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APPLICATION OF PLASMA-POWDER AND ELECTRIC ARC COATINGS TO INCREASE TRIBOCORROSION RESISTANCE OF STEELS IN CHLORIDE-CONTAINING MEDIA WITH HYDROGEN SULFIDE AND AMMONIA

V.I. Pokhmurskyi[1], **M.S. Khoma**[1], **I.O. Ryabtsev**[2], **Ye.F. Pereplyotchikov**[1], **V.A. Vynar**[1], **V.M. Gvozdetskyi**[1], **Kh.B. Vasyliv**[1], **N.B. Ratska**[1], **V.R. Ivashkiv**[1] and **Ye.M. Rudkovskyi**[1]
[1]G.V. Karpenko Physical-Mechanical Institute of the NAS of Ukraine
5 Naukova Str., 79060, Lviv, Ukraine. E-mail: khomams@gmail.com
[2]E.O. Paton Electric Welding Institute of the NAS of Ukraine
11 Kazymyr Malevych Str., 03150, Kyiv, Ukraine. E-mail: office@paton.kiev.ua

The work was performed within the framework of the complex program of the NAS of Ukraine «Problems of life and safe operation of structures, constructions and machines», 2011–2020. The corrosion and tribocorrosion characteristics of plasma-powder and electric arc coatings on pipe steels in chloride-containing media with hydrogen sulfide and ammonia were studied. It was established that the corrosion resistance of the coatings applied by plasma-powder surfacing and electric arc spraying is improved with an increase in pH of the solution. It was shown that the coatings deposited by the plasma method with the powder of 08Kh17N35S3R alloy were the most resistant to corrosion and mechanical fracture in these media. It was established that electric arc coatings sprayed from the flux-cored wire 75Kh19R3S2 reduce the corrosion current density of carbon steels in a hydrogen sulfide solution by 40 %. In the same medium on the surface of the coatings sulfide compounds are formed, which act as a solid lubricant during friction, facilitating a reduction in wear of the material by 40−42 %. The electric arc coatings produced by the flux-cored wire 75Kh19R3S2 were proposed to be used to restore damaged surfaces of parts and protect them from corrosion and abrasive wear in the hydrogen sulfide media. 14 Ref., 5 Tables, 4 Figures.

Keywords: plasma-powder surfacing, electric arc coatings, corrosion, tribocorrosion, chlorides, hydrogen sulfide, ammonia

Corrosion and mechanical wear occurs during friction of parts in aggressive media and is often the reason for reducing the life of many parts of equipment and structures in the oil, gas, petrochemical and municipal industries, as for example, stop valves, end seals, rolling bearings, etc. [1−3].

The main methods for restoration and improvement of serviceability of surfaces of parts operated under the conditions of corrosion and mechanical wear include plasma-powder surfacing [4, 5] and electric arc spraying of protective coatings from flux-cored wires [3, 6−8].

Plasma-powder surfacing is used to improve the physical and mechanical characteristics of working surfaces and restoration of worn parts. In particular, using this method the surfaces of parts of stop valves are deposited: gate valves, seats, rods and other parts of oil and gas equipment [4−10]. The use of powders based on Ni, Fe, Cr, B, Si, etc. allows regulating the chemical composition of deposited layers and expands the range of their functional properties [6−8].

Electric arc metallization (EAM) using flux-cored wires is one of the widespread methods of deposition wear-resistant coatings, the cost of which is 2−3 times lower than that of plasma-powder surfacing [6]. During melting of flux-cored wires in the electric arc a melt is formed, which during dispersion into droplets, forms an electric arc coating with a high structural heterogeneity. The combination of hard and soft components provides their high wear resistance. To improve the corrosion and tribocorrosion resistance of coatings, to the charge of flux-cored wires chromium compounds are added and to reduce the porosity of the sprayed layer, FeMn and FeSi are introduced, which form a low-melting eutectic. Comprehensive investigations of corrosion and tribocorrosion properties of coatings with different chemical composition, produced by plasma-powder surfacing

