

HEAT-RESISTANT THERMAL SPRAYED COATINGS BASED ON FeAlCr INTERMETALLIDE WITH CeO₂ ADDITIVES*

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The paper presents the results of studying the heat resistance of coatings, produced by the methods of plasma (PS) and high-velocity oxy-fuel spraying (HVOF), using composite powder based on FeAlCr with addition of 2 wt.% CeO₂, as well as by the methods of electric arc metallization (EM) and activated electric arc metallization (AM) with using of flux-cored wire of the following composition: 98(82Fe + 16Al + 2Cr) + 2CeO₂ (wt.%). Composite powder was prepared by the method of mechanochemical synthesis (MS) by treating a mixture of powder components in a planetary-type mill. Heat resistance testing was performed in air at 800, 900 and 1000 °C for 7 h by weight method. Coating structure after heat resistance testing was studied with application of metallographic and X-ray structural analysis (XRD). It is found that during testing of coatings produced by PS and HVOF methods the delamination phenomenon is observed, whereas coatings produced by AM and EM methods preserve a tight bond strength with the substrate. Obtained kinetic curves of heat resistance showed that in the entire time interval of testing at 800–1000 °C the oxidation mechanism follows the parabolic law. The data of kinetic dependencies were used to plot the parametric heat resistance diagrams, allowing evaluation of fatigue life time of the studied protective coatings in the temperature range of 800–1000 °C. The highest heat resistance is found in FeAlCrCeO₂ coatings produced by AM and EM methods with using of flux-cored wire. At 1000 °C it exceeds the resistance of steel 45 by 23–26 times, and corresponds to heat resistance of 08Cr17Ti steel. 12 Ref., 2 Tables, 8 Figures.

Keywords: thermal spraying, electric arc spraying, iron-aluminium intermetallics, mechanochemical synthesis, composite powder, flux-cored wire, parametric heat resistance diagram, FeAlCr–CeO₂ system

One of the modern actual tasks of surface engineering is the development of coatings and their technologies of deposition that provide protection of parts, structural elements and components of equipment from high-temperature corrosion and wear, in particular, heat power units and devices operating in combustion flows of different kinds of fuels. These include heating surfaces of boilers of heat power plants, waste burning plants, as well as elements of recuperators. The development of new designs of recuperators, which allow increasing the degree of using heat of exhaust gases by 15–20 %, is associated with the need in providing the protection of their elements by using of coating with an increased heat resistance.

In this regard, Fe₃Al and FeAl iron intermetallics, characterizing by a high heat resistance at 600–1000 °C and resistance to erosion wear under attack of gas flows, are promising materials as functional protective coatings for such practical purpose [1]. Their advantage over nickel intermetallics is the increased resistance to high-temperature corrosion in sulfur-containing gas environments [1, 2].

Theoretical and experimental works performed in the field of heat resistance of iron intermetallics showed that by optimizing the content of alloying elements, in particular chromium, it is possible to increase their resistance to high-temperature corrosion and mechanical properties [3, 4]. Another possibility of increasing heat resistance of high-temperature Fe- and Ni-alloys and coatings based on them is associated with the use of rare-earth metals alloys and oxides as alloying additives [5–7]. The results of experimental investigations of the effect of CeO₂ additives in the intermetallic FeAl-coating produced by HVOF methods showed that with its content being 2–5 wt.%, the resistance of FeAl–CeO₂ material is increased by 2.0–2.5 times not only to oxidation, but also to erosion wear at 700–800 °C. In addition, it was found that introduction of CeO₂ reduces the rate of depletion of aluminum content in the coating, thus increasing the life time of protective properties of the coating [8].

The results of practical application of FeAl-coating in the conditions of a waste burning plant confirmed its effectiveness of protecting the surface of

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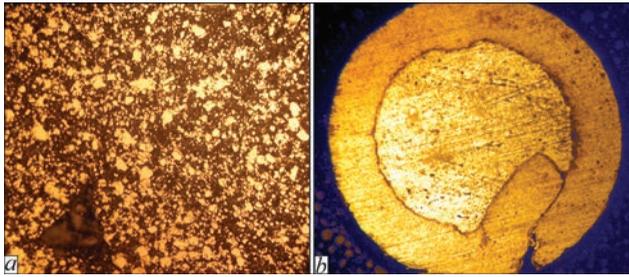


Figure 1. Microstructure ($\times 400$) of powder FeAlCr + CeO₂ produced by the method of MS (a) and cross-section of flux-cored wire Fe + Al + Cr + CeO₂ (b)

the equipment of such enterprises from corrosion and erosion wear [9].

