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DEVELOPMENT OF ELECTRIC ARC SPRAY COATINGS FOR RECONDITIONING RODS OF HYDRAULIC CYLINDERS OF MINING EQUIPMENT, USING FLUX-CORED WIRES*

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The paper outlines the main requirements to flux-cored wires based on ferroalloys of Fe–Cr–C and Fe–Cr–B systems with more than 12 wt.% chromium for electric arc spraying of wear- and corrosion-resistant coatings. It is found that, unlike steel, presence of 12 wt.% chromium in flux-cored wire charge does not ensure corrosion resistance of coatings in neutral water solutions. The causes for that were studied. It is experimentally established that corrosion resistance of coatings containing more than 12 wt.% chromium is inversely proportional to their chemical microheterogeneity. High effectiveness of application of coating impregnation with inhibited 3 % solution of Hydroway 1060 to prevent aggressive environment penetration through pores in the coating to the substrate is demonstrated. Synergistic compositions of sodium benzoate + benzyl benzoate inhibitors were developed, which provide up to 99.14 % degree of corrosion protection of the coating steel substrate. 12 Ref., 1 Table, 8 Figures.

Keywords: *arc spray coatings, flux-cored wires, ferroalloys, chemical heterogeneity, corrosion resistance, oxide, carbide, boride, inhibitor*

A considerable part of structural elements of critical machines and mechanisms, in particular, hydraulic cylinders of mine, mining and utility equipment, are exposed to corrosion-abrasion wear during long-term operation under stringent loading conditions in neutral water environments (Figure 1).

In most of the cases, electrolytical chromium plating method is used for protection from corrosion-abrasion wear. However, because of its carcinogenic wastes, alternative technologies are actively sought in industrialized countries. Leading world companies (Metco, Castolin, TAFA, Deloro, Nanosteel) apply thermal coating technologies for this purpose [1–3]. Among these technologies electric arc spraying of coatings is characterized by high productivity at the lowest cost that attracts particular interest [4–6]. Solid stainless wires of 40Kh13 or 08Kh18N10T type are often used to form corrosion-resistant electric arc spay coatings (EASC). However, coatings from them are characterized by low hardness and wear resistance and quite high cost [7, 8].

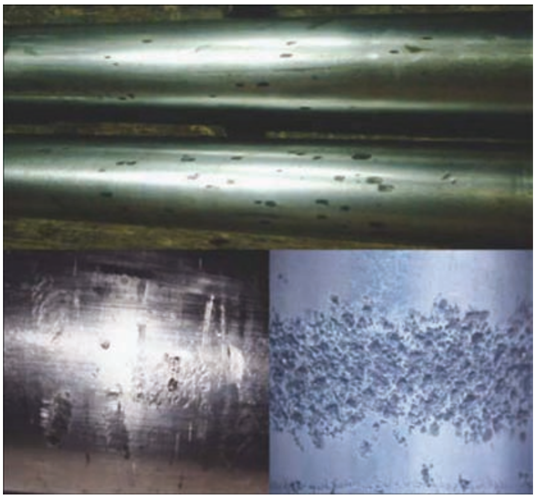

Figure 1. Damage of rod surface: local corrosion, bruises, burrs, abrasive wear

Methodological aspects of research. Flux-cored wires (FCW) of Fe–Cr–C and Fe–Cr–B systems were manufactured in a sheath of low-carbon steel 08 kp (rimmed). Used as charge materials were powders of high-carbon ferrochromium, ferrochromeboron, chromium, ferrosilicium, ferrophosphorus and self-fluxing alloy PG-10N-01. Coefficient of FCW filling was equal to 25–27 %. Electric arc spray coatings 1.2–1.5 mm thick were applied with FMI-2 metallizer from 08Kh18N10T steel and FCW of optimized compositions of 1.8 mm diameter on samples from 12Kh1MF steel. Modes of coating deposition were as follows: current of 150 A, arc voltage of 32–34 V.

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Spraying was performed by an air jet under pressure of 0.4–0.8 MPa from 150 mm distance.

