https://doi.org/10.15407/tpwj2019.10.04

DIFFUSION HEAT-RESISTANT COATINGS FOR STAINLESS AND CARBON STEELS

A.L. BORISOVA[1], **N.I. KAPORIK**[1], **T.V. TSYMBALISTA**[1] and **M.A. VASILKOVSKAYA**[2]
[1]E.O. Paton Electric Welding Institute of the NAS of Ukraine
11 Kazymyr Malevych Str., 03150, Kyiv, Ukraine. E-mail: borisov@pwi.ru.kiev.ua
[2]I. M. Frantsevich Institute of Problems of Materials Science
3 Krzhyzhanovskogo Str., 03680, Kyiv, Ukraine. E-mail: kiparis-gpk@ukr.net

The paper presents the results of investigation of heat-resistant diffusion coatings on steel 08Cr7Ti and steel 45, produced by aluminizing and chromoaluminizing methods in powder mixtures at a temperature of 900–950 °C during 2–5 h. On the kinetic dependencies of oxidation of the specimens with coatings in the temperature interval of 800–l000 °C, the parametric diagrams of thermal shock resistance were plotted. They allow evaluating endurance of protective coatings at any temperatures up to 1000 °C. 8 Ref., 3 Tables, 7 Figures.

Keywords: *aluminizing, chromoaluminizing, heat-resistant coatings, microstructure, phase composition, oxidation kinetics, thermal shock resistance parameter*

All types of protective coatings, including heat-resistant ones, can be divided into two main groups by the nature of their formation: diffusion and layered coatings [1].

I — diffusion-type coatings, the composition of which is the product of interaction of the saturating medium with the base metal. They are produced by saturating the surface of protected metal by one or more elements to form a protective layer.

II — layered-type coatings deposited on the surface of protected metal of a heat-resistant material, for example, applying the methods of thermal spraying.

The coatings of diffusion type are the most widely used. Their advantage is a good bond strength with the base and a relatively simple technology of deposition, the disadvantage is a high temperature of formation and rather active diffusion interaction with the base.

Layered-type coatings are as a rule deposited on cold or slightly preheated base, but they have weaker bond strength with the base than diffusion coatings and require the use of more complex equipment.

Combining the methods of forming protective coatings, obviously, will significantly reduce disadvantages of both groups.

During 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», heat-resistant coatings of two types were developed. The results of investigations of the coatings produced by the methods of thermal spraying using composite powder FeAlCr with the addition of 2 wt.% CeO_2, were published in [2]. This paper is devoted to the solution of the same problem by using diffusion-type coatings.

The most promising diffusion methods for producing heat-resistant coatings on steels include aluminizing and chromoaluminizing processes [3–6]. Moreover, in addition to thermal shock resistance, diffusion saturation of the surface of metals and alloys with aluminum and simultaneous or consequent saturation with aluminum and chrome leads to increase in corrosion and erosion resistance. Among numerous methods of aluminizing and chromoaluminizing, the method of saturation in powder mixtures obtained the most widespread and industrial application.

It is known that structure, phase composition, protective properties and endurance of coatings depend on such factors as composition of powder mixture, temperature and time of diffusion saturation, content of alloying elements, and many other factors, in connection with which the solution of the problem of increasing endurance and efficiency of specific parts requires additional investigations.

In the present work, the processes of aluminizing and chromoaluminizing of steel 08Cr17Ti (used for outer secondary radiators of recuperators) and steel 45 (to investigate the possible replacement of alloy steel with carbon steel) were investigated.

Methods and materials. The processes of aluminizing and chromoaluminizing were carried out in special containers with a seal at a temperature of 900–950 °C during 2–5 h. The main components of the powder mixtures were:

- powder of aluminum parting dust (source of aluminum during aluminizing), a mixture of powders of chrome and aluminum (during chromoaluminizing);

