GASOABRASIVE WEAR RESISTANCE AT ELEVATED TEMPERATURES OF COATINGS PRODUCED BY THERMAL SPRAYING

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Thermal spraying is becoming ever wider accepted to produce reconditioning and protective coatings for various functional purposes. However, service life of such coatings has not been studied well-enough so far. This work is a study of the mechanism of formation of electric arc sprayed coatings from flux-cored wires of Fe–Cr–B–Al alloying system. It is found that gasoabrasive wear resistance of coatings from flux-cored wires depends on coating hardness, stresses of the first kind in the coating and on composition of oxide films, which form at spraying and at elevated temperatures during gasoabrasive wear testing. Oxide films initially form on the drop surface during spraying. In addition, in air the porous electric arc sprayed coatings are found to have oxidation on the surface and inside the coating (interlamellar oxidation) and oxidation on the boundary between the coating and steel base. It is shown that the high resistance to gasoabrasive wear is observed in coating, in which tensile stresses are transformed into compressive stresses as a result of the process of inner interlamellar oxidation during isothermal soaking at testing temperature of 400–600 °C, leading to increase of coating volume and improvement of its cohesion strength as a result of its reinforcement by interlamellar films of 100–150 nm thickness. Optimum content of alloying elements and their influence on gasoabrasive wear resistance of coatings are determined. Positive influence of residual compressive stresses in the coatings on gasoabrasive wear is shown. Proposed coatings will become applied in power engineering enterprises. 13 Ref., 1 Table, 12 Figures.

Keywords: *thermal spraying, coatings, flux-cored wires, gasoabrasive wear*

Electric spraying process is a sufficiently simple and inexpensive one among thermal spraying methods [1]. Recent introduction of electrodes in the form of flux-cored wires (FCW) for thermal spraying enabled widening the field of application of this method and producing reconditioning and protective coatings for various functional purposes [2–5], in particular for protection from corrosion and gasoabrasive wear of heating elements of thermal electric power stations [6–12]. However, service life of such coatings has not yet been well enough studied that restrains wide-scale application of this method.

The paper is devoted to investigation of the influence of alloying elements on coating structure, their mechanical characteristics, wear resistance at gasoabrasive wear and gas corrosion resistance at higher temperature.

Experimental procedure and studied materials. Coatings were applied by thermal spraying with EM-14 metallizer, spraying FCW of 1.8 mm diameter. Powders of boron-containing compounds (ferrochromium boron FKhB-2 and boron carbide), pure metals (chromium, tungsten and aluminium), as well as aluminium-magnesium alloys were used as charge components. Developed FCW were compared with those of foreign companies (Table), which are used for part protection from gasoabrasive wear. Strip from steel 08kp (rimmed) of 0.4 mm thickness and 10 mm width was used as wire sheath. Coefficient of FCW filling with the charge was 22–35 wt.%. Modes of coating deposition were as follows: I = 150–160 A, U_a = 32–34 V. FCW was sprayed by an air jet under the pressure of 0.60–0.65 MPa with 140–150 mm spraying distance. Coating phase composition was studied in DRON-3 diffractometer with computer recording of diffractograms. CuK_α-radiation was used at U = 32 V and I = = 15 mA. Scanning step was 0.05.

Coating structure and chemical composition after spraying and oxidation were studied in the Carl Zeiss scanning microscope EVO-40 XVP

Calculated FCW composition, wt.%

FCW grade	B	Cr	Al	W	Mo	Si	Other	Fe	Wire trade mark
PP-Kh6R3Yu2	3	6	2	–	–	–	–	Base	FMI
PP-Kh6R3Yu6	3	6	6	–	–	–	–	Same	FMI-2
PP-Kh6R3Yu14	3	6	14	–	–	–	–	»	FMI-11
PP-70Kh6R3Yu6	3	6	6	–	–	–	–	»	FMI
ПП-70V6R3Yu6	3	–	6	–	–	–	–	»	FMI-7
PP-500Kh20R5M10 V10B10G5S2	5	20	–	10	10	2	10Nb	»	EndoTec DO 390N
PP-Kh30M15Yu4	–	22	5	–	–	–	–	»	EuTronic Arc 509
PP-Kh29R4S2G2	4	29	–	–	–	2	2Mn	»	Praxair and TAFA 95MXC

with microanalysis system EVO-4XVP. Microhardness was determined in PMT-3 hardness meter.

In confidence interval of 0.95 and with minimum experiment number (four) relative error of determination of cohesive and adhesive strength and wear resistance parameters did not exceed 5 %.

Samples of electric arc sprayed coating material for determination of the modulus of elasticity by the method of three-point bending were prepared as follows. One surface (of 100 × 20 mm size) of 100 × 20 × 6 mm samples from steel 20 was coated with tin 2 of 40–50 μm thickness and subjected to jet treatment with corundum for preparation of tinned surface for spraying.