Completeness of fusion of the charge and sheath in coatings (chemical microheterogeneity) was assessed by the coefficient of microheterogeneity (K_{MH}) introduced by us [9], and by electrochemical procedure of moving capillary [10]. K_{MH} coefficient characterizes the deviation of the content of each of the alloying elements within an individual lamel from its average content in the coating. In order to determine K_{MH} coefficient, integral content of a specific alloying element in a section of 100 mm^2 area was compared with its local content in rectangular sections of 35.10^{-4} mm^2 area, which by their size are comparable with average area of lamels in coatings. Determination of coating K_{MH} was performed in not less that 10 sections, located at a distance of minimum 5 mm from each other by the width of the spraying spot, which was equal to 25–30 mm. K_{MH} value of these sections was averaged.

Corrosion properties were determined in potentiodynamic mode in SVA-1BM unit by three-electrode schematic: working electrode (sample) — reference electrode (silver-chlorine of EVL-1M1 type) — auxiliary electrode (platinum). Rate of change in potential was equal to 2 mV/s. Corrosion currents were determined by extrapolating linear sections of polarization curves to corrosion potential.

Investigation results and their discussion. When EASC are produced by spraying FCW of Fe–Cr–C and Fe–Cr–B systems, no common pool is formed and chromium-containing charge does not completely dissolve in the steel sheath melt, because of the transience of wire melting processes. This results in strong chemical microheterogeneity of the coatings that significantly influences their corrosion resistance.

It is found that unlike solid consumables, presence of 12 wt.% chromium in FCW charge does not provide corrosion resistance of EASC in neutral water environments. This is caused by the following:

- non-uniform distribution of chromium in coating lamels, because of their high chemical microheterogeneity. Drops, forming from FCW melt (unlike drops formed from solid wire), have markedly different composition, which is determined by the completeness of fusion of charge components with each other and with the steel sheath;
- transition of a certain part of chromium into carbides (for Fe–Cr–C alloying system) and into borides (for Fe–Cr–B alloying system) that essentially reduces its content in the coating solid solution;
- depletion of chromium content in the coating solid solution as a result of oxide formation from a certain part of it.

It is experimentally established that during spraying of EASC with FCW of Fe–Cr–C and Fe–Cr–B systems, coatings of the following three types can form, depending on the completeness of fusion of FCW charge and its steel sheath (Figure 2). FCW charge does not fuse with the steel sheath melt, and chemically microheterogeneous coating forms, which consists of lamels formed separately from the steel sheath with inclusions of refractory charge particles (Figure 2, *a*). Here, the lamels differ strongly by their chemical composition and chromium concentration in them. K_{MH} for this type of coatings practically is in the range of 0.3–0.99. This is type I. FCW charge is partially fused with the sheath. In this case, coating lamels differ less by chemical elements content, in particular, also by chromium concentration. For this coating K_{MH} can be in the range of 0.1–0.3 (Figure 2, *b*). This is type II. Charge components are completely fused with each other and its sheath, forming chemically homogeneous melt (Figure 2, *c*). This is type III. In this case, FCW calculated chemical composition corresponds to actual composition of each formed coating lamel by more than 90 %, and K_{MH} will be less than 0.1.

It is found that to provide corrosion resistance to coatings from FCW in neutral water environments their microstructure should correspond to third coating type (Figure 2, *c*) and should have K_{MH} equal to not less than 0.1 by chromium.

