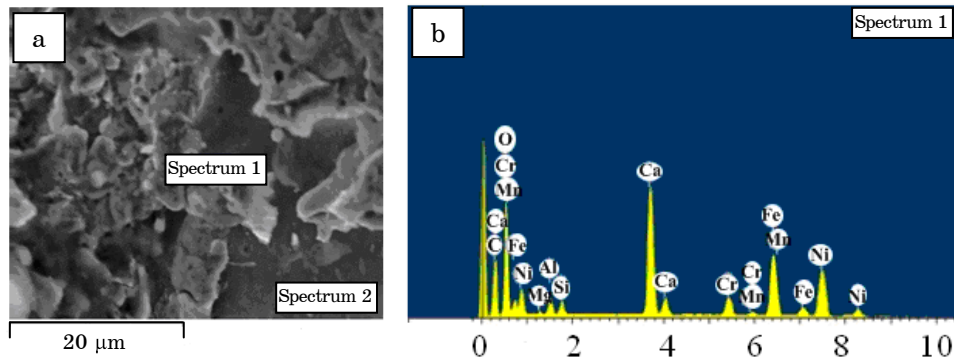


Fig. 8 – Structure and elemental composition of PG-10N-01 coating: secondary emission image of the surface (a); elemental composition (b)

Fe in the coatings deposited by the plasma detonation method has the bcc-lattice before electron irradiation, the lattice parameter is increased in comparison with that in the substrate ($a_{sub} = 2,864 \text{ \AA}$), especially for PG-10N-01 coating ($a = 2,8707 \text{ \AA}$, Table 1). In PG-19N-01 coating the α -phase of Fe is formed only in some depth of the coating (Table 1). After electron

irradiation the Fe_7Ni_3 phase with the bcc-lattice and the lattice parameter $a = 2,8610 \text{ \AA}$ (Table 1) is formed in PG-19N-01 coating; and the intensity of Fe peaks on the X-ray diffraction pattern sharply decreases (Fig. 4b), and in PG-10N-01 and PGAN-33 coatings the α -phase of Fe is still observed, but we note the change in the lattice parameter of the α -phase of Fe in comparison with that before irradiation (Table 1).

Table 2 – Results of the elemental analysis (wt.%) of the plasma detonation PG-10N-01 coating

Spectrum	O	Mg	Al	Si	Ca	Cr	Mn	Fe	Ni
1	36,57	0,30	1,59	1,38	14,80	4,00	0,32	18,78	22,25
2	0,82	–	0,40	0,37	–	9,03	0,42	4,10	84,86
max	36,57	0,30	1,59	1,38	14,80	9,03	0,42	18,78	84,86
min	0,82	0,30	0,40	0,37	14,80	4,00	0,32	4,10	22,25

Formation of the doping compounds with the material of eroded electrode, assumed before [9, 10], is not confirmed in the given case. Mo oxides are formed only in PGAN-33 after irradiation, but Mo enters into the composition of this coating powder (4 wt.%). Regular increase in the coating adhesion to the substrate and corrosion resistance of the irradiated samples is observed. Corrosion potentials in sea water of the substrate (steel 3) and PG-19N-01 coating are sufficiently high: $\varphi_{cor} = -0,38 \text{ V}$ (for the substrate) and $\varphi_{cor} = -0,49 \text{ V}$ (for the coating), but the corrosion rate of the substrate is essentially higher: $i_{cor}(\text{substrate}) = 3,7 \text{ mm/h}$ and $i_{cor}(\text{coating}) = 2,2 \text{ mm/h}$. Corrosion rate of the given coating before irradiation was not measured. Coating before irradiation had tendency to the corrosion when etching in a chloroacetic electrolyte (change in the coloring, fracture).

By the methods of the electron diffraction microscopy of thin foils it was established that PG-19N-01 coating deposited by the plasma detonation method on the steel 3 substrate represents the matrix, which is formed of nano-grains of different orientation with separate crystalline particles (Fig. 9a). Ordering in the distribution of crystalline elements is not observed, linear sizes of elements are different: from 50 to 500 nm, particles are equiaxed. Particle surface is non-uniform (Fig. 9b). Microelectron diffraction pattern of microcrystallites is point (Fig. 10a), in contrast to the ring microelectron diffraction pattern of nanocrystalline matrix (Fig. 11).