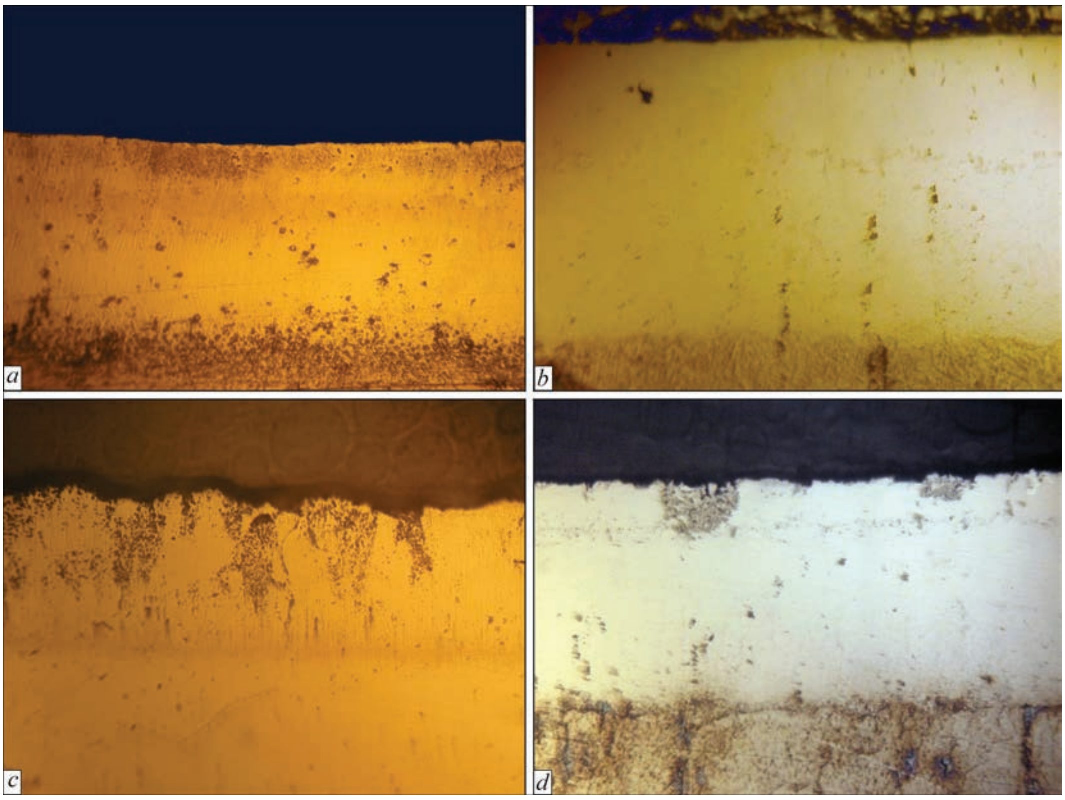

Figure 1. Microstructure (×400) of aluminized (*a*, *b*) and chromoaluminized (*c*, *d*) steel 08Cr17Ti and steel 45