V.I. Pokhmurskyi — http://orcid.org/0000-0003-1042-829X, M.S. Khoma — https://orcid.org/0000-0002-0951-3975,
I.O. Ryabtsev — https://orcid.org/0000-0001-7180-7782, V.A. Vynar — http://orcid.org/0000-0002-5314-7052

Table 1. Chemical composition of powders for plasma-powder surfacing, wt.%

Powder grade	C	Cr	Si	Mn	Ni	Fe	B
PR-06Kh17N80S3R3	0.6–0.9	15–17	2.7–3.7	–	Base	≤5.0	2.3–3.0
PR-01Kh17N8S6G	0.05–0.12	15–18	4.8–6.4	1–2	7–9	Base	–
PR-08Kh17N35S3R3	0.8	18	3.5	≤ 1.0	35	35	2.5

and electric arc spraying of powder materials have a significant importance for restoration of serviceability and increasing the life of equipment operated in corrosive-active media at the presence of hydrogen sulfide, chlorides and ammonia.

The aim of this work is to investigate the possibility of using plasma-powder and electric arc coatings to restore serviceability and increase the service life of friction units in the equipment of oil and gas, refining and municipal industries, which are operated in corrosive media.

Investigation procedure. Plasma-powder surfacing, the technology of which is developed by the PWI, was performed in the universal installation OB2184 on the basis of the device A1756 [4, 5]. The chemical composition of powders for surfacing is given in Table 1. Surfacing mode: current is 250–300 A, powder feed is 3 kg/h, deposition rate is 6 m/h, amplitude of oscillations of the plasmatron is 10 mm, their frequency is 45 min^{-1}. The consumption of carrier, plasma-forming and shielding gases (argon) is 3 l/h, 2 and 12 l/min, respectively. The beads deposited under these conditions, had a width of 25–35 mm and a height of 6.0–6.6 mm during two-beads surfacing.

Electric arc metallization was performed according to the technology developed by the G.V. Karpenko PMI [3, 6–9]. The coatings were produced by spraying electrode flux-cored wires PD-60Kh15R2GS and PD-75Kh19R3S2 with the use of the electric arc metallizer EM-17 with a modified spraying system, where an electric arc burns in the channel of the spraying head, which allows producing fine-dispersed coatings. Surfaing conditions: current is 150 A, operating voltage is 32 V, distance from the nozzle to the spraying surface is 150 mm, compressed air pressure is 0.65 MPa. Sheath of flux-cored wires is made of steel 08kp (rimmed) (0.05–0.11 % C; ≤ 0.02 % S; 0.025–0.5 % Mn; 0.04 % P), chemical composition of the charge is given in Table 2.

Corrosion-mechanical wear of materials was studied in the installation of friction with a reciprocating motion of the indenter according to the scheme ball-plane [2]. The counterbody is a corundum ball with a diameter of 9 mm. The applied normal load is 10 N, the length of the friction track is 16 mm, the speed of the indenter movement is 0.003 m/s. The specimens for investigations were polished to a roughness R_z = = 2.5 μm. The nature of the change in the investigated parameters during tribocorrosion tests was recorded by an analog-digital device using a personal computer with a measurement step of 0.25 s. The degree of wear of the specimens after friction was determined by the width of the track formed as a result of interaction of the ball with the surface of the coating, the hardness of which is significantly lower than that of corundum.

Tb le 2 Chemical composition of charge of flux-cored wires, wt.%

Powder wire grade	Composition of charge
PD-60Kh15R2GS	FeCr 72 %; B_4C 13 %; FeSi 10 %; FeMn 5 %
PD-75Kh19R3S2	Cr 72 %; FeSi 13 %; B_4C 10 %

To determine the elastic-plastic properties of structural components of the produced coatings, in particular Meyer microhardness, the method of dynamic indentation was used. For this purpose the device Micron-gamma was applied [11].

Electrochemical investigations under static conditions and during friction were performed using the potentiostat IPC-ProM. The electrode potentials of the specimens in corrosive media were measured relative to the saturated chloride-silver reference electrode. The auxiliary electrode is platinum. The media for corrosion and tribocorrosion tests are: free-aerated 3% solution of NaCl, pH 7; 3 % solution of NaCl + 0.025 % of NH_4OH, pH 9–10; 3% solution of NaCl + H_2S (saturated), pH 4.