Six samples were fastened on the forming surface of a hexagon and 1.5 mm coating from FCW was deposited. Spray-deposited plates were ground from end faces and over the sprayed side down to coating thickness of 1 mm. Prepared samples were placed into a heated furnace, where the temperature was 50 °C higher than tin melting temperature. At heating of coated steel plates the tin layer melted and coating spalled spontaneously due to internal stresses. As a result, beam-type samples of 100 × 20 × 1 mm size from coating material were made. Modulus of elasticity of electric arc sprayed coatings was determined by bending method, and calculation was performed as follows [13]:

$$E = \frac{L_v^3(P_2 - P_1)}{4bh^3(Z_2 - Z_1)},$$

where L_v is the distance between base cutters, mm; P_1, P_2 is the magnitude of first and second load, g; b is the plate width, mm; h is the plate thickness, mm; Z_1, Z_2 are the indicator readings at the first and second loading, mm.

Investigation of gasoabrasive wear at elevated temperatures (up to 600 °C) was conducted in a laboratory unit with application of mechanical acceleration of abrasive (in particular, quartz sand < 200 μm) with particle velocity of 10–40 m/s, and 30° angle of incidence.

Figure 1 gives the schematic of a unit for testing coatings for gasoabrasive wear at higher temperature.

The unit consists of electric furnace *1* (temperature is regulated with accuracy of ±2 °C), abrasive feeding device *2*, DC electric motor *3*, module of adjustment of engine revolutions *4*. To eliminate the edge effects resulting from coating tearing off by abrasive jet on sample edges, they were tightly fastened to each other on the inner side of ring *5* (Figure 1, *a*).

Assembly of abrasive feeding and acceleration (Figure 1, *b*, *c*) consists of inner pipe fixed rigidly, through which the abrasive is uniformly supplied to abrasive acceleration assembly. External pipe, which is fixed on bearings in the case, is designed to transfer the torque to abrasive acceleration assembly. Bearings are air-cooled.

Samples were made from steel 12Kh1MF of 20 × 40 × 6 mm size, and 10 μm of nickel was deposited on all the sample surfaces by galvanizing to eliminate the uncontrolled increase of sample weight, because of oxidation of their unsprayed surfaces at elevated temperatures. Nickel layer was removed by machining from one side of the sample (20 × 40 mm). This surface was subjected to corundum jet treatment and electric arc coating of 1000 μm thickness was deposited layer-by-layer in six passes.

Sprayed surface of samples was ground to 700 μm thickness. Experimental investigations were conducted at 30° angle of abrasive attack and abrasive velocity of 36 m/s, which was set by varying the speed of revolution of DC electric motor *3* from adjustment module *4* (see Figure 1, *a*). Wear resistance of coated samples was determined by their weight loss with up to 0.0002 g accuracy.

Experimental results and their discussion. *Influence of FCW charge composition on coating*

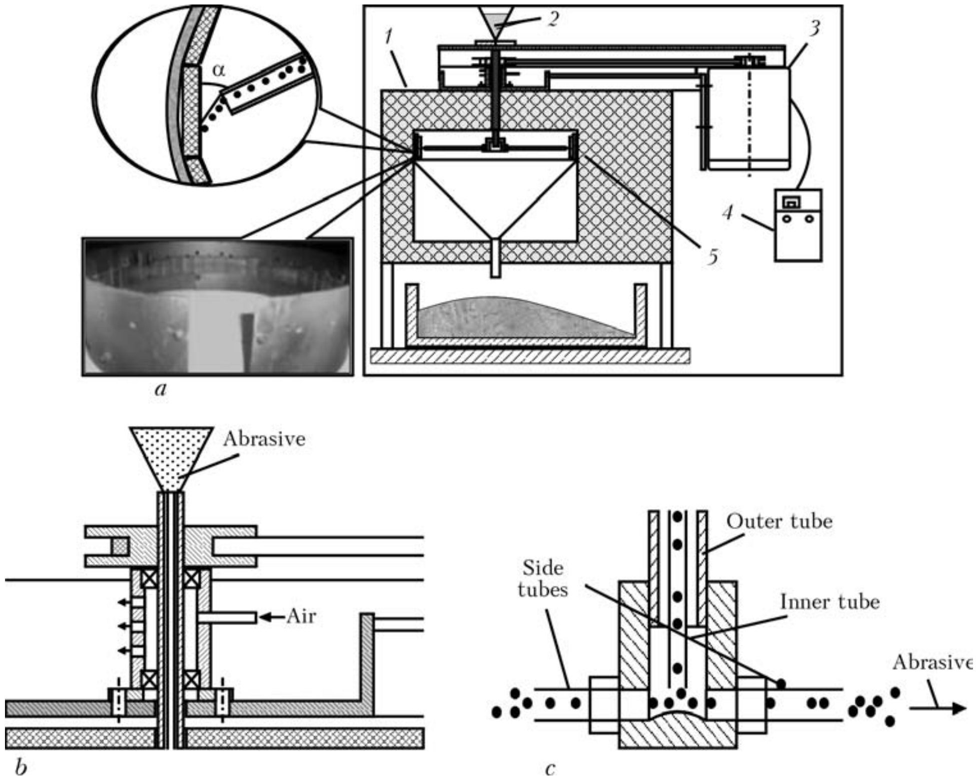

Figure 1. Schematic of unit for gasoabrasive wear testing of coatings at elevated temperature (*a*), and assemblies for abrasive feeding (*b*) and acceleration (*c*) (for designations see the text)