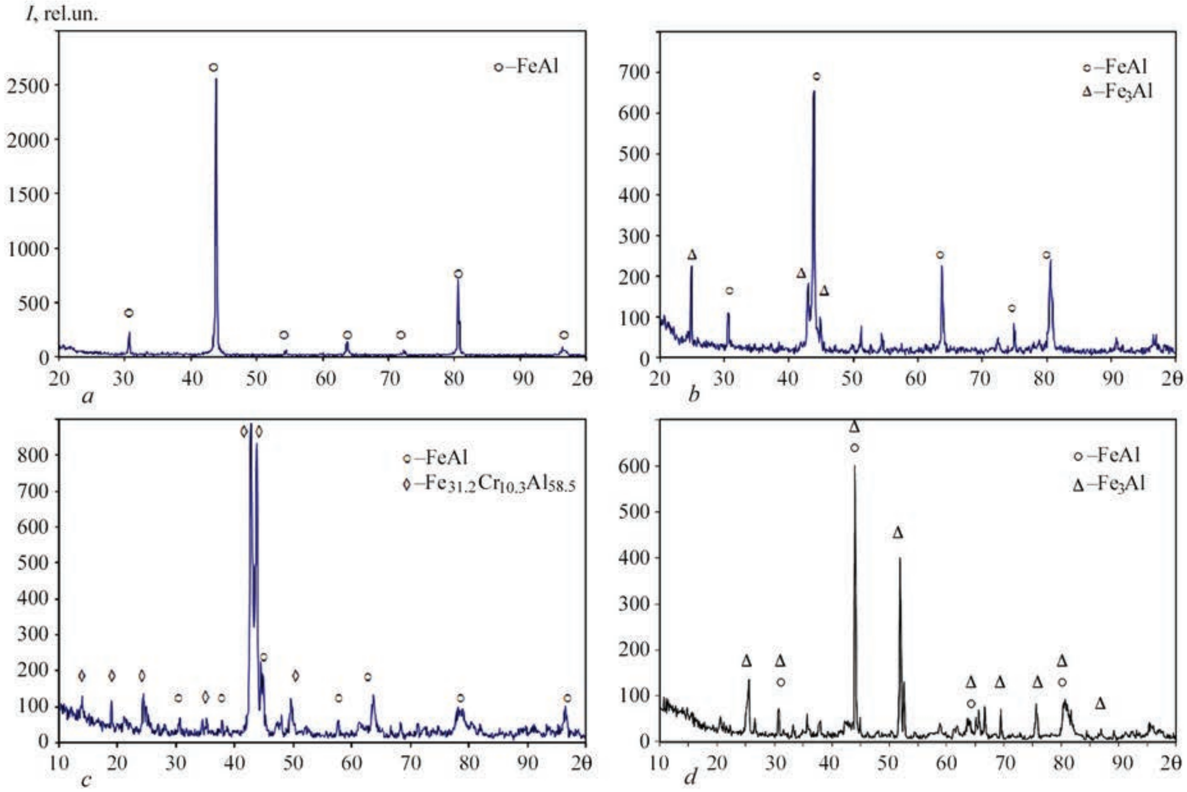

Figure 2. X-ray patterns of diffusion coatings on steel 08Cr17Ti (*a*, *c*) and steel 45 (*b*, *d*) produced by the methods of aluminizing (*a*, *b*) and chromoaluminizing (*c*, *d*)

Table 1. Characteristics of heat-resistant coatings

Coating	Characteristics of coating					
	Thickness, μm		Microhardness, MPa		Phase composition	
	08Cr17Ti	Steel 45	08Cr17Ti	Steel 45	08Cr17Ti	Steel 45
Aluminized	160±15	230±20	3240±450	2560±490	FeAl	FeAl, Fe_3Al
Chromoaluminized	200±10	205±10	3340±630	2800±690	FeAl, $Fe_{31.2}Cr_{10.3}Al_{58.5}$	FeAl, Fe_3Al

- aluminum fluoride powder AlF_3 (process activator);
- aluminum oxide powder (inert additive that prevents sintering of aluminum powder particles and a mixture of aluminum with chrome);
- titanium hydride powder (to remove oxygen remainders from powder mixture).

X-ray structural analysis (XRD) was performed by applying the X-ray diffraction meter DRON-3 in CuK_α-radiation with a graphite monochromator. The phases were decoded using the ASTM hardware components.

Cutting of specimens with coatings was performed in the machine-tool Isomet 1000. The cut specimens were filled with protacryl of grade M, grinding was performed using an abrasive paper with a grain size from 600 to 1200, and polishing was performed using diamond discs from 80–40 to 20–14 in the machine-tool Row Rathenow Metasines. The final polishing was performed in a felt disc using a chrome oxide suspension. To reveal the microstructure, etching of the specimens was carried out in an alcohol solution NHO_3 for steel 45 and HF for steel 08Cr17Ti. Metallographic examinations were performed with the use of the microscope Neophot 32 equipped with a digital photo camera. Microhardness was measured by using of the microhardness tester PMT-3 at a load of 50 g. The number of measurements was at least 50.

Results and discussion. Figure 1 presents the microstructure. Figure 2 shows X-ray patterns of diffu-