The microstructure of the surfaces was studied by metallographic method in a scanning electron microscope EVO 40XVR with a system of micro-X-ray spectral analysis using an energy-dispersion spectrometer INCA ENERGY 350.

Results of investigations and their discussion. *Plasma-powder surfacing*. Deposited layers (Figure 1) from the powders PR-01Kh17N8S6G (base Fe), PR-06Kh17N80S3R3 (base Ni) and PR-08Kh17N35S3R3 (base Ni–Fe) having different composition and structure were investigated. It was found that they have a heterogeneous structure, which determines their micromechanical, corrosion-electrochemical and tribocorrosion properties. The deposited iron-based layer has two structural components with a microhardness of 6.0–6.5 and 7.5–8.0 GPa. In the nickel-based layer after surfacing, three components with a microhardness of 6.0–7.0, 7.0–8.5 and 15 GPa are formed. The highest microhardness (~ 15 GPa) is predetermined by the presence of borides of type FeCrB. The coating with

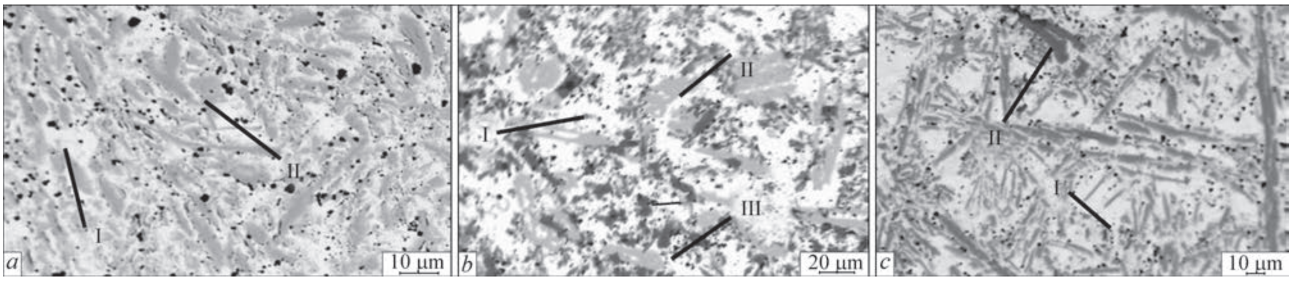

Figure 1. Microstructure of layers deposited by the method of plasma-powder surfacing: *a* — 01Kh17N8S6G (Fe base); *b* — 06Kh17N80S3R3 (Ni base); *c* — 08Kh17N35S3R3 (Ni–Fe base)

an iron-nickel base contains two components with a microhardness of 7.0–7.5 and 10.1–12.2 GPa. Nickel and nickel-iron based coatings, as compared to iron-based coatings, are characterized by a higher microhardness of structural components, which is associated with the presence of boron and a higher concentration of carbon in the powders (0.6–0.9 % against 0.12 %, respectively).

The electrochemical behavior of deposited layers in corrosion-active chloride-containing media with the addition of hydrogen sulfide and ammonia was studied (Table 3). It was found that application of plasma-powder layers makes it possible to reduce the corrosion current density of steel 17G1SU, which was chosen for comparison by about 2 orders. With an increase in the hydrogen index of the medium from pH4 to pH9, it is observed that the corrosion current density of alloys 01Kh17N8S6G and 06Kh17N80S3R3 is decreased by 7–15 %, and that of 08Kh17N35S3R3 is decreased by three times. The corrosion rate is determined by anodic processes in a solution of 3 % of NaCl + NH_4OH and cathodic processes in 3 % of NaCl and 3 % of NaCl + H_2S. In terms of corrosion resistance in the investigated media, the layer deposited by the powder on Ni–Fe base is inferior to two other, its corrosion current density is $(0.47–1.60)\cdot10^{-3}$ against $(0.56–0.80)\cdot10^{-3}$ mA/cm^2. However, under conditions of tribocorrosion in pair with a ceramic corundum ball coating based on Ni–Fe has the lowest values of the coefficient of friction and material loss in all the investigated media (Table 4), which indicates its higher resistance to fracture. In a hydrogen sulfide medium, the width of the wear track of this coating and the friction coefficients are 3–4 times lower than the original steel, and in neutral and alkaline solutions — by 30–50 %, which indicates a significant effect of corrosion products on friction and wear. In particular, during friction sulfide films formed on the friction surface in a solution of 3 % of NaCl + H_2S, perform the function of lubricant, which reduces the coefficient of friction and the width of the wear track.