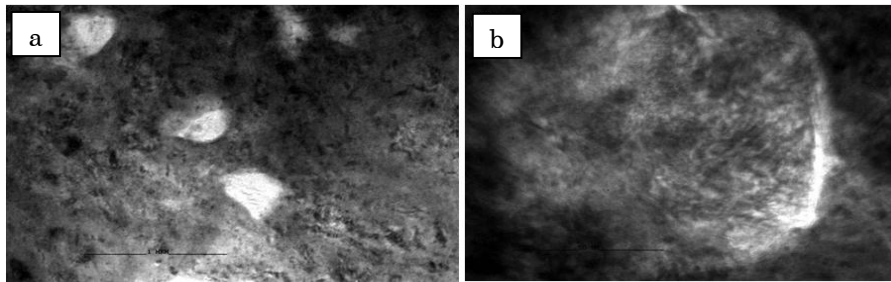


Fig. 9 – Electron microscope image of the microstructure of powder PG-19N-01 coating deposited by plasma jet on the steel substrate: general view of the microstructure (a); image of a crystalline particle (b)

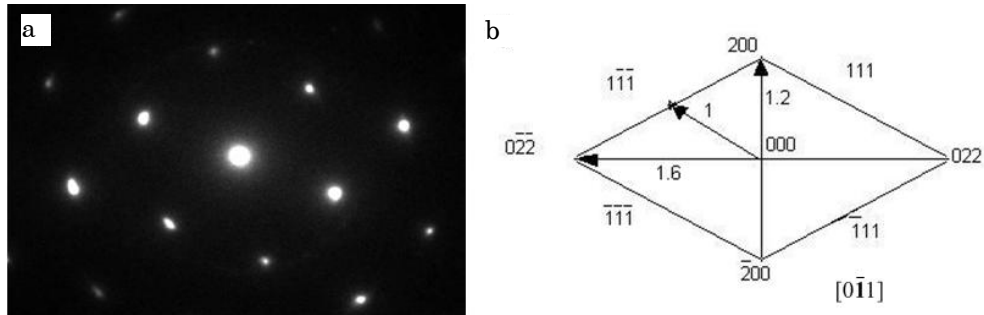


Fig. 10 – Electron diffraction pattern of a crystalline particle (a) and scheme of its interpretation (b)

We have interpreted the electron diffraction pattern of the matrix in PG-19N-01 coating. On the ground of the data of the X-ray structural analysis material contains the phase based on Ni, which has the fcc-lattice with the matrix parameter $a = 3,5250 \text{ \AA}$ (Table 1). According to the electron diffraction pattern (Fig. 10b) this parameter is equal to $3,5303 \text{ \AA}$. Parameter of the fcc-lattice of microcrystallite in the coating is $a = 3,5235 \text{ \AA}$ that is closed to the data of the X-ray structural analysis (CrNi_3 -phase, fcc-lattice with the parameter $a = 3,5520 \text{ \AA}$). Volume fraction of microcrystallites in the coating material determined using TEM images is about 15%.

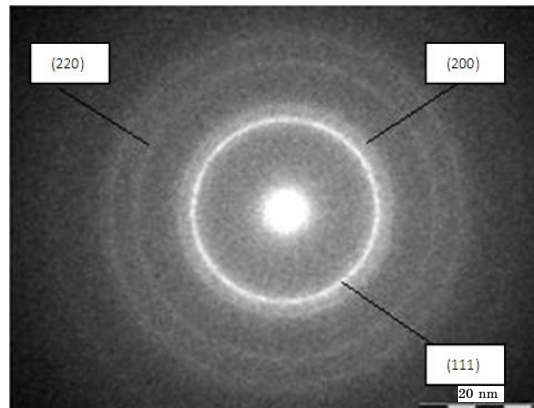


Fig. 11 – Electron diffraction pattern of the PG-19N-01 coating matrix with indexes of the corresponding crystallographic planes

In the middle of the coating at high magnification it is possible to see in the matrix the mixture of variously oriented nanograins (Fig. 12a, b), which is similar to the structure shown in Fig. 1c. But the nanograin boundaries are not expressed, a clearly defined symmetry in the arrangement of nanograins with certain orientation of atomic planes is absent. Therefore we can not state with confidence that ordering in the microstructure formed by the nanograin mixture is observed. However, on the electron diffraction patterns one can clearly see the point reflections, which are superimposed on the ring electron diffraction pattern of the coating matrix (Fig. 12c). Sizes of the separate nanograins are of the order of 2-3 nm, but point reflections imply about the alignment of microregions with identically oriented crystal lattice. However, boundaries of these formations are not expressed.