structure. To study the composition of the drops formed at FCW spraying by an air jet, they were trapped in a snow target, and the cuts on sections were studied. It is established that minimum drop size was 15 μm, and maximum was 400 μm. Fraction of 18–50 μm size amounted to 50 wt.%, 50–150 μm size to 40 wt.%, and amount of drops larger than 150 μm was small at 10 wt.%. During spraying of FCW of Fe–Cr–B–Al alloying system, the charge and sheath do not have enough time to fuse completely because of the transiency of melting processes, so that a heterogeneous melt and drops of three types form:

- drops of metal melt, based on Fe alloyed with 3–5 % Cr, 6–14 % Al and B, are surrounded by Al_2O_3 oxide, the particles of which grow as round islets on drop periphery (Figure 2, *a*);
- drops of metal melt, based on Fe alloyed with 3–5 % Cr, 2–4 % Al and B, are surrounded by an oxide film $(FeCr)_2O_3$, which is located between ferrochrome dendrites (Figure 2, *b*);
- round drops of pure oxide Al_2O_3 $(FeAlCr)_2O_3$ and $(FeCr)_2O_3$ (Figure 2, *c*).

When hitting the spraying surface, molten drops are badly deformed and solidify in layers as lamels, separated by oxide films (Figure 3, *a*). Phase analysis of electric arc sprayed coatings revealed that at formation of coatings using FCW with B_4C + Fe charge, coating matrix phase is Fe_α with inclusions of Fe_3C ferric carbide and free B (Figure 3, *b*, *c*). In this case, interaction of boron carbide with iron melt at spray-deposition of coatings runs by the following reaction: $Fe + 1/3B_4C = 1/3Fe_3C + 4/3B$. Adding Cr-containing elements to FCW charge promotes disappearance of free B in the coating structure, whereas interaction of boron carbide with Cr proceeds by the following reaction: $Cr + 2/7B_4C = 4/7CrB_2 + 1/7Cr_3C_2$.

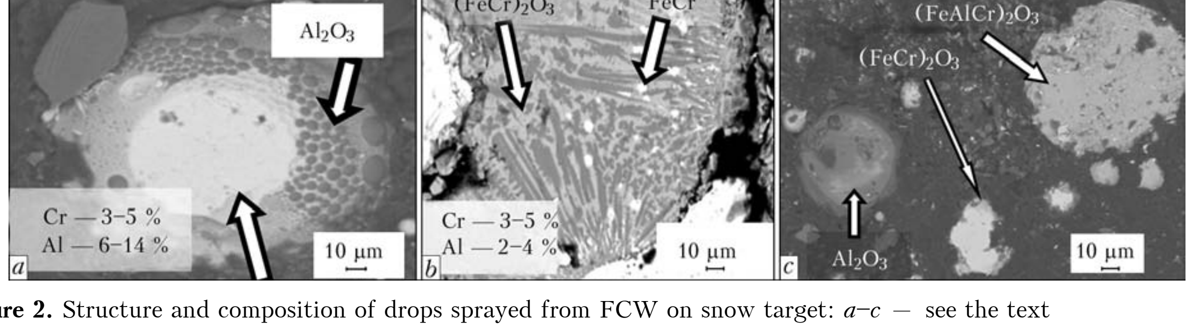

Figure 2. Structure and composition of drops sprayed from FCW on snow target: *a*–*c* — see the text

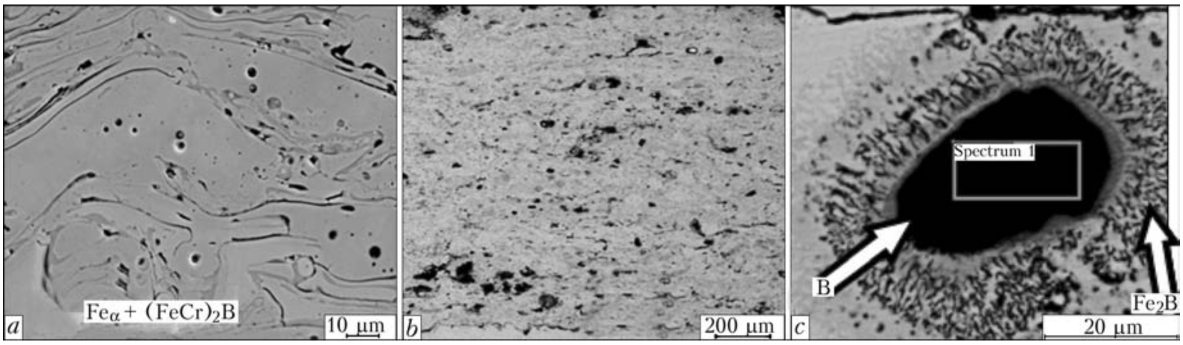

Figure 3. Structure of electric arc sprayed coatings: *a* — FCW with $(FeCr)_2B$ + Fe charge; *b* — FCW with B_4C + Fe charge; *c* — same, boron inclusions in the coating