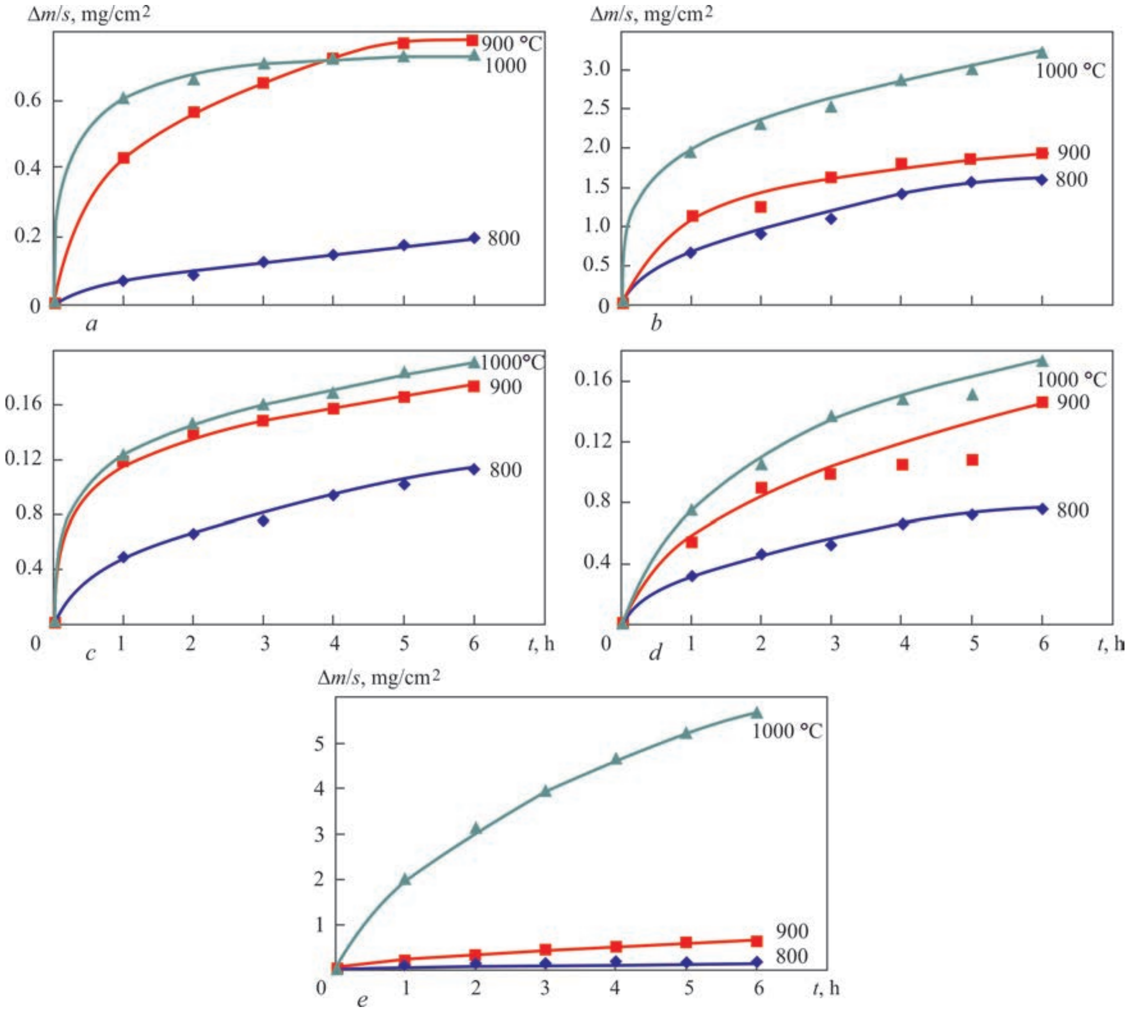

Figure 3. Kinetic dependencies of oxidation of aluminized (*a*, *b*) and chromoaluminized (*c*, *d*) steel 08Cr17Ti (*a*, *c*) and steel 45 (*b*, *d*) and also unprotected steel 08Cr17Ti (*e*)