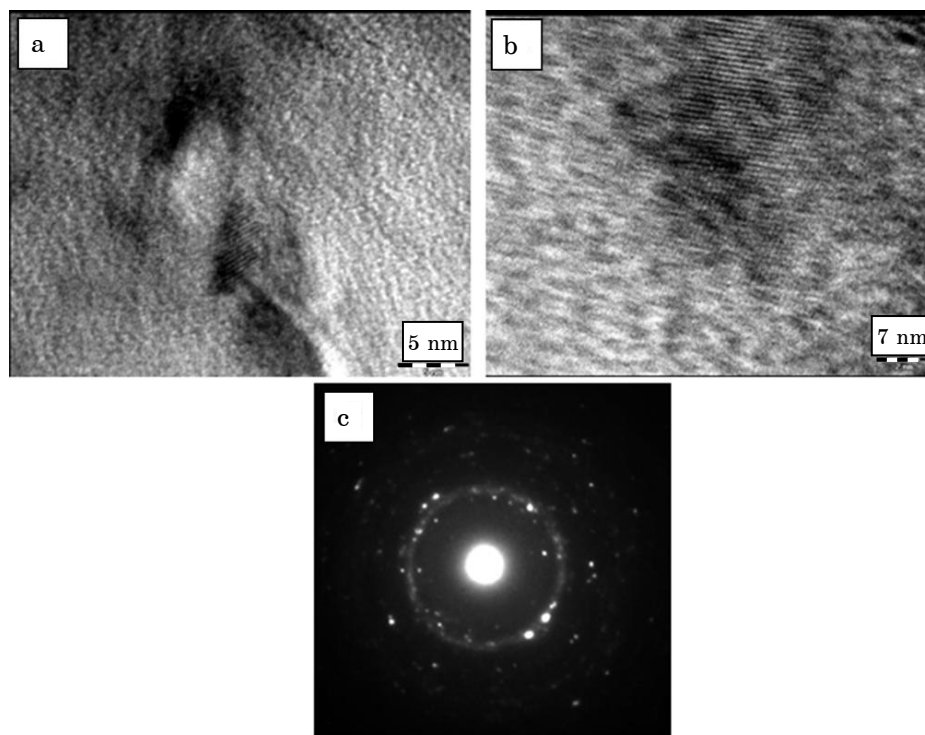


Fig. 12 – Electron microscope image of the microstructure of powder PG-19N-01 coating deposited by plasma jet on the steel substrate: pictures of nanoregions of different crystallographic orientation (a, b) and microelectron diffraction pattern of the region illustrated in a (c)

Presence of extensive defects of the microstructure (Fig. 13) is also typical for the given foils.

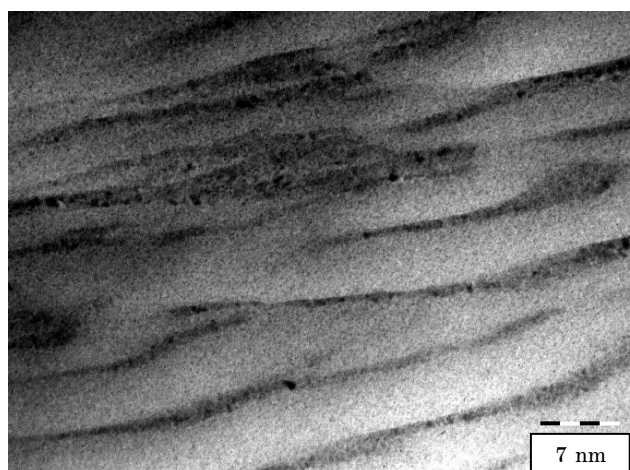


Fig. 13 – TEM image of the PG-19N-01 surface deposited by plasma jet on the steel substrate

4. DISCUSSION OF THE EXPERIMENTAL RESULTS

We assume that the structure and phase constitution of the coatings based on Ni-Cr deposited by the plasma detonation method has general features.