The development of the technology of thermal spraying of protective FeAl-coatings is connected with the solution of the problem of starting materials production. The deposition of FeAl-coatings by high-velocity oxy-fuel spraying can be carried out using both powders as well as flux-cored wires [9, 10].

In the present work, deposition of coatings was carried out by both plasma and high-velocity oxy-fuel spraying using powders based on FeAl, as well as electric arc spraying of coatings from flux-cored wires based on FeAl with introduction of CeO₂.

Objects of investigations and experimental procedure. For manufacture of samples with heat-resistant coatings by thermal spraying methods, a composite powder (CP) of the following composition was prepared (wt.%): 98(82Fe + 16Al + 2Cr) + 2CeO₂.

As starting materials, the following powders were used: Fe, 63–160 μm ; Al, 40–100 μm ; Cr < 100 μm ; CeO₂ < 40 μm .

Production of the composite powder was performed by the method of mechanochemical synthesis (MS), which was carried out in the planetary-type mill «Activator 2SL» (JSC «Activator», Novosibirsk, Russia) at a rotation speed of central disk being 1000 rpm, and that of drums, rotating in the opposite direction, being 1500 rpm. The MS process was carried out in the atmosphere of air for 5 h. During the MS process, the water cooling of drums and planetary-type mechanism was performed. To eliminate sticking of the treated charge material onto the drum wall and grinding bodies at the beginning of the MS

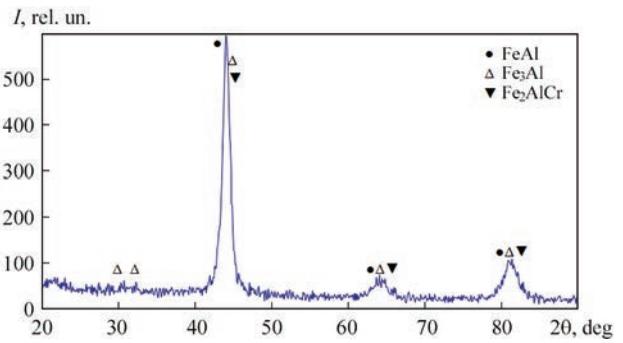


Figure 2. X-ray pattern of MS-powder FeAlCr + CeO₂ produced in the planetary-type mill during 5 h

process, a surface-active substance (oleic acid, in the amount of 0.3 wt.%) was added to the mixture.

For deposition of coatings using the methods of electric arc metallization (EM) and activated electric arc metallization (AM), a flux-cored wire (FCW) of 1.85 mm diameter was manufactured (Figure 1, b) at a thickness of sheath of 0.5 mm of low-carbon rimmed steel 08. As a filler, a mechanical mixture of powders Al, Cr, and CeO₂ in a ratio of 80:10:10 (wt.%) was used. The degree of filling is 14 vol.%, the calculated composition of the flux-cored wire (wt.%) is 98 (82Fe + 16Al + 2Cr) + 2CeO₂.

The microstructure of the MS-powder FeAlCr + CeO₂ and the cross-section of the flux-cored wire FeAlCr + CeO₂ are shown in Figure 1.

As was shown by the results of X-ray phase analysis (XRD) (Figure 2), during the MS process, a composite powder is formed containing the phases FeAl, Fe₂AlCr, Fe₃Al, which after the operation of conglomeration was used for deposition of coatings by plasma (PS) and high-velocity oxy-fuel (HVOF) spraying methods.

Plasma spraying (PS) of coatings was carried out by using of the installation UPU-8M with the following parameters: $I = 500 \text{ A}$, $U = 45 \text{ V}$, the rate of plasma-forming gas (Ar + N₂) was 25 l/min, the spraying distance was $L = 120 \text{ mm}$. For spraying, a powder with a particle size <40 μm was used.