As shown by experimental data, presence of just high-carbon ferrochromium (FCW 140Kh14) does

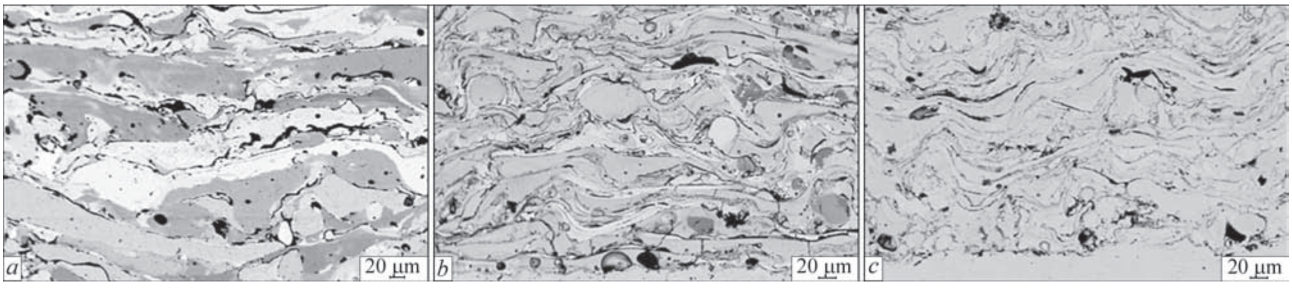


Figure 2. EASC typical structures, depending on the degree of fusion of FCW charge components with its sheath: *a* — just high-chromium charge; *b* — high-chromium charge with addition of PG-10N-01; *c* — high-chromium charge with addition of ferrosilicium and ferrophosphorus

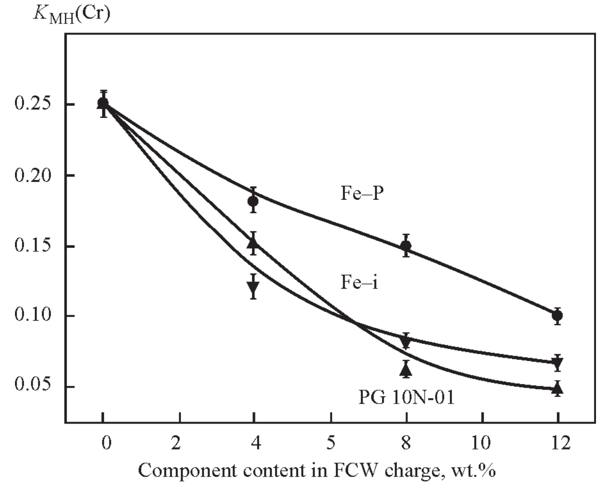


Figure 3. Influence of the content of FCW charge components on coefficient K_{MH} (Cr)

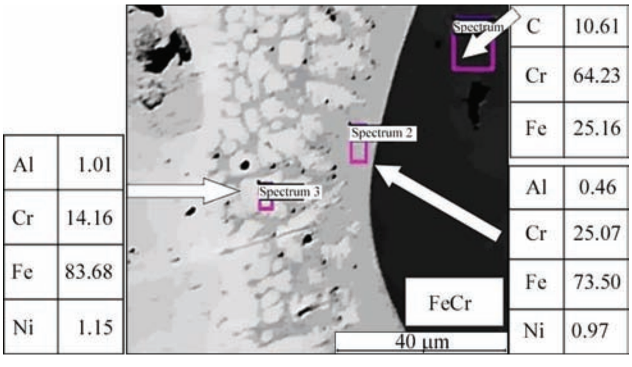
not provide sound fusion of FCW charge and sheath (Figure 2, *a*). It is found that powders of ferrosilicium (Fe–Si), ferrophosphorus (Fe–P) or self-fluxing alloy (PG-10N-01) should be added to FCW charge (alongside ferrochromium or ferrochomeboron, which provide the required chromium content and hardness to the coating), in order to improve fusion and achieve uniform distribution of chromium in coating lamels. These powders can form low-temperature eutectics between FCW charge components and its sheath. It was found that this allows reducing chemical heterogeneity of coatings to the level of K_{MH} (Cr) = 0.05 (Figure 3).

It is experimentally established that eutectic melting of charge components promotes formation of a considerable quantity of low-melting melt inside FCW, in which refractory components of ferrochromium are dissolved (Figure 4). This also provides smelting of the melt with the inner surface of FCW sheath already at 2–3 mm distance from the arc active spots. As a result, chemical heterogeneity of the coatings is strongly reduced, as the time of metal staying in the liquid phase becomes longer (Figure 5).