A clear relationship between tribotechnical characteristics and the rate of corrosion of deposited layers is observed. As pH of the medium grows, the density of corrosion currents for layers with different base decreases, and the coefficient of friction and material losses increase (Table 3). The mechanisms of contact interaction of layers are determined by structural heterogeneity and tribological characteristics of separate structural components. Thus, during contact interaction of surface layers of 06Kh17N80S3R3 with a ceramic

Table 3. Density of corrosion currents, coefficient of friction and width of friction tracks of the layers deposited by the method of plasma-powder surfacing in different media

Medium	01Kh17N8S6G (base Fe)			06Kh17N80S3R3 (base Ni)			08Kh17N35S3R3 (base Ni–Fe)		
	i_{cor}, mA/cm^2	*B*, μm	μ	i_{cor}, mA/cm^2	*B*, μm	μ	i_{cor}, mA/cm^2	*B*, μm	μ
3 % of NaCl+H_2S (pH 4)	0.00075	180	0.10	0.0006	210	0.13	0.0016	140	0.09
3 % of NaCl (pH 7)	0.00065	190	0.21	0.0008	230	0.16	0.0019	160	0.10
3 % of NaCl+0.025 % NH_4OH (pH 9)	0.00065	260	0.41	0.00056	300	0.35	0.00047	190	0.31

Table 4. Coefficients of friction and width of wear track of electric arc coatings in different media

Medium	60Kh15R2GS				75Kh19R3S2			
	E, mV	*i*, mA/cm^2	μ	*B*, μm	*E*, mV	*i*, mA/cm^2	μ	*B*, μm
3 % of NaCl + H_2S (pH 4)	–586	0.053	0.30	350	–626	0.052	0.25	240
3 % of NaCl (pH 7)	–525	0.034	0.38	510	–525	0.024	0.30	480
3 % of NaCl + 0.025 % NH_4OH (pH 9)	–468	0.024	0.50	490	–468	0.022	0.55	400

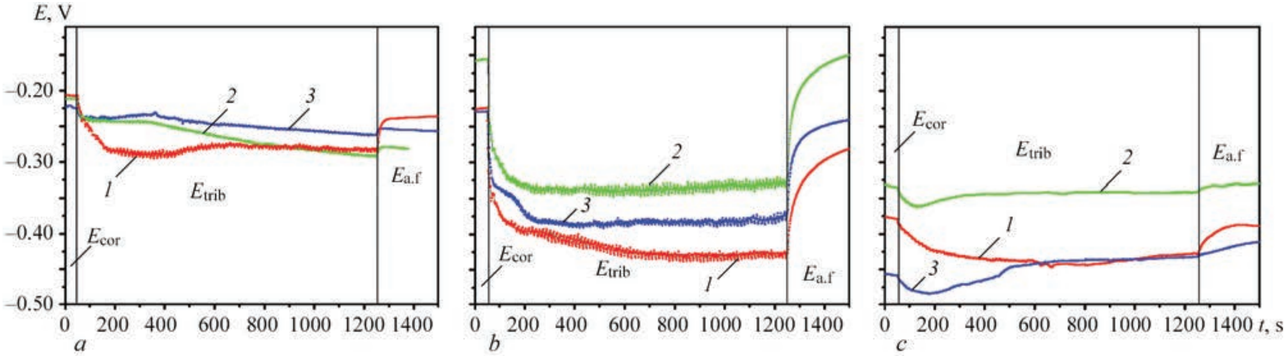

Figure 2. Change of electrode potentials of the surface of alloys during friction in 3 % of NaCl (*a*), 3 % of NaCl + NH_4OH (*b*), 3% of NaCl + H_2S (*c*): coatings based on Fe (*1*), Ni (*2*) and Ni–Fe (*3*)