Coating by HVOF spraying was deposited under the following process parameters:

- rate of propane-butane is 0.2 m³/h, pressure is 4.5 atm;
- oxygen rate is 0.5 m/h, pressure is 7 atm;

Table 1. Characterization of thermal coatings produced from the MS-powder FeCrAl + CeO₂ (PS, HVOF) and FCW Fe + Al + Cr + CeO₂ (EM and AM)

Method of deposition	Thickness, μm	H μ , MPa	Phase composition
PS	250–300	3890 \pm 1180	FeAl, Fe ₃ Al, FeCr, CeAlO ₃
HSFS	250–300	3376 \pm 683	FeAl, Fe ₃ Al, Fe ₂ AlCr, CeAlO ₃ , Al ₄ Ce
AAM	125–210	2458 \pm 31	Fe, Al, FeAl, Fe–Cr, CrO
EAM	440–700	2150 \pm 433	FeAl, Fe ₃ Al, Fe–Cr

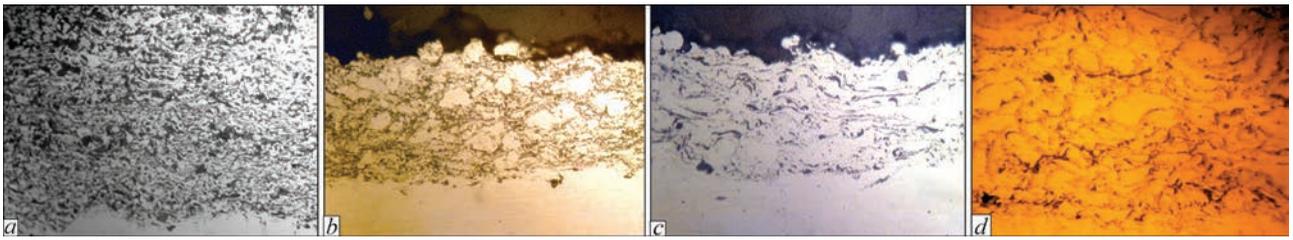


Figure 3. Microstructure ($\times 400$) of coatings: PS (a), HVOF (b) from MS-powder FeAlCr + CeO₂ and AM (c), EM (d) from flux-cored wire FeAlCr + CeO₂

• pressure of transporting gases (air and nitrogen) is 6 atm;

- spraying distance is 120–150 mm;
- particle size is $< 63 \mu\text{m}$.

The study of the heat resistance of coatings was carried out in the temperature range of 800–1000 °C in a specially designed installation by periodic weighing directly in the furnace at the test temperature.

The obtained results were compared with the test results of stainless steel 08Cr17Ti and steel 45, and for steel 45 the test temperatures were 700 and 800 °C due to its low heat resistance.

Producing coatings by the method of activated arc metallization was carried out using the AM-installation using of the following parameters:

- air pressure is 6 atm;
- propane-butane pressure is 3 atm;
- voltage is 30 V, current strength is 250 A;
- spraying distance is 100 mm.

Parameters of the coating process by the method of electric arc metallization, carried out using the metal spray gun EM-14, were the following:

- air pressure is 6.5 atm;
- voltage is 36 V, current is 80 A;
- spraying distance is 100–120 mm.

Coatings were deposited on samples of steel 45 with a diameter of 10 mm with the shape of an acorn.

Experimental results and discussion. A metallographic analysis of sprayed coatings (Figure 3) showed that in all cases on the surface of samples of steel 45 dense coatings are formed that are homogeneous in structure and composition, without defects and delaminations at the interface with the substrate.

Using the XRD method, it was found that during the process of coating deposition from the powder FeAlCr + CeO₂ by PS and HVOF methods, the coatings which were formed, contain the products of interphase interaction of the spray composite powder, as well as oxides Fe₃O₄, FeAl₂O₄, and CeAlO₃, that is the