Coating structure at elevated temperatures. Unlike solid materials in porous electric arc sprayed coatings oxidation in air at elevated temperatures occu both on coating surface and inside it (interlamellar oxidation) (Figure 4, *a*, *b*). In addition, oxidation occurs on the boundary between the coating and steel base (Figure 4, *c*). As a result of 8–10 % porosity of the coatings oxygen penetrates into the steel base even at coating thickness of 0.5–0.8 μm. Total oxygen content in the initial coating is equal to 2.5–3.0 wt.%. After soaking for 100 h at 550 °C oxygen content in the coating rises up to 4–5 wt.%, at 100 h soaking at 700 °C — up to 8.0–9.5 wt.%. Here coating oxidation rate is 10–30 times lower than that of steel.

At the temperature of 600–700 °C oxide films of hematite Fe_2O_3 form on steel surface, growing in the form of needle-like projections 100–200 nm thick (Figure 5, *a*). On coatings with not more than 2 % Al (PP-Kh6R3Yu2) oxide films of hematite alloyed by chromium and aluminium $(FeCr)_2O_3$ are formed, growing on the surface in the form of strobiloidal protrusions of 5–10 μm thickness (Figure 5, *b*). Oxide films of hematite alloyed by aluminium $(FeAl)_2O_3$ form on Kh6R3Yu6 and Kh6R3Yu14 coatings with higher aluminium content, which grow on the surface in the form of monolithic film (Figure 5, *c*). Oxide films 0.2–2.0 μm thick form between coating lamels. These films contain particles of matrix metal phase 100–300 μm long, strongly bonded to matrix phase (Figure 5, *d*).

Two-layer oxide film forms on the boundary between coating and base. The part adjacent to the coating has an increased content of aluminium, and the part adjacent to the base has higher iron. Oxide film is embedded into the coating as though by anchors, and strongly binds it to the steel base.

Influence of testing temperature on coating mechanical characteristics. During long-term soaking at testing temperature of 600 °C, hardness of all the coatings decreases and is stabilized on the level of *HV* 500–550, because of coarsening of strengthening phase — $FeCr_2B$ borides. So, as shown by metallographic analysis, after spraying boride size does not exceed 100 nm, and after soaking for 5000 h at 600 °C, their size increases to 300–500 nm (Figure 6, *a*, *b*). Long-term soaking of coatings at testing temperature of 600 °C promotes increase of their cohesion strength (Figure 7).

Such an effect is predetermined by reinforcement of coating structure by thin (less than 1 μm) oxide films (see Figure 5, *d*). Here, the coating acquires a composite structure. The greatest strengthening is observed for a coating from

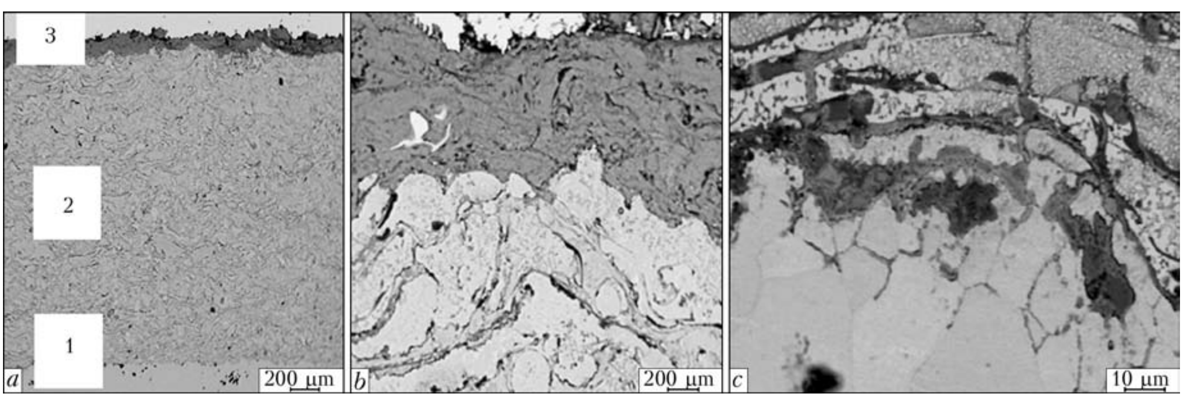

Figure 4. Coating structure after soaking at 600 °C for 2000 h: *a* — total coating structure (*1* — base (12Kh1MF steel); *2* — coating; *3* — oxide film on coating surface); *b* — transition zone between coating and oxide film on coating surface; *c* — transition zone between coating and base metal