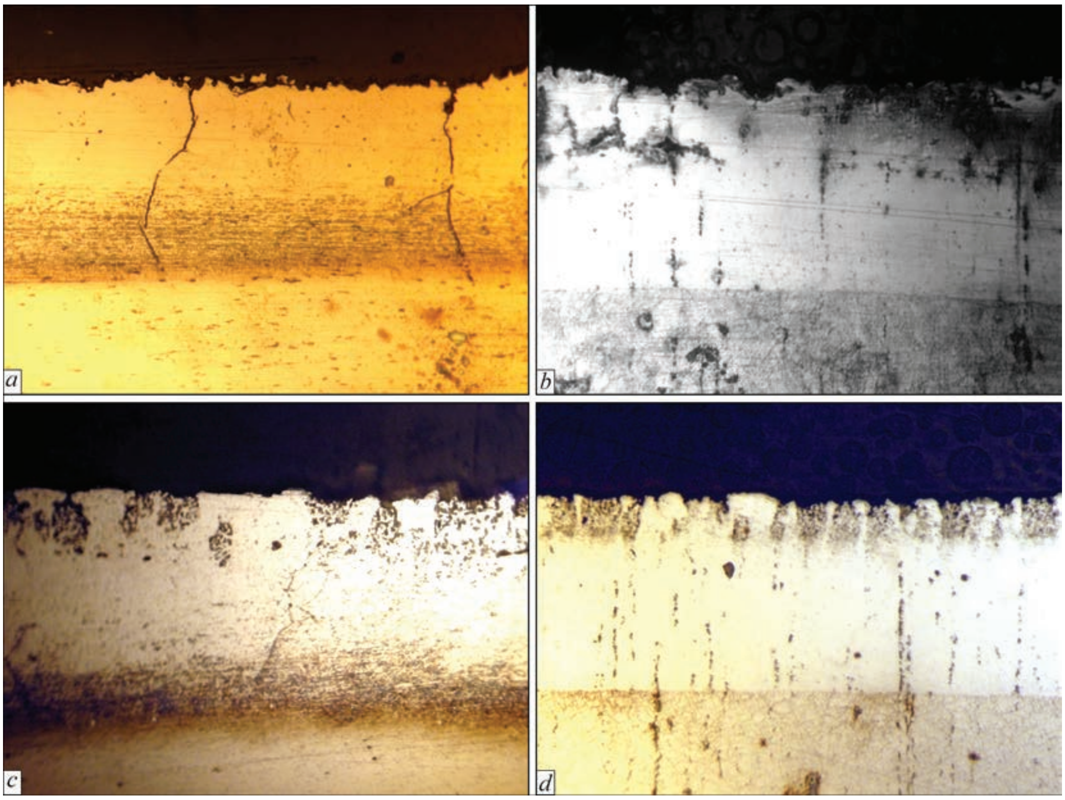

Figure 4. Microstructure (×200) of aluminized (*a*, *b*) and chromoaluminized (*c*, *d*) steel 08Cr17Ti (*a*, *c*) and steel 45 (*b*, *d*) after tests on thermal shock resistance at a temperature of 1000 °C during 5 h

sion coatings on steel 08Cr17Ti and steel 45, and in Table 1 their characteristics are given.

As follows from the presented data, at diffusion saturation of steels with aluminum, on their surface layers of iron intermetallide are formed, which differ in thickness and hardness. As is known, chrome inhibits the diffusion of aluminum into iron, which results in a smaller thickness of aluminized layer on steel 08Cr17Ti as compared to that of steel 45, while its hardness increases due to the presence of chrome. It should be noted, that beyond the region of intermetallide FeAl, the region of solid solution of aluminum in iron is located, spreading to the depth up to 400 μm (for steel 08Cr17Ti) and to 600 μm (for steel 45). Its microhardness is smoothly decreased in the direction to the core (from 2000 to 1500 MPa).

During chromoaluminizing of steel 08Cr17Ti in the surface layer of the coating, two intermetallides were revealed: FeAl alloyed with chrome, and $Fe_{31.2}Cr_{10.3}Al_{58.5}$ (a phase close to Fe_3CrAl_6 as to its composition), and on steel 45 — FeAl and Fe_3Al alloyed with chrome. The microhardness of these coatings is slightly higher than that of the aluminized layers on the same steels.

Typical kinetic dependences of oxidation of diffusion coatings and unprotected steel 08Cr17Ti are shown in Figure 3, *a* and Figures 4 and 5 demonstrate microstructure and X-ray diffraction patterns of coatings after tests on thermal shock resistance at a temperature of 1000 °C.

As follows from the presented data (Figure 3), the mechanism of oxidation of diffusion coatings submits to the parabolic temporal law in the entire studied temperature range of 800–1000 °C. Judging by the results of X-ray diffraction analysis (Figure 5, Table 2), the main changes in phase composition during oxidation of diffusion coatings are the formation of aluminum oxide Al_2O_3 in the surface layers, behind which there is a region of intermetallides FeAl or Fe_3Al (in case of aluminizing) or intermetallides FeAl and Fe_3Al alloyed with chrome (in case of chromoaluminizing), gradually passing into solid solutions. Judging by the

Table 2. Characteristics of coatings after tests on thermal shock resistance at a temperature of 1000 °C during 5 h

Coating	Characteristics of coating					
	Thickness, μm		Microhardness, MPa		Phase composition	
	08Cr17Ti	Steel 45	08Cr17Ti	Steel 45	08Cr17Ti	Steel 45
Aluminized	320±15	320±20	2780±560	2370±400	FeAl, Al_2O_3	FeAl, Al_2O_3
Chromoaluminized	290±5	300±10	3260±520	2230±320	$(F, Cr)_3Al$, Al_2O_3	$(Fe_2Cr)Al$, Al_2O_3