First of all, the layered structure. On the example of the analysis of PG-19N-01 coating it is established for certain that intermetallic CrNi_3 -phase with the fcc-lattice is formed on its surface. It is typical that Cr compounds are formed only in thin surface layer of the coating that is confirmed by the different analysis methods, namely, TEM, XRD, and ESCA. Thickness of the layer, which contains the compounds based on Cr, was not defined exactly in this experiment, but such compounds were not discovered neither at the depth of about 75 μm from the surface, nor at the depth of 150 μm , in the joint region with the substrate. We suppose that non-uniform temperature profile formed along the sample depth under the action of plasma jet is the determinative reason of non-uniform phase formation is. Based on the data of [14], solubility of Cr in Ni sharply decreases with temperature. In whole, one can consider, that thin layer containing oxides and carbides, and phases with the coating elements as well, which are badly soluble at high temperatures, is formed on the free coating surface.

The main layer of the coating has sufficiently uniform phase structure, in the given case this is γ -phase, solid solution based on Ni, and α -phase based on Fe, which obviously penetrates from the side of the substrate.

Secondly, increase in the weight fraction of Fe in the coating in comparison with the initial composition is typical for all coatings. Since Fe can penetrate from the substrate only, one can assume a sharp increase in the diffusion coefficients, and possibly, mechanism of the radiation-induced diffusion becomes the dominant one. We initially assumed the possible appearance of Fe on the surface as the result of the hit of the sprayed substrate under the action of plasma jet on the surface of deposited powder particles. The "dust" cloud of Fe atoms, which after the plasma action are attracted back to the electrically charged substrate, is formed. Assumption was based on the fact, that under the action of plasma jet the essential spraying of the substrate material [15] occurs. But the fact, that in PG-19N-01 coating the α -phase of Fe is discovered only from the side of the coating adjoining to the substrate, refutes this assumption. On the other hand, it is impossible to exclude the possibility that due to the turbulent motion of a liquid during melting of a part of the substrate surface and coating the agitation of their components occurs.

Observed change in the lattice parameter of α -Fe (Table 1) in the coatings in comparison with the substrate allows to suppose the possibility of change in the lattice parameter due to doping by Cr atoms (the atomic radius is 130 pm) with larger atomic size than Fe (126 pm) or by Ni atoms with smaller atomic size (124 pm). The authors of [16] observed such increase in the parameter under implantation of Cr atom into the center of Fe cubic cell, i.e., under substitution of the central Fe atom by Cr atom. Observed in our experiment formation of Fe_7Ni_3 compound with the bcc-lattice in PG-19N-01 after irradiation with the reduced lattice parameter in comparison with α -Fe forces to suggest that this formation flows according to the substitution mechanism of Fe atoms in the lattice by Ni atoms, but we did not determine in this experiment which exactly places in the Fe lattice Ni takes. New compounds based on Cr appear in this coating after irradiation that

also implies about the decrease in the Ni fraction in solid solution. Also in PGAN-33 coating parameter of α -Fe decreased in comparison with the same before irradiation. Isolation of the phases with Cr is not observed in PGAN-33 coating, i.e., all Cr atoms are in the bound state in solid solution. We note that only PGAN-33 does not contain Fe in the composition of coating powder. However, in PG-10N-01 coating after irradiation compounds based on Cr appear, but the lattice parameter of α -Fe increases. Possibly, α -Fe lattice with interstitial Ni atoms in this coating experiences tensile stresses. Analysis of the phase composition of the given coatings implies sooner about very fast diffusion, than about mechanical agitation of the melted coating and substrate. The results we have obtained are in agreement with the data obtained by the authors of [17]. It was established in [17] that irradiation by high-current electron beams leads to the essential morphological, structural, and phase changes in the surface layers in WC-Co alloy; arouses intensified mass transfer with the diffusion coefficients, which exceed 8-9 orders the coefficients of radiation-induced diffusion under irradiation of materials by continuous particle flows of the middle density; leads to the surface homogenization as a result of the melting and mutual dissolution of the phase components, and to the formation of intermetallic compounds as well.