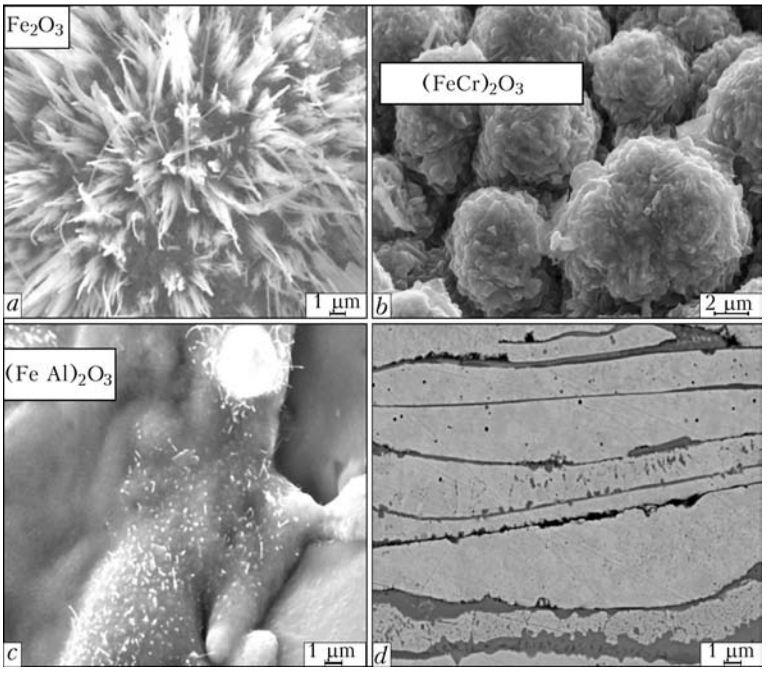

Figure 5. Structure of surface films: *a–c* — see the photoars; *d* — lamels

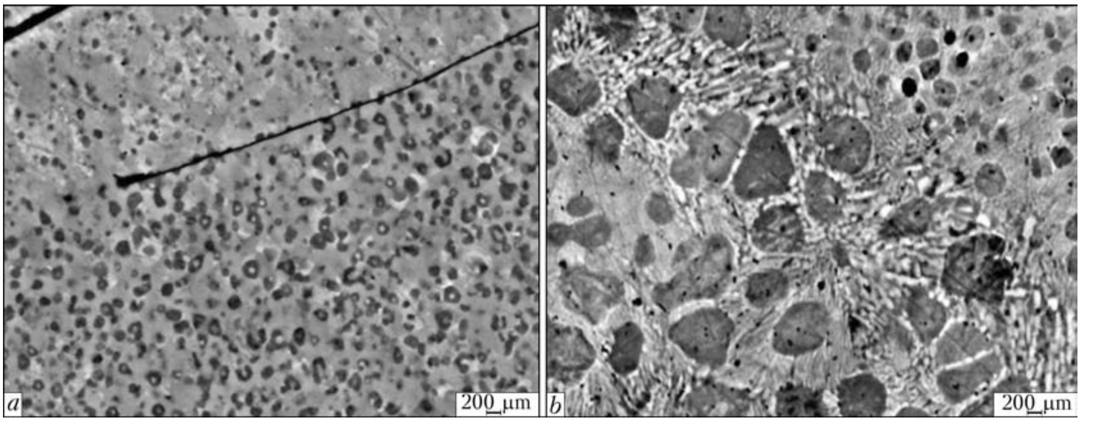

Figure 6. Structure of coatings with borides after spraying (*a*) and after soaking at 600 °C for 5000 h (*b*)

FCW Kh6R3Yu14, that is related to coating reinforcement by aluminium oxide films.

Modulus of elasticity of spray-deposited coatings without heat treatment is in the range of 50,000–70,000 MPa. At increase of testing temperature above 350 °C, the modulus of elasticity of FCW 70V6R3Yu6 coating rises almost 3 times, and for a coating from FCW Kh6R3Yu14 — by 70 % (Figure 8, *a*) [13]. Increase of modulus of elasticity is determined by inner interlamellar oxidation and it is directly proportional to the amount of oxide phase in the coating. So, the modulus of elasticity of 70V6R3Yu6 coating after spraying is equal to 52,000 MPa, and oxide phase amount is 4 wt.%; after soaking for 100 h at 600 °C the value of the modulus of elasticity rises up to 180,000 MPa, and amount of interlamellar oxide phase is 14 wt.% (Figure 8, *b*).

Long-term exposure of samples at the temperature of 600 °C also leads to an essential decrease of tensile stresses in the coating. Two time

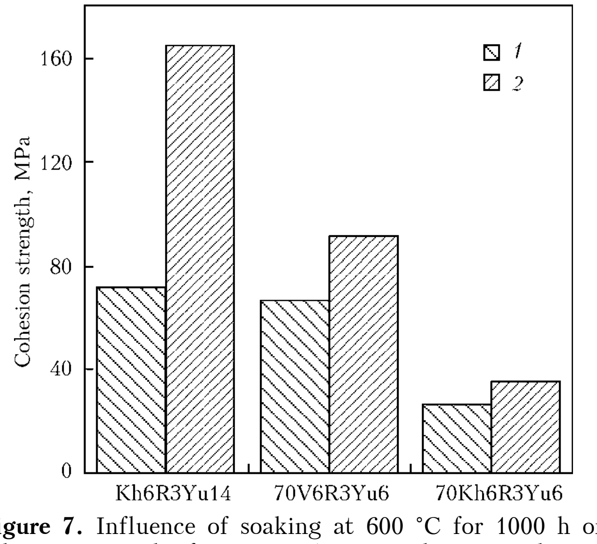

Figure 7. Influence of soaking at 600 °C for 1000 h on cohesion strength of coatings: *1* — initial; *2* — soaking