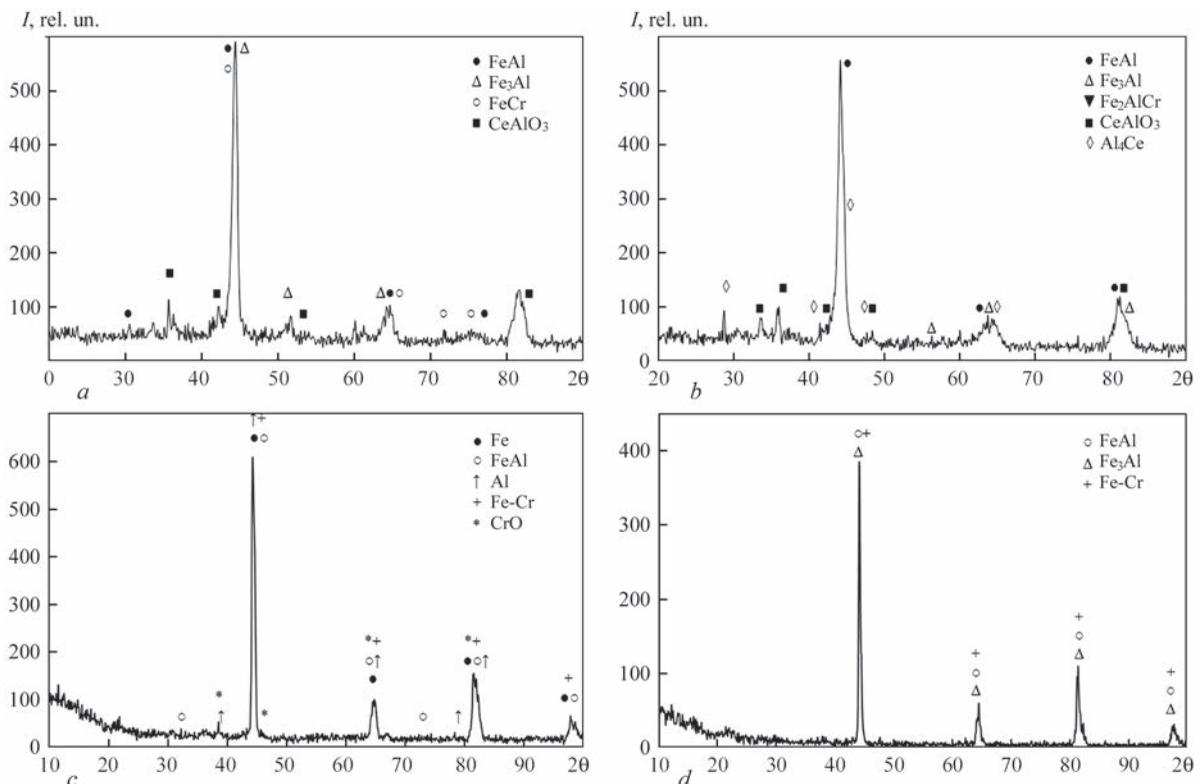


Figure 4. X-ray patterns of coatings: PS (a), HVOF (b), from MS-powder FeAlCr + CeO₂ and AM (c), EM (d) from flux-cored wire Fe + Al + Cr + CeO₂

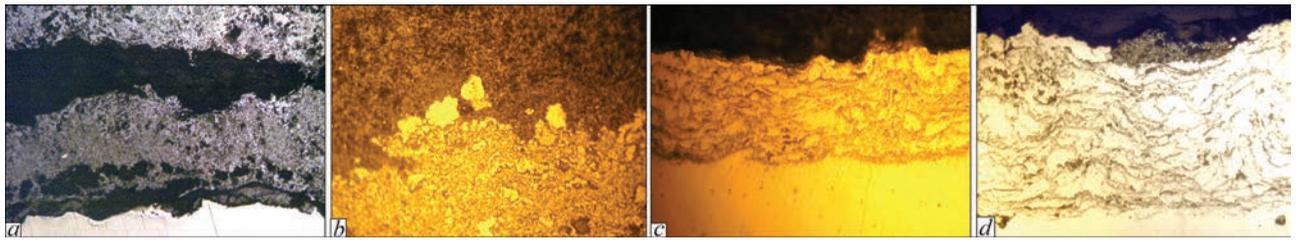


Figure 5. Microstructure ($\times 400$) of TS-coatings produced from MS-powder FeAlCr + CeO₂ using the method of PS (a), HVOF (b) and Fe + Al + Cr + CeO₂ produced using methods of AM (c) and EM (d), after tests on heat resistance at 1000 °C

result of CP FeAl + CO₂ components oxidation during spraying process. In terms of qualitative composition, the coatings do not practically differ (Figure 3, a, b) and (Figure 4, a, b), but only a higher content of oxides in plasma coatings can be noted as compared to HVOF, which is probably connected with a higher degree of dispersion of sprayed particles.

In the AM- and EM-coatings, oxide phases as well as traces of CeO₂ were not detected after applying the XRD method (Figure 4, c, d). The difference between the phase composition of AM- and EM-coatings formed by spraying from flux-cored wires is in the fact, that in the AM-coating, the reaction between the wires components Fe and Al during the spraying process does not completely occur and these elements are contained in a pure form.