ball, brittle components with a high microhardness (15 GPa) enter the friction zone. This is manifested in low values of the friction coefficient, but more intensive wear according to the mechanism of microcutting, the losses of material are approximately 45% higher than in the coating on iron-nickel base. In the matrix of layers of 01Kh17N8S6G and 08Kh17N35S3R3, the brittle component is absent and solid phases are uniformly distributed in the plastic matrix, which corresponds to the Charpy–Bochvar rule [12], and the contact interaction takes place in the absence of abrasive wear element, which explains a high resistance of tribocorrosion.

By changing the electrode potentials during corrosion-mechanical wear, it is possible to qualitatively evaluate the fracture and formation of secondary structures in the zone of frictional interaction [13]. It is shown (Figure 2) that the largest difference between the corrosion potentials in the initial state (E_{cor}), tribocorrosion during friction (E_{trib}) and surface potentials after friction ($E_{a.f}$) for all deposited layers is characteristic for the medium of 3 % of NaCl + NH_4OH. This indicates the formation of dense secondary structures on the surface of the contact zone, which are destroyed with the beginning of a frictional interaction. During steady friction, the secondary structures are intensively destroyed and restored, which is manifested in the tribopotential oscillations, which indicate a high rate of surface repassivation and fracture of the material according to the mechanism of oxidative wear. As pH index of the medium decreases, the rate of repassivation processes is reduced, which are minimal in the hydrogen sulfide medium. The difference between these potentials is insignificant and local oscillations of the tribopotential are almost absent, which indicates the incompatibility of the initial surface films of corrosion products. The coefficient of friction under such conditions is the lowest as compared to other media. The frictional interaction of layers with the counter-body occurs from the formation of secondary structures that reduce the adhesion between the surfaces.

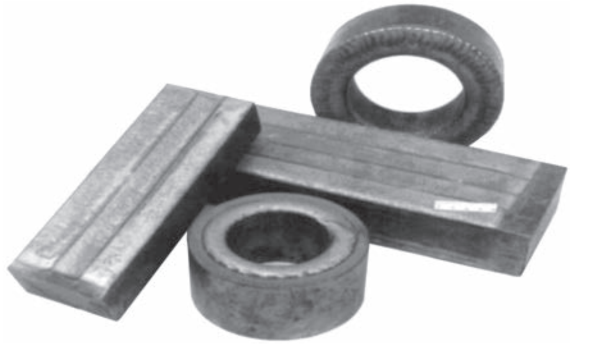

Figure 3. Parts of stop valves deposited by the plasma method using the powder PR-08Kh17N35S3R

It was found that the difference between the potentials of corrosion, tribocorrosion and passivation correlates with the hardness of the coatings. In particular, this is clearly observed when comparing the material 01Kh17N8S6G (Ni–Fe base) and 08Kh17N35S3R3 (Ni–Fe base) in the investigated media. The biggest difference between the potentials as well as local oscillations of the tribopotential are typical to the deposited layer of complex carbides, which is associated with a greater surface damage because of a lower hardness in the surface layers of the coating.

Plasma surfacing from the powder PR-08Kh17N-35S3R was proposed for depositing protective layers on a surface of parts of stop valves (Figure 3) with the aim of improving their corrosion and tribocorrosion resistance in aggressive media and it was used at the PJSC «Konotop armature plant».

Electric arc spraying. To restore worn or damaged surfaces and improve the service characteristics of parts, thermal spraying is widely used [3, 6–9]. This method makes it possible to significantly extend the life cycle of parts by creating a layer of coatings with the specified properties on their surface. During spraying, thermal buckling of a part does not occur and physicochemical properties of the base material are not changed. The ability to repair parts instead of replacing them helps to reduce costs and increase the efficiency of production.