To prevent chromium transition into oxides during drop formation at coating spray-deposition, it is proposed to add to FCW charge composition such elements as Al, Ti, Si, B in which free energy of oxide formation is smaller than that for chromium oxides, and for this reason the oxides of these elements form faster. Thus, addition of up to 2 wt.% Al or Si to FCW charge partially prevents formation of chromium-containing oxides and leads to running of alumo- and silicothermic reactions of chromium reduction from its oxides. On the whole, this promotes transition of almost entire quantity of chromium from the composition of FCW charge into the coating solid solution.

At the same time, it is impossible to prevent formation of chromium-based carbides and borides during solidification of coating drops on the sprayed surface. Therefore, the quantity of chromium which will participate in their formation should be taken into account and compensated. For FCW of Fe–Cr–C and Fe–Cr–B systems calculation formulas are proposed for determination of the quantity of chromium in them (taking into account the quantity to be consumed in formation of carbides and borides), sufficient to provide EASC corrosion resistance in neutral water environments [11]. When performing calculations by the proposed formulas, it was found that for coatings from FCW of Fe–Cr–B system it is necessary to provide greater content of chromium than for coatings from FCW of Fe–Cr–C system. After all, chromium-containing carbides form only in the coating ferritic phase, the quantity of which in the coating structure can be easily limited by FCW charge component composition, whereas chromium-containing borides in coatings from FCW of Fe–Cr–B system form in all the present phases. Performed calculations allowed optimizing the compositions of 140Kh14N2TYu FCW of Fe–Cr–C system and 70Kh20RZGS2Yu FCW of Fe–Cr–B system by the quantity of chromium in them.

Corrosion properties of coatings. Electrochemical studies showed that corrosion resistance (I_{corr}) of coatings of Fe–Cr–C system in 3 % water solution of NaCl is inversely proportional to their chemical mi-



Al	1.01
Cr	14.16
Fe	83.68
Ni	1.15

C	10.61
Cr	64.23
Fe	25.16

Al	0.46
Cr	25.07
Fe	73.50
Ni	0.97

Figure 4. Ferrochromium dissolution in the melt of 140Kh14N2TYu FCW

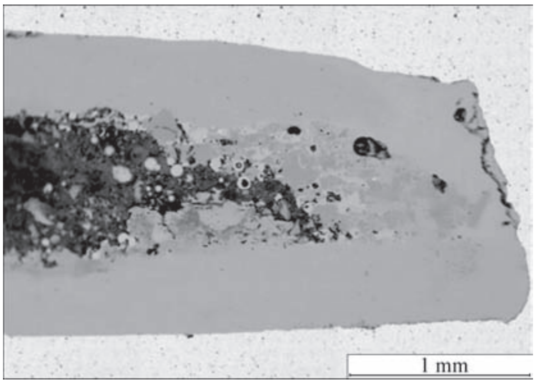


Figure 5. Influence of the content of self-fluxing alloy PG-10N-01 in FCW charge on smelting of the charge and sheath

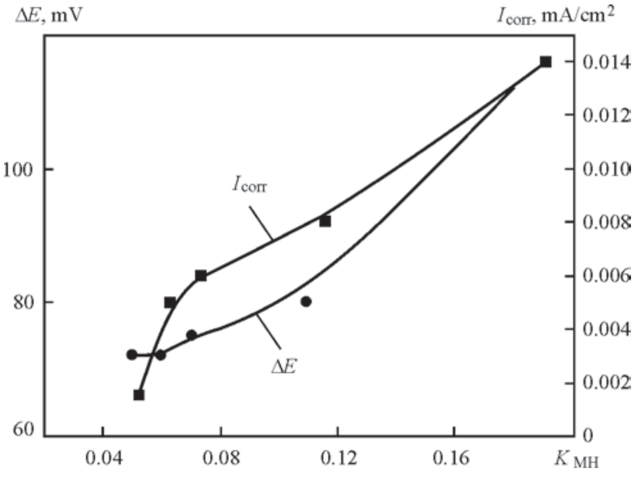


Figure 6. Dependencies of density of corrosion current I_{corr} and electrochemical microheterogeneity of coating ΔE on coefficient K_{MH} in 3 % water solution of NaCl