The results of metallographic analysis of coatings, that passed a heat resistance test showed, that plasma

and thermal coatings (Figure 5, a, b) are cracked and delaminated from the substrate during oxidation, where as coatings deposited by electric arc metallization (AM and EM), are tightly bonded to the substrate and do not delaminate even after testing at a temperature of 1000 °C for 5 h. According to the results of XRD (Figure 6), for all types of coatings, including in EM- and AM-coatings, on their surface iron oxides and complex iron-chromium oxides and CeAlO₃ oxide were found, which were not revealed in the initial state.

Figure 7 presents kinetic dependences of oxidation of thermal coatings and unprotected steels 45 and 08Cr17Ti in the temperature range of 800–1000 °C in air. The nature of the curves indicates that the oxidation mechanism in all the cases submits to the parabolic temporal law in the entire investigated temperature range of 800–1000 °C.

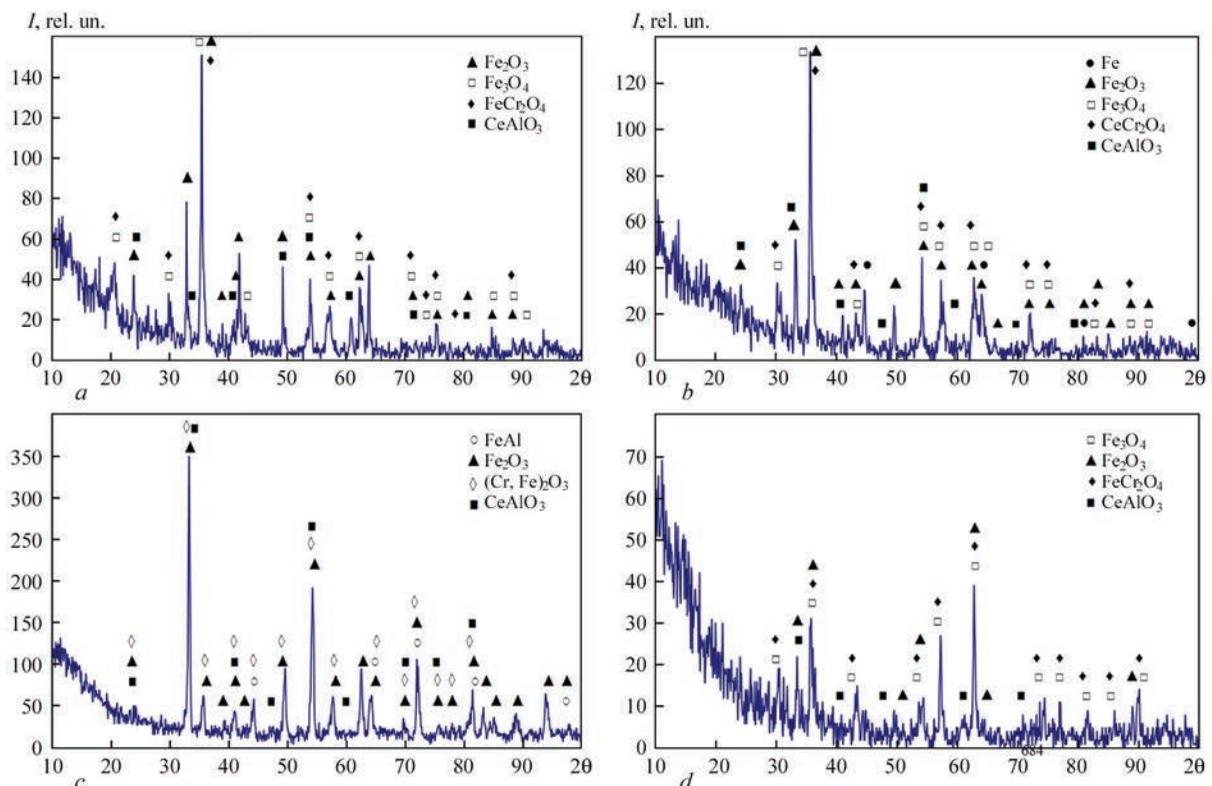


Figure 6. X-ray patterns of TS-coatings: PS (a), HVOF (b) from MS-powder FeAlCr + CeO₂, and AM (c) and EM (d) from flux-cored wire Fe + Al + Cr + CeO₂ after heat resistance tests at 1000 °C