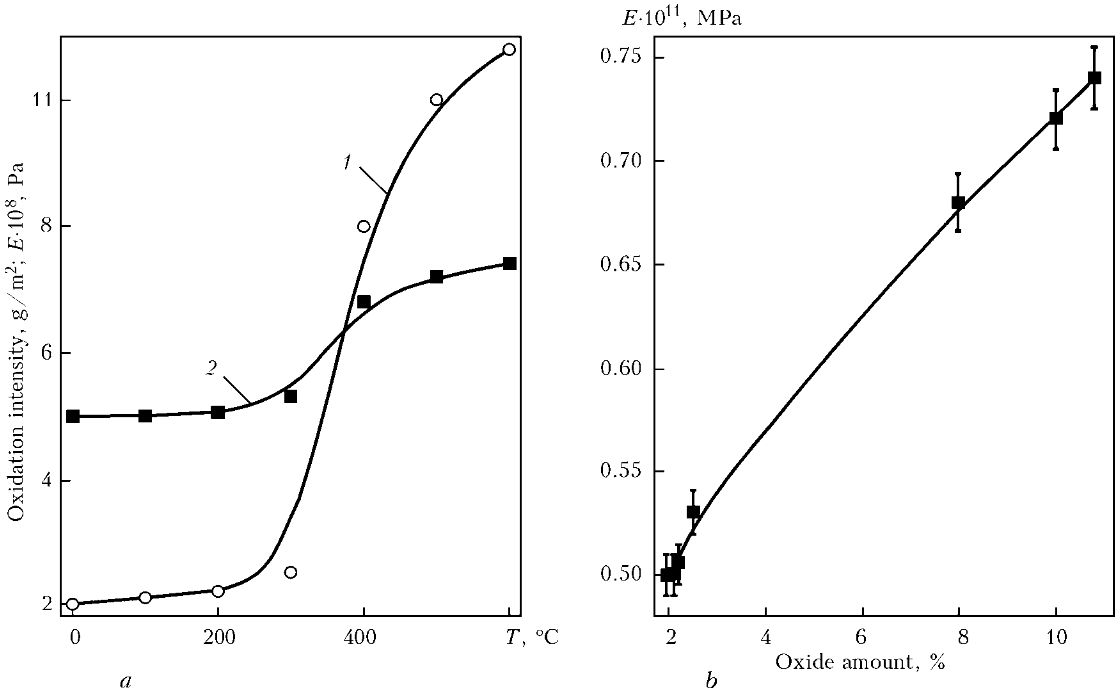

Figure 8. Temperature influence on oxidation intensity (*1*) and modulus of elasticity (*2*) of coatings (*a*), and of amount of interlamellar oxides in the coating on modulus of elasticity (*b*)

stages and two mechanisms are determined, by which lowering of tensile stresses in the coating proceeds (Figure 9).

So, at the first stage which lasts up to 20 h at 600 °C stress lowering occurs due to decomposition of austenite in the coating structure, that is accompanied by increase of coating volume. At the second stage with increase of soaking time above 20 h, compressive stresses rise, because of running of just the process of intralamellar oxidation of the coating

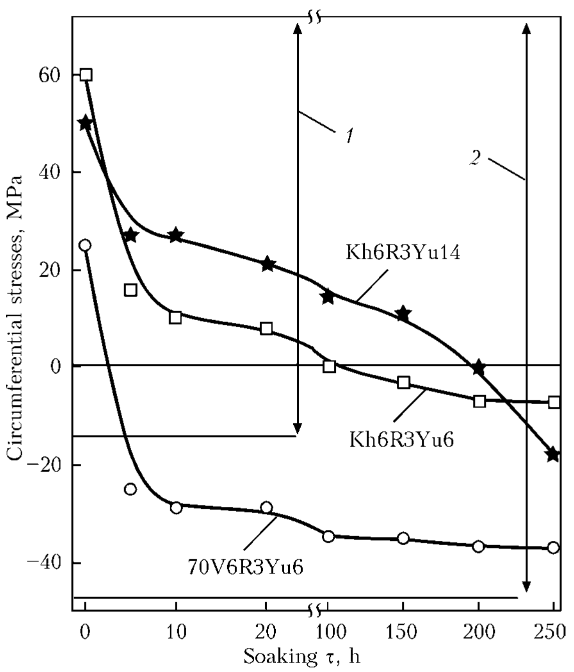

Figure 9. Influence of soaking at 600 °C on stress level in coatings: *1* — first; *2* — second time stage

and increase of the amount of oxide phase, that essentially increases the coating volume.