croheterogeneity by the content of chromium, determined by K_{MH} coefficient, as well as electrochemical microheterogeneity, determined by the technique of moving capillary, which were found to correlate with each other (Figure 6). With reduction of K_{MH} coefficient (Cr) from 0.2 to 0.05 the density of corrosion current decreases practically by an order from 0.014 to 0.0015 mA/cm^2, and comes to the level of corrosion currents of 0.0008 mA/cm^2, which were recorded for a coating, formed from stainless wire 08Kh18N10T. At the same time, it was found that increasing corrosion resistance of the coatings proper does not allow providing reliable protection of metal bases, on which coatings were formed, from the impact of corrosive environment, as a result of their natural porosity.

To prevent penetration of working environment through the pores inside the coating (to the metal base), it was proposed to pre-impregnate the coatings with mineral oil I-20, or 3 % water solution of Emulsol of Hydroway-1060 grade, which is used as working fluids in hydraulic cylinders for various purposes.

Preliminary studies indicated the need for development of effective inhibited compositions based on sodium benzoate, sodium silicate and benzyl benzoate, which are environmentally safe.

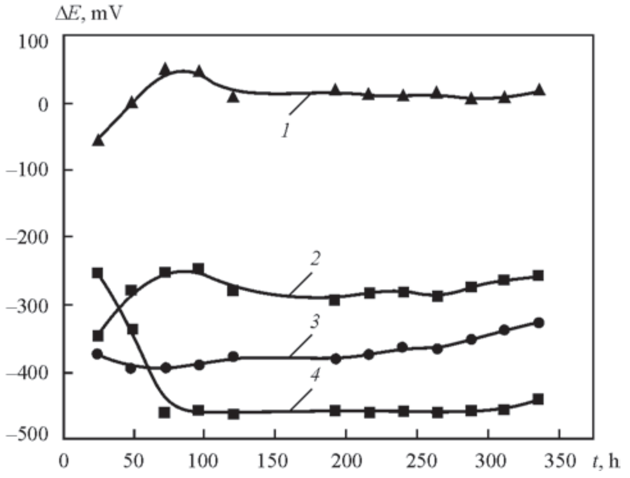


Figure 7. Change of electrode potential ΔE of coating from 140Kh14N2TYu FCW with the time of its soaking in the environment of «acid rain», impregnated with different fluids: *1* — 3 % Emulsol + SB + BB; *2* — 3 % Emulsol; *3* — I20 oil; *4* — without impregnation

At long-term testing of coatings in «acid rain» environment, their electrode potential stopped at the level of -450 mV (Figure 7), that means that the fluid had passed through the spray-deposited coating to the steel base. After coating impregnation with 3 % solution of Hydroway-1060 Emulsol its potential effectively shifts to positive values and stops at the level of –265 mV, whereas impregnation with 3 % solution of Hydroway-1060 Emulsol, inhibited by a synergistic composition from a mixture of 1 g/l of sodium benzoate (SB) and 1 g/l of benzyl benzoate (BB), shifts its potential to the positive region and sets it as the level of 20 mV. Now, this means that this inhibited working fluid for hydraulic cylinders not only prevents fluid access inside the coatings to the steel base, but also effectively inhibits its surface, as well as the forming surfaces — the interlamelar space of the coatings.