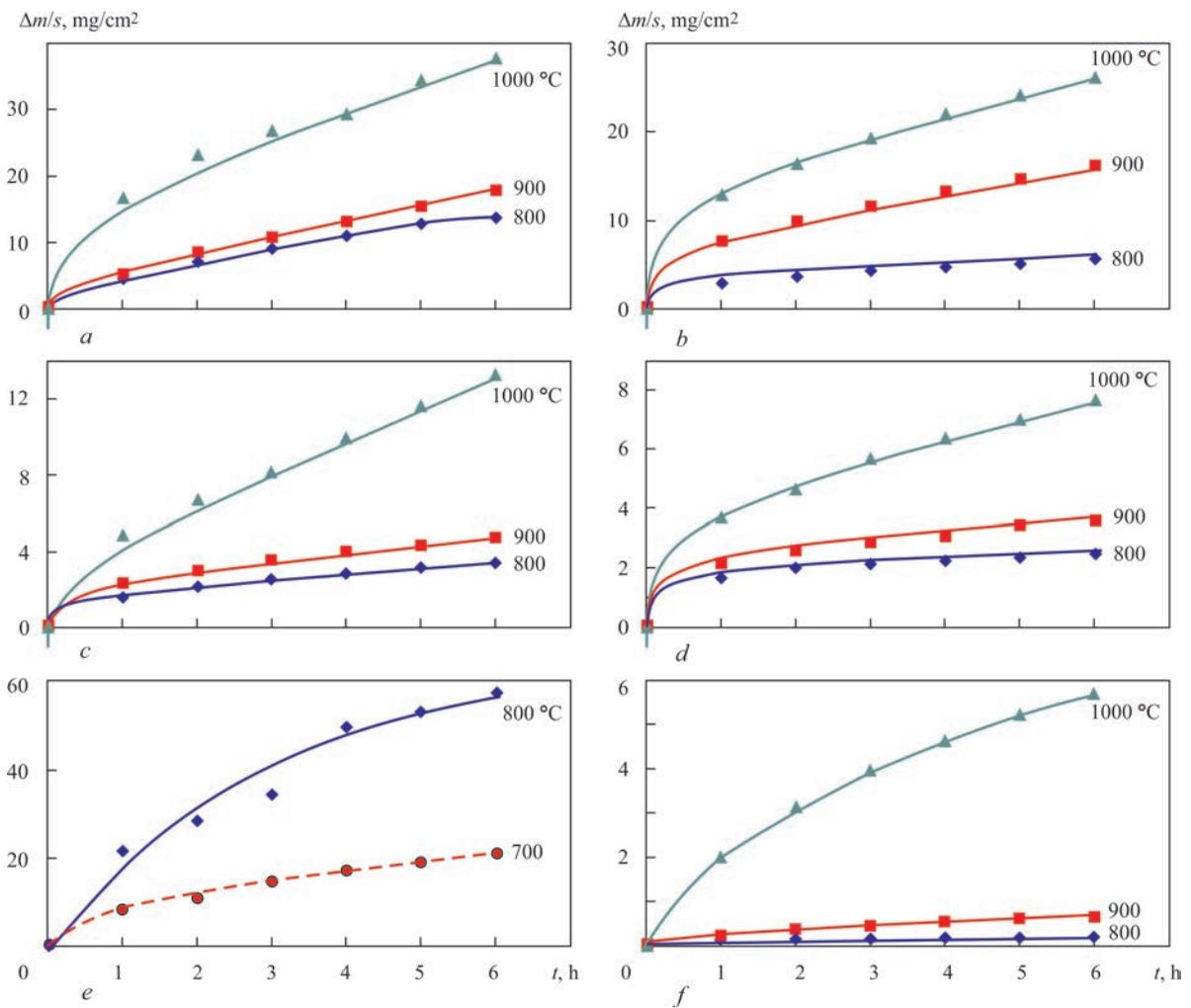


Figure 7. Kinetic dependences of oxidation of thermal sprayed coatings and unprotected steels at temperatures of 800, 900 and 1000 °C in air: *a* — PS; *b* — HVOF produced from MS-powder FeAlCr + CeO₂; *c* — AM; *d* — EM from FCW Fe + Al + Cr + CeO₂; *e* — steel 45; *f* — steel 08Cr17Ti