Gasoabrasive wear resistance of electric arc sprayed coatings. With increase of boron content in the coating up to 2.5 wt.%, gasoabrasive wear resistance of coatings becomes higher. Increased content of boron in the coatings above 2.5 wt.% leads to increase of tensile stresses in the coating and appearance of a net of microcracks in it, that lower coating wear resistance. As the same time, with increase of aluminium content in FCW with 2.5 wt.% B, gasoabrasive wear resistance of coatings rises monotonically (Figure 10, *a*). Replacement of FKhB master alloy by B_4C in FCW charge only slightly, by 15 %, lowers the wear resistance, so that these components can be irreplaceable (Figure 10, *b*).

Investigations for gasoabrasive wear resistance of coatings from FCW with varying content of aluminium of 2, 6, 14 wt.% showed that below 350 °C gasoabrasive wear resistance of coatings and steel rises only slightly (Figure 11), but at lowering of aluminium content in FCW coating wear resistance becomes significantly lower than that of steel.

This is related to the fact that at spraying of coatings from FCW with a low content of aluminium they develop considerable tensile stresses, relaxation of which occurs through formation of a net of microcracks. With increase of aluminium content, a more heterogeneous coating forms, and much lower tensile stresses develop, due to their relaxation by plastic defor-

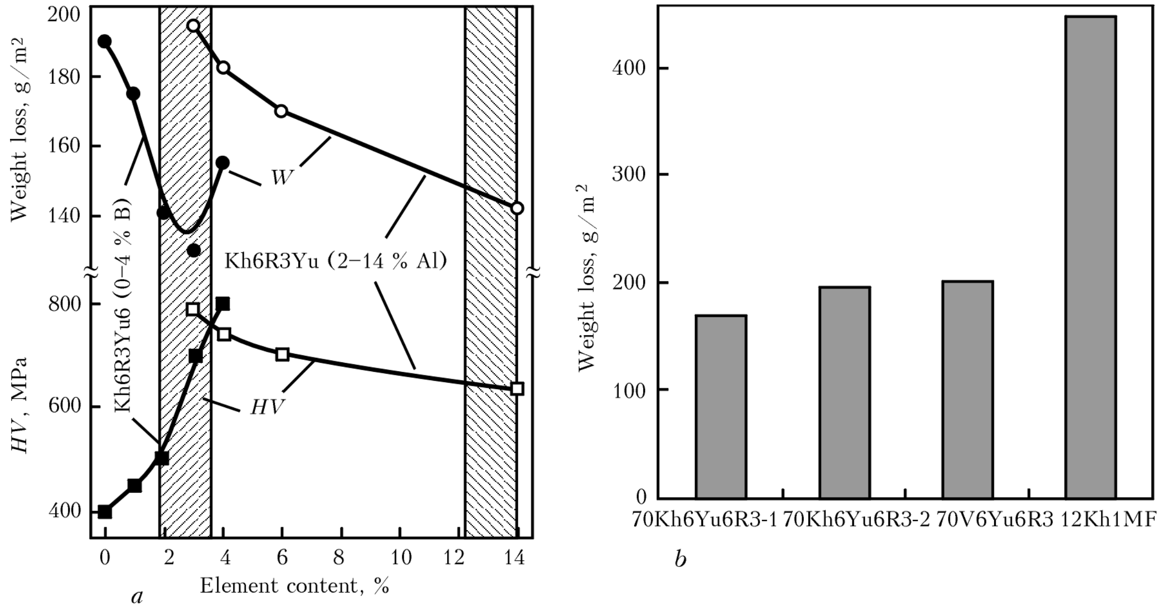

Figure 10. Influence of boron (Kh6R3Yu6 with 0–4 % B) and aluminium (Kh6R3Yu with 2–14 % Al) on hardness and gasoabrasive wear resistance *W* of coatings (*a*), and influence of FKhB (70Kh6Yu6R3-1) and B_4C (70Kh6Yu6R3-2) master alloys in FCW charge on gasoabrasive wear (*b*)

mation in the less hard coating lamels. With increase of testing temperature above 350–400 °C steel wear resistance drops abruptly, and that of the coating rises — to a greater extent for coatings with lower aluminium content. This is related to lowering of tensile stresses in the coatings as a result of interlamellar oxidation of microcracks and their filling by gas corrosion products, which increase the coating volume, leading to lowering of tensile stresses and their transformation into compressive stress. Therefore, a more significant lowering of tensile stresses is observed in coatings with a ramified net of cracks due to additional filling of microcracks by oxides.

However, gasoabrasive wear resistance also depends on morphology of oxide film, which forms on coating surface. Monolithic oxide film $(FeAl)_2O_3$ forms on the surface of coatings with 14 wt.% Al, which ensures 4 times higher wear resistance than in 12Kh1MF steel and 30 % higher value than for coating from FCW Kh6R3Yu2.

Gasoabrasive wear resistance of coating from FCW Kh6R3Yu14 was compared with that of coatings spray-deposited from EndoTec DO 390N, Praxair and TAFA 95MXC FCW alloyed by a large amount of chromium, molybdenum and niobium, which were used for structure protection from gasoabrasive wear (see Figure 11).