The coatings produced by electric arc spraying from the flux-cored wires PD-60Kh15R2GS and PD-75Kh19R3S2 were investigated. They have a heterogeneous structure consisting of a martensitic

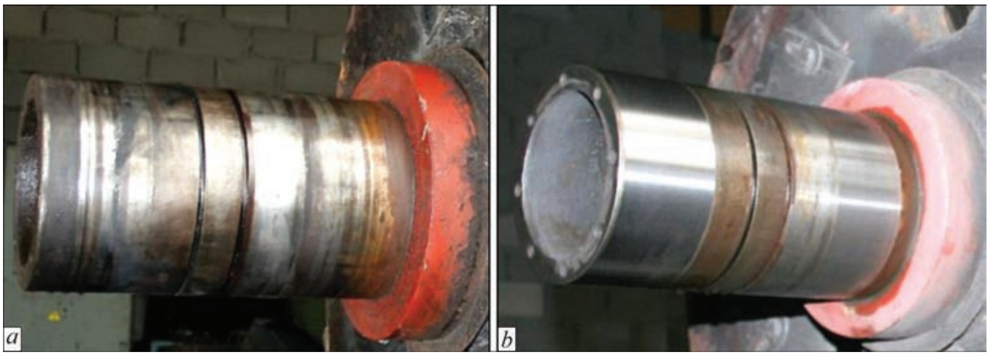

Figure 4. General appearance of damaged shaft of centrifuge of wastewater treatment plants in the initial state (*a*) and after electric arc spraying and grinding (*b*)

matrix strengthened by fine-dispersed inclusions of FeCrB and $FeCr_2B$ borides. The hardness of the coatings is *HV* 545–545, cohesive strength is 140–150 MPa [3]. The presence of ferrochrome-boron and chromium in the charge provides a high content of chromium in the coating.

The electrochemical characteristics of sprayed coatings in the media containing ammonia, hydrogen sulfide and chlorides were investigated. On the obtained polarization curves passivation regions are absent, which indicates electrochemically active dissolution of materials. After electric arc spraying, the values of the electrode potentials in all corrosive media are shifted to the region of positive values by 60–70 mV. The corrosion currents density of sprayed coatings in hydrogen sulfide and chloride solution is reduced by 40 % as compared to the initial material (Tables 4, 5). In ammonia solution, the corrosion currents of the base material and coatings have the lowest values. The corrosion rate of electric arc coatings is controlled by cathode processes. It was established that the corrosion rate of coatings from PD-75Kh19R3S2 is lower than from PD-60Kh15R5GS, which is associated with a higher concentration of chromium (Tables 4, 5).

The width of the friction track and the values of the friction coefficients of both electric arc coatings are the lowest in 3 % of NaCl + H_2S, and the highest are in 3 % solution of NaCl. The tribological characteristics of coatings from PD-75Kh19R3S2 are better than those from PD-60Kh15R2GS, in particular, in 3 % of NaCl + H_2S its wear is lower by a third (Table 4). The parameters of friction and wear of coatings are determined by their chemical composition, heterogeneity of the structure, ratio of strength characteristics of its components, relief, etc. The most effective electric arc coatings were revealed in the solution of 3 % of NaCl + H_2S, where the width of the wear track after spraying decreased by 40–42 % (Tables 4, 5).

The highest values of friction coefficients were revealed during friction of coatings in a medium containing ammonia. Probably, in the solution on the surface secondary structures are formed, which are destroyed during friction and play the role of abrasive. This facilitates an increase in the coefficient of friction and wear of the material. Depassivating chlorine ions in the medium initiate corrosion of coatings and the combined action of corrosion and mechanical factors during friction leads to a decrease in wear resistance. In the hydrogen sulfide medium, the wear and friction coefficients of electric arc coatings are the lowest, which is associated with the formation of sulfide-containing films on the surface, which act as a solid lubricant during friction, reducing the adhesive component of contact interaction, which reduces friction and wear coefficients [2, 13, 14]. In addition, during friction, sulfides can fill the pores in the coating, improving its homogeneity, which facilitates an increase in the corrosion resistance of the material.