After exposure for 168 h the electrode potential shifts to the anode zone, that characterizes formation of specific compounds on the surface, having iron cations and benzoate anions in their composition. A characteristic feature of benzoate-containing compounds is their adsorbing on the steel surface, creating rather dense passive film, which prevents interaction of corroding environment and steel surface. This results in a significant reduction of corrosion currents of coating

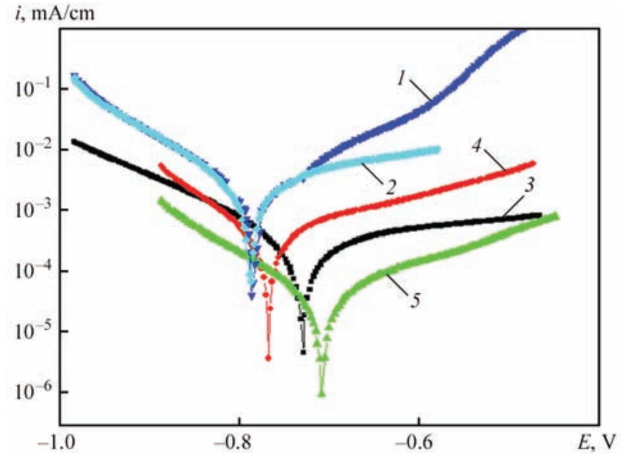


Figure 8. Corrosion resistance of coating substrate — 12Kh1MF steel, in the solution of 3 % NaCl and 3 % emulsion of Hydroway-1060 Emulsol, inhibited with synergistic composition, soaking for 168 h. Environment composition is 1:1. *1* — 12Kh1MF in 3 % NaCl; *2* — 12Kh1MF in 3 % water emulsion of Emulsol; *3* — 1 g/l of sodium benzoate; *4* — 1 g/l of sodium benzoate + 1 g/l of sodium silicate; *5* — 1 g/l of sodium benzoate + 1 g/l of benzyl benzoate

Density of corrosion current of 12Kh1MF steel at application of various inhibitors

Corrosion current density	12Kh1MF steel in chlorine-containing environment with different inhibitors				
	12Kh1MF + 3 % NaCl	12Kh1MF*	SB*	SB + SS*	SB + BB*
T = 24 h					
$I_{corr}\cdot10^{-4}$, mA/cm^2	8.94	5.9	2.72	0.86	0.72
T = 168 h					
$I_{corr}\cdot10^{-4}$, mA/cm^2	14.4	22.2	2.13	3.96	0.35
*3 % emulsion of Emulsol in chloride-containing medium.					

substrate material, compared to current in an uninhibited environment (Figure 8).

As a result of conducted electrochemical studies in chloride-containing medium, the synergism phenomenon is observed at the combination of 3 % emulsion of Emulsol with 1 g/l of sodium benzoate and 1 g/l of benzyl benzoate, as I_{corr} is reduced up to 6 times, compared with the case, when individual inhibitors were used (see Table).

Calculation of the effectiveness of the action of inhibitors performed by the formula for determination of the degree of protection [12], showed that inhibition in 3 % emulsion of Hydroway-1060 Emulsol in chloride-containing environment of sodium benzoate provides the degree of protection Z(SB) = 90.41, and that of sodium silicate Z(SB + SS) = 82.16, whereas the solution of 1 g/l of sodium benzoate + 1 g/l of benzyl benzoate provides the best degree of corrosion protection of 12Kh1MF steel (Z(SB + BB) = 99.14). During coating service in inhibited Emulsol environment metal inhibition proceeds through formation of adsorption passive films on the surface that is the result of interaction of cations of ionized metal with ionic residue of inhibitors.

Conclusions

1. 140Kh14N2TYu, 70Kh20RZGS2Yu flux-cored wires of Fe–Cr–C and Fe–Cr–B systems were developed, which allow forming electric arc spray coatings with low coefficient of chemical microheterogeneity K_{MH} (Cr) = 0.05–0.07 and with corrosion resistance on the level of coating sprayed with stainless wire from 08Kh18N10T steel, as well as wear resistance on the level of galvanic chromium coating.

2. Synergistic compositions of inhibitors were developed, which are added to 3 % emulsion of Hydroway-1060 Emulsol and effectively protect both the electric arc spray coating, and metallic material of its substrate from corrosion in chloride-containing environment with degree of protection Z(SB + BB) = = 99.14 %.

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