Such FCW also have a higher content of boron and carbon, that ensures coating hardness on the level of *HV* 1100–1200. This causes microcracking in the coatings at their spraying. High content of alloying elements (chromium, molybdenum, vanadium) in these coatings essentially slows

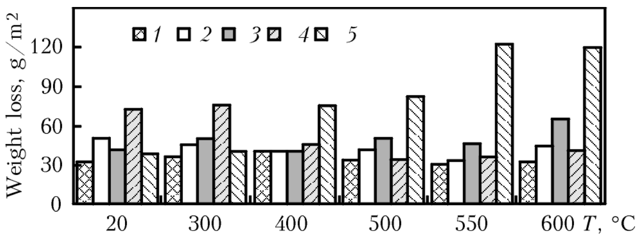

Figure 11. Influence of testing temperature on gasoabrasive wear resistance of various coatings from 12Kh1MF steel: *1* — Kh6R3Yu14; *2* — Kh29R4S2G2; *3* — 500Kh20R5M10 V10B10G5S2; *4* — Kh30M15Yu4; *5* — 12Kh1MF

down their inner interlamellar oxidation. For this reason, tensile stresses in the coating do not essentially decrease with time, as it takes place in the less alloyed coatings, and, therefore, their gasoabrasive wear resistance is much lower than that in the coating from FCW Kh6R3Yu14.

Coatings from FCW ensure a high wear resistance under two conditions. First, FCW charge should contain such alloying elements, which cause dispersion hardening in the coating structure. Secondly, such a content of chromium and aluminium in the coating should be provided as to create the prerequisites for inner interlamellar oxidation at an optimum rate of 0.5 g/(m^2·h) (Figure 12) and, therefore, achieve the transformation of tensile stresses into compressive stresses and formation of a continuous strong oxide film $(FeAl)_2O_3$ on coating surface.

Coatings from FCW studied in this paper, have passed production trials and are applied for protection of economizer and shield pipes from gasoabrasive wear in Burshtin TPS, as well as in Polish thermal power stations.

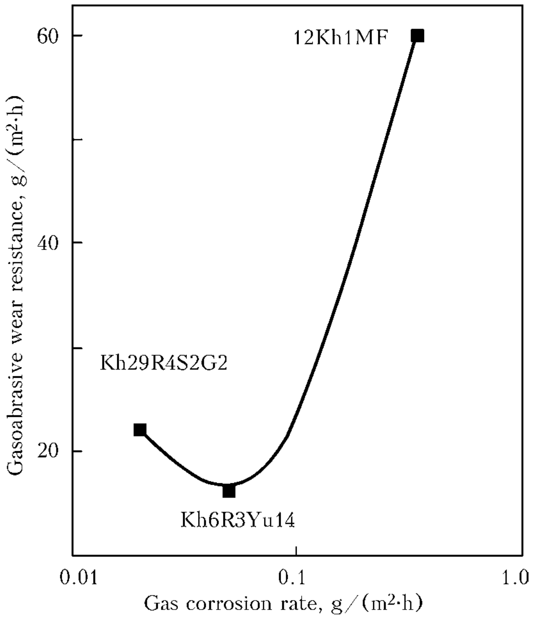

Figure 12. Influence of gas corrosion rate on gasoabrasive wear resistance of coatings and 12Kh1MF steel (testing temperature of 600 °C)

Conclusions

1. Procedure of investigation of gasoabrasvie wear of coatings was improved. It simulates the operation of TPS boilers as close as possible, allows eliminating edge effects, which arise as a result of coating tearing off on the edges of samples by an abrasive jet, and avoiding uncontrolled increment of sample mass due to oxidation of their non-sprayed surfaces at elevated temperatures.

2. To determine the modulus of elasticity of the coating by three-point bending method, a procedure of making beam samples from uncoated material without a substrate was proposed. Dependence of variation of modulus of elasticity of electric arc sprayed coatings of Fe–Cr–B–Al system on temperature and soaking time was established. It is shown that the modulus of elasticity of the coatings is directly proportional to the amount of oxide phase, formed under the conditions of long-term soaking at elevated temperatures.

3. It is also shown that gasoabrasive wear resistance of coatings from FCW depends on coating hardness, stresses of the first kind in the coating and on the type of oxide film, which forms at elevated temperature during testing.

4. High resistance to gasoabrasive wear is demonstrated by coatings, in which tensile stresses are transformed into compressive stresses as a result of the process of inner interlamellar oxidation during isothermal soaking at testing temperatures of 400–600 °C, that leads to increase of coating volume, and of its cohesion strength as a result of its reinforcement by interlamellar films of 100–150 nm thickness.

5. A connection between the morphology of surface oxide films and coating gasoabrasive wear resistance is established and it is found that high resistance to gasoabrasive wear is demonstrated by coatings, forming a dense film of iron oxide alloyed by aluminium.

6. A new composition of FCW Kh6R3Yu14 was developed for deposition of high-temperature coatings capable of dispersion strengthening in operation and improving the wear resistance of 12Kh1MF steel 12 to 14 times, and its gasoabrasive wear resistance by 2.5–4 times.

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