Electric arc coatings produced from the flux-cored wire PD-75Kh19R3S2 were proposed to be used to restore damaged surfaces of parts and protect them from corrosion and abrasive wear in hydrogen sulfide media. The coatings were deposited to the surface of the shafts in the centrifuges of the wastewater treatment facilities of LMKP Lvivvodokanal and passed the test and industrial inspection.

Table 5. Electrode potentials, corrosion current density, friction coefficient and width of friction tracks of steel 17G1SU (base) in different media

Medium	*E*, mV	*i*, mA/cm^2	*B*, μm	μ
3 % of NaCl + H_2S (pH 4)	–660	0.08	580	0.28
3 % of NaCl (pH 7)	–580	0.04	310	0.25
3 % of NaCl + 0.025 % NH_4OH (pH 9)	–530	0.025	360	0.41

Conclusions

1. Corrosion and tribocorrosion characteristics of plasma deposits from the powders based on iron (PR-01Kh17N8S6G), nickel (PR-06Kh17N80S3R3) and Fe–Ni system (PR-08Kh17N35S3R3) and coatings produced by electric arc spraying using the wires PD-60Kh15R2GS and PD-75Kh19R3S2 in the media containing chlorides, hydrogen sulfide and ammonia were investigated.

2. In the deposits produced from the powders 01Kh17N8S6G and 08Kh17N35S3R3, two structural components with a microhardness of 6.0−6.5 and 7.5−8.0 GPa and 7.0−7.5 and 10.1−12.2 GPa were revealed. The deposited layer from the nickel-based powder PR-06Kh17N80S3R3 has three components with a microhardness of 6.0−7.0, 7.0−8.5 and 15 GPa. An increased microhardness of structural components is associated with the presence of boron and a higher concentration of carbon in the powder. The highest microhardness (~ 15 GPa) is predetermined by the presence of borides of FeCrB type.

3. The coatings produced by electric arc spraying from the flux-cored wires PD-60Kh15R2GS and PD-75Kh19R3S2 have a structure consisting of a martensitic matrix strengthened by fine-dispersed inclusions of borides FeCrB and $FeCr_2B$. The hardness of coatings is *HV* 545−545, cohesive strength is 140−150 MPa.

4. As a result of tests it was shown that deposits from the powder based on Fe−Ni and electric arc coatings from the wire PD-75Kh19R3S2 have the highest resistance to corrosion-mechanical wear in corrosive-active media.

5. It was found that depositing layers by the plasma method from the powder PR-08Kh17N35S3R allows reducing the corrosion rate by approximately 2 orders in the media containing chlorides, ammonia and hydrogen sulfide. During friction in a hydrogen sulfide medium, the width of the wear track and the friction coefficients are 3−4 times smaller than that of the initial steel, and in neutral and alkaline solutions — by 30−50 %.

6. Plasma-powder surfacing by the powder PR-08Kh17N35S3R was proposed for depositing protective coatings on the surface of gate and stop valves in order to improve their corrosion-mechanical properties and it was used at the PJSC «Konotop Armature Plant».

7. It was established that the corrosion rate of electric arc coatings sprayed from the flux-cored wire PD-75Kh19R3S2 in ammonia solution is commensurated with the corrosion rate of carbon steel. In chloride and chloride-hydrogen sulfide solutions, deposition of coatings reduces the corrosion rate of steel by almost 40 %. In the presence of hydrogen sulfide in the medium, on the surface of the coatings sulfide compounds are formed, which act as a solid lubricant during friction, reducing the adhesive component of the contact interaction, which facilitates the reduction in wear of the material by 40−42 %.

8. Electric arc coatings produced from the flux-cored wire PD-75Kh19R3S2 were proposed to be used to restore damaged surfaces of parts and protect them from corrosion and abrasive wear in hydrogen sulfide media. The coatings were deposited on the surface of the shafts in the centrifuges of the wastewater treatment plants of LMKP Lvivvodokanal and successfully passed the test and industrial inspection.

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