Table 2. Results of calculation of parameters of heat resistance of EM-coatings

Temperature, K	$10^3/T, 1/K$	Oxidation time, h	$\lg t$	Specific increment of mass, mg/cm^2	$\lg q$	$(Qlge)/RT$	Heat resistance parameter <i>P</i>
1074	0.932	1	0	1.646	0.216	8.53	8.53
		2	0.301	1.964	0.293		8.2
		3	0.477	2.063	0.314		8.05
		4	0.602	2.178	0.338		7.9
		5	0.699	2.292	0.36		7.8
		6	0.778	2.397	0.379		7.75
1173	0.852	1	0	2.078	0.318	7.8	7.8
		2	0.301	2.492	0.396		7.5
		3	0.477	2.805	0.448		7.3
		4	0.602	3.038	0.482		7.2
		5	0.699	3.404	0.53		7.1
		6	0.778	3.511	0.545		7.02
1273	0.785	1	0	3.718	0.57	7.2	7.2
		2	0.301	4.671	0.67		6.88
		3	0.477	5.748	0.76		6.71
		4	0.602	6.424	0.81		6.58
		5	0.699	7.058	0.848		6.49
		6	0.778	7.672	0.885		6.41

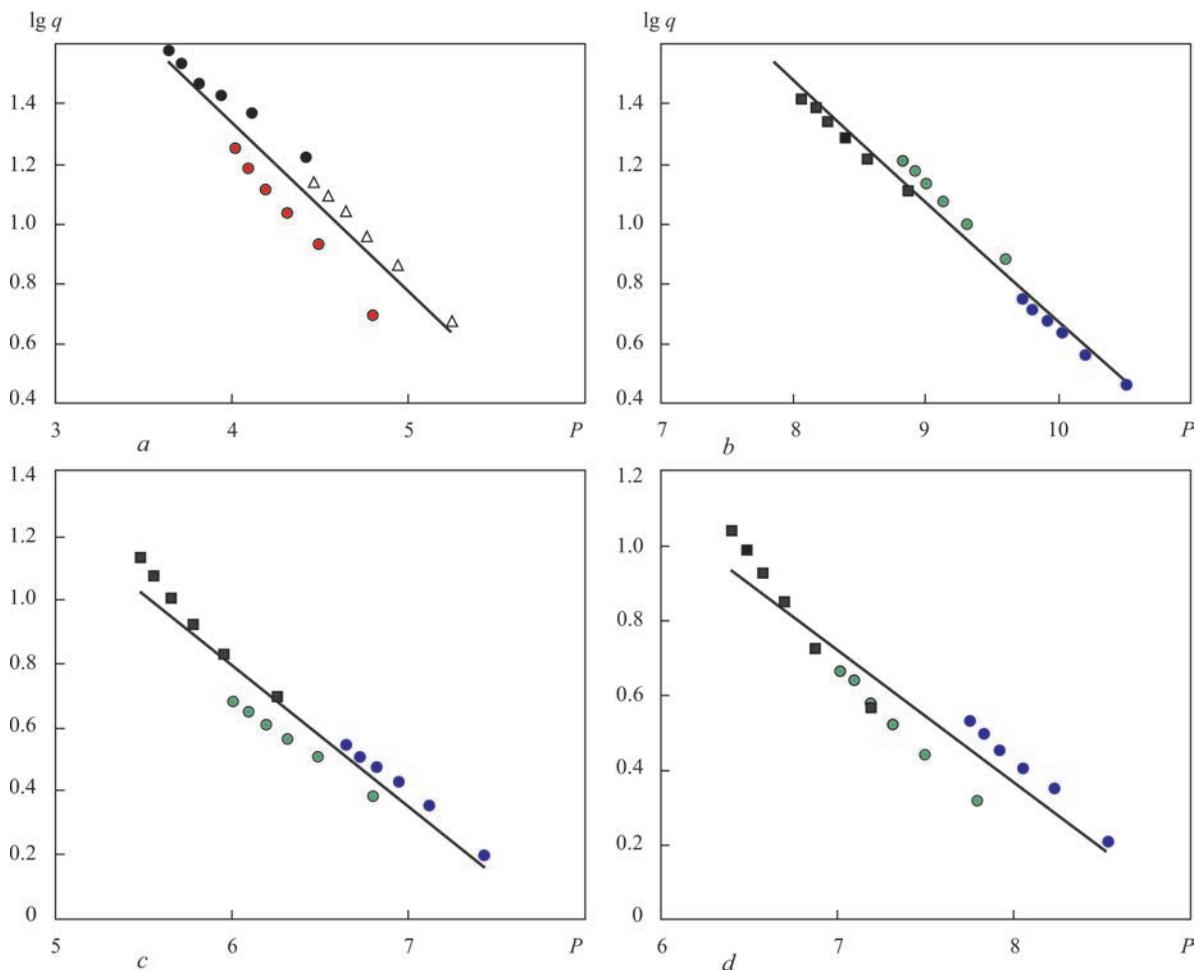


Figure 8. Parametric diagrams of heat resistance for PS (a) and HVOF (b) EM (c) and AM (d) according to results of tests on heat resistance at the temperatures of 800–1000 °C for 1–6 h

One of the important characteristics of protective heat-resistant coatings is the prediction of their service life. Such a prediction can be made by plotting parametric heat resistance diagrams [11].