It is necessary to note that carbide strengthening phase in alloys based on Ni-Cr at the temperatures of 700-800 °C coagulates much faster than intermetallic one that leads to the fast softening of alloys [18]. Therefore, alloys with intermetallic hardening are more preferable for the work in the high-temperature region. Intermetallic compounds are formed in PG-19N-01 and PG-10N-01 coatings after electron irradiation and in PG-19N-01 directly after plasma detonation deposition of the coating (Table 1).

Thirdly, we assume that nanocrystalline structure discovered in PG-19N-01 coating is typical for all coatings deposited by the plasma detonation method and is partly typical for the substrate layer adjoining to the coating. One of the reasons is high microstructure imperfection conditioned by the impact action of plasma jet on the surface and sharp temperature gradient in the coating that can lead to the appearance of severe deformation in the coating. As a result, for the mechanical stress relieving the substructure composed of nanograins of different crystallographic orientation with high and continuous misorientation is formed in the coating, and this is confirmed by the typical ring electron diffraction patterns. Typical for polycrystals features of diffraction contrast, namely, changes in its intensity on the boundaries, which are necessary for the reveal of the grain boundaries, are absent at an arbitrary orientation of foil in goniometer. We assume that we observe the structure similar to the fragmented one with misorientation of fragments-nanograins similar to the observed under crystal polygonization. Slight peak spreading on the electron diffraction pattern is the confirmation of this assumption for PGAN-33 and PG-10N-01 coatings.

Ring pattern of microdiffraction (Fig. 11) implies about high values of the local internal stresses as well. Possibly, level of internal stresses slightly decreases due to their partial relaxation under fragmentation. Level of local internal stresses in thin substructure can be estimated using the formula $\sigma \approx E\Delta h\chi$, where E is the Young modulus; Δh is the characteristic dimension of the dislocation charge region; χ is the corresponding component of the curvature tensor of crystallographic planes parallel to an electron beam [19]. Calculated in [19] by this formula level of stresses for TiN/Cu coating depo-

sited on the stainless steel 12X18H10T by the vacuum-arc scattering method is about 5-9 GPa, as well as found in works [20, 21] values of the long-range compression stresses for TiN, Ti-Si-N coatings. In our experiment the value of Δh can be taken equal to the nanograin size ($\Delta h \approx 2-3$ nm), the values of tensor component χ of the lattice bend-torsion in the nanograin cross-section were not determined, but it is obvious that such small value of Δh will condition the essential reduction of the level of internal stresses. Such stresses can not be measured by the ordinary techniques of the X-ray structural analysis, since size of the coherent scattering zone is closed to the interatomic spacing. Therefore, high curvature zones of the lattice do not participate in the formation of diffraction pattern, and by the X-ray structural analysis methods it is possible to measure only the internal stresses of less defective regions of the material microstructure.

We have to note the presence of slightly raised diffuse background on the microdiffraction pattern (Fig. 10) that implies about existence of amorphous component. However, X-ray pattern of the given coating does not have an expressed X-ray halo. Therefore we assume that amorphization of a part of the coating basically occurs in the foil due to long-term etching by Ar ions (12 hours, the beam energy is 5 keV).

Due to the substantial thickness of the coating (150 μm) the conjugation problem of the high-strength and brittle surface film with the main volume of material with lower strength and high plasticity is absent. Deformation process passes on the same structural level all over the whole coating volume and the transition to the substrate layer. Basically, structure of PG-19N-01 coating is a nanocrystalline one along its whole thickness with small volume fraction (of the order of 15%) of intermetallic CrNi_3 microcrystallites. We assume that the structure and phase state of the coating is determined by the following factors: deformation influence of plasma jet, distribution of temperature profile in the coating material, and non-uniform concentration of elements in the coating.

Phenomenon of the formation in the coating material of the areas, which contain nanograins with different crystallographic orientation, discovered in PG-19N-01 coating is very important. It is seen in Fig. 12a that the given region is formed on the defect with increased surface boundary energy that is typical for the observed areas with nanograins. We suppose that for initiation of the areas with ordered nanograins, the presence of additional defect energy besides the free energy gain due to the ordering of atoms is profitable in the given case. The fact of nanostructure formation in the coatings deposited by the plasma detonation method is new though such assumptions were expressed earlier. Nanostructures are stable at room temperatures, are observed in coating foils deposited some months and even years ago.