The heat resistance parametric diagram represents the dependence of the mass loss (increase) of the coating material during oxidation on the heat resistance parameter. The heat resistance parameter is a physical value, whose rate of change over time is proportional (with the opposite sign) to the intrinsic oxidation rate of the coating material, calculated from the values of relative losses (increase) of its mass [12].

The procedure for plotting parametric diagrams consists in determining the values n and Q , where n is the index of degree of parabolic dependence of the oxidation process and Q is the activation energy.

The value n is determined from the experimental kinetic dependence (Figure 7) of the specific increment (loss of mass) q on time t : $q^n = Kt$ (K is the oxidation rate constant), which during plotting in the logarithmic coordinates $\lg q - \lg t$ is transformed into a linear dependence

$$n \lg q = \lg K + \lg t \text{ or } \lg q = \frac{1}{n}(\lg K + \lg t).$$

Hence, $n = \text{ctg}\alpha$ in the coordinates the time is $\Delta m/s \text{ mg/cm}^2$, where α is the inclination angle of the straight line to the axis of abscissa, or can be calculated by the formula:

$$n = \lg(t_2 / t_1) / \lg(q_2 / q_1), \quad (1)$$

where q_1 and q_2 (g/cm^2) is the specific increase (loss) of mass of coating during the oxidation time, equal to t_1 and t_2 , respectively. The accuracy of calculating the value of the exponent n by the formula (1) is the higher, the farther the values t_1 and t_2 are apart from each other.

The activation energy Q of the oxidation process is determined using the temperature dependence $K = K_0 \exp(-Q/RT)$ through the tangent of the angle φ formed by the straight line after taking the logarithm: $\lg K = \lg K_0 - \lg e$.

Activation energy can also be calculated using the formula:

$$Q = n \lg(q_2 / q_1) R / \lg e \left(\frac{1}{T_1} - \frac{1}{T_2} \right), \quad (2)$$

where e is the basis of natural logarithms; R is the universal gas constant; q_1 and q_2 are the specific increase (loss) of mass at the temperatures T_1 and T_2 , respectively.

As in the calculation of the value n , in this case it is recommended to choose the values of T_1 and T_2 , which are sufficiently far apart from each other.

The value of the heat resistance parameter is determined on the basis of the activation energy of the coating oxidation process, calculated according to formulas (1) and (2), and also using the results of tests carried out to obtain the dependences $\lg q - \lg t$ and $\lg q - 1/T$:

$$P = \frac{Q \lg e}{RT} - \lg t. \quad (3)$$

The results of calculating the heat resistance parameter on the example of an EM-coating of flux-cored wire Fe + Al + Cr + CeO₂ are given in table 2, parametric diagrams — in Figure 8.

Conclusion

As a result of carried out investigations, it was found that thermal coatings produced from composite powder FeAlCr + CeO₂ and flux-cored wire Fe + Al + Cr + CeO₂ can protect steel 45 from oxidation, however, to a different extent, depending on the method of deposition.

Thus, at the temperature of 800 °C, the resistance of PS-coatings exceeds steel 45 by more than 1.6 times, HVOF-coatings by 12.5 times, and AM- and EM-coatings by 23 and 26 times, respectively. AM- and EM-coatings remain stable in the oxidizing environment at the level of stainless steel 08Cr17Ti almost up to 1000 °C. This allows recommending to substitute steel 08Cr17Ti with a cheaper steel 45 with AM- or EM-coating of flux-cored wire Fe + Al + Cr + CeO₂ for deposition to external secondary radiators of recuperators.

Note. The article was prepared on the basis of the results of fulfillment of the project of the Program «Resurs-2» P5.1.2 «Improving life time and effectiveness of recuperative heat exchangers by deposition of heat-resistant radiating coatings to protect heating surfaces, operating in combustion flows, and modernization of inner secondary emitters».

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