During air cooling of the coating deposited by the plasma detonation method the decay of supersaturated solid solution based on Ni occurs. This solution has non-uniform concentration of chemical elements due to non-uniform particle distribution of the coating powder. Powder particles were melted while depositing, and displacement of Fe atoms from the substrate to the surface occurred as well. We assume that microscopic regions of γ -phase with the same orientation of crystal lattice are formed during cooling. Coherent binding between arisen new regions with ordered atomic arrangement and ambient volumes of initial unordered solid solution generates distortions in crystal lattice that is appeared in the hardness increase. Appearance of

point reflexes (Fig. 12c) on the ring electron diffraction pattern of the coating is the confirmation of such region formation. Formed structures are stable at room temperatures, decrease in the strength properties is not observed.

Formation of the chromium-enriched layers on the coating surface has caused concern due to the tendency of Cr to the formation of compounds with N. Increase in the hardness of the surface layer occurs in this case, but simultaneously the Cr content in the coating decreases, and as a result the corrosion resistance is deteriorated [22]. However, such phases were not discovered on the coating surface; air cooling is permissible for them. Microcrystalline intermetallics formed on the surface of PG-19N-01 coating, on the contrary, improve its corrosion and strength properties.

Structure and phase constitution of the coatings based on Ni-Cr deposited by the plasma detonation method and exposed to the treatment of an electron high-current beam also has common features. Firstly, smoothing of the surface relief and formation of the coating fine-grained structure with micron grain sizes are typical for such coatings after melting by an electron beam. Secondly, formation of the multiphase dense coatings with intermetallic hardening compounds, oxides, and carbides. Thirdly, high hardness, of the order of 5 GPa, and good corrosion resistance in sea water.

5. CONCLUSIONS

By the TEM methods we have revealed the formation of nanocrystalline γ -phase based on Ni and microcrystalline CrNi_3 phase (the crystallite size is from 50 to 150 nm) in PG-19N-01 coating before irradiation, extensive microstructure defects, and areas consisting of nanoregions (the nanograin size is 2-3 nm) with different crystallographic orientation of the lattice. By the microelectron diffraction patterns we have determined the parameters of micro- and nanocrystalline phases: 3,5235 Å ($a = 3,5520$ Å by the XRD data) and 3,5303 Å ($a = 3,5250$ Å by the XRD data), respectively. We have assumed that nanostructure with crystallographically disoriented nanograins is formed in the coating for the mechanical stress relief.

Layered structure of the coatings deposited by the plasma detonation method is established for certain. Thin layer (its thickness is not more than 50 μm), which contains oxides, carbon, or carbides, is formed on the surface of the coatings, as well as the phases with coating elements, which are poor soluble at high temperatures (Cr is such element in the given case). The main coating layer has sufficiently uniform phase structure, it is the γ -phase in the given case; solid solution based on Ni; and also the α -phase based on Fe, which obviously penetrates from the substrate side; in this case parameter of the α -phase in the coating is changed in comparison with the substrate. Probably, penetration of Fe into coating material is conditioned by the radiation-induced diffusion.

Fine-grained microstructure with high hardness, of the order of 5 GPa, is formed in the coatings after irradiation; coatings possess good adhesion to the substrate and corrosion resistance in sea water: high corrosion potential $\varphi_{\text{cor}} = -0,49$ V and low corrosion rate $i_{\text{cor}} = 2,2$ mm/h for PG-19N-01 coating. All coatings become multiphase with intermetallic strengthening compounds, oxides, and carbides. Improvement of the coating properties after treatment by an electron beam is achieved both due to phase transformations and roughness smoothing of the coating surface during melting. Described in the

given work techniques of the coating deposition and modification by electron irradiation can be recommended to obtain the corrosion-stable solid coatings.

The results obtained allow to present the simplified model of the PG-19N-01 coating structure before irradiation as a duplex Cr-Ni coating; thickness of Cr layer is about 50 μm . This model will be the basis for calculation of temperature profiles under electron irradiation. Comparison of the calculated temperatures and phase diagrams of Cr-Ni will allow to suggest about phase composition of the coating depending on the parameters of an electron beam during irradiation.

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