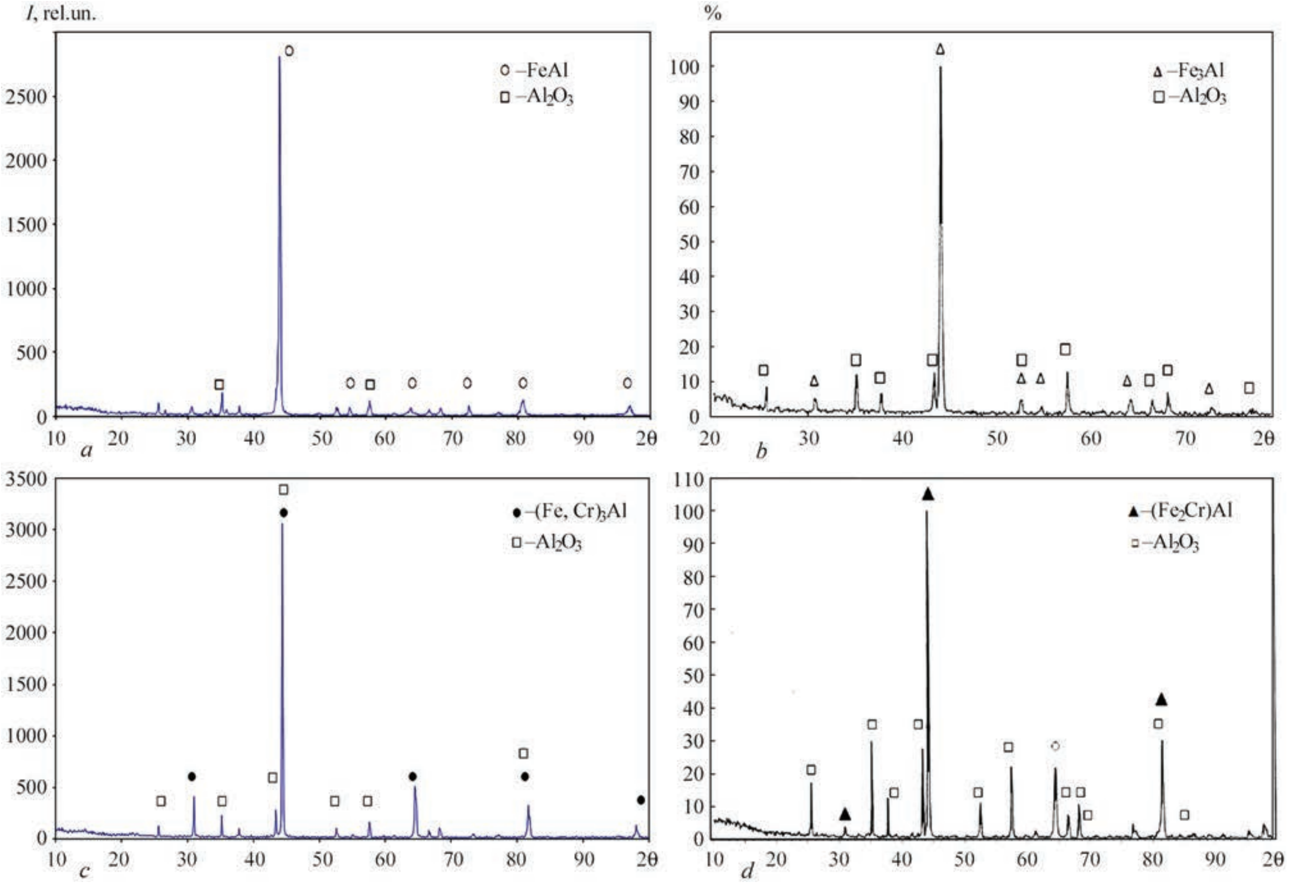

Figure 5. X-ray patterns of aluminized (*a*, *b*) and chromoaluminized (*c*, *d*) steel 08Cr17Ti (*a*, *c*) and steel 45 (*b*, *d*) after tests on thermal shock resistance at a temperature of 1000 °C during 5 h

results of X-ray spectral microanalysis, the content of aluminum in the coating decreases both as a result of the formation of an oxide film, as well as due to its resorption in the base. Thus, for example, on the surface of chromoaluminized steel 08Cr17Ti in the initial state (Figure 6, *a*), the content of aluminum is about 31 wt.%, which corresponds to the composition of intermetallide FeAl, gradually decreasing at a depth of about 150 μm to 15 % (approximate content of Al in Fe$_3$Al), and then to 2 % at a depth of 600 μm. After oxidation at a temperature of 1000 °C during 6 h, these values amount approximately to about 20 %, respectively, and in the surface layer to about 15 wt.% at a depth of about 200 μm (Figure 6, *b*).

Comparing the microstructure of diffusion coatings in the initial state (Figure 1) and after oxidation at a maximum temperature of 1000 °C (Figure 4), the presence of longitudinal (in depth) cracks on steel 08Cr17Ti and their practical absence on steel 45 can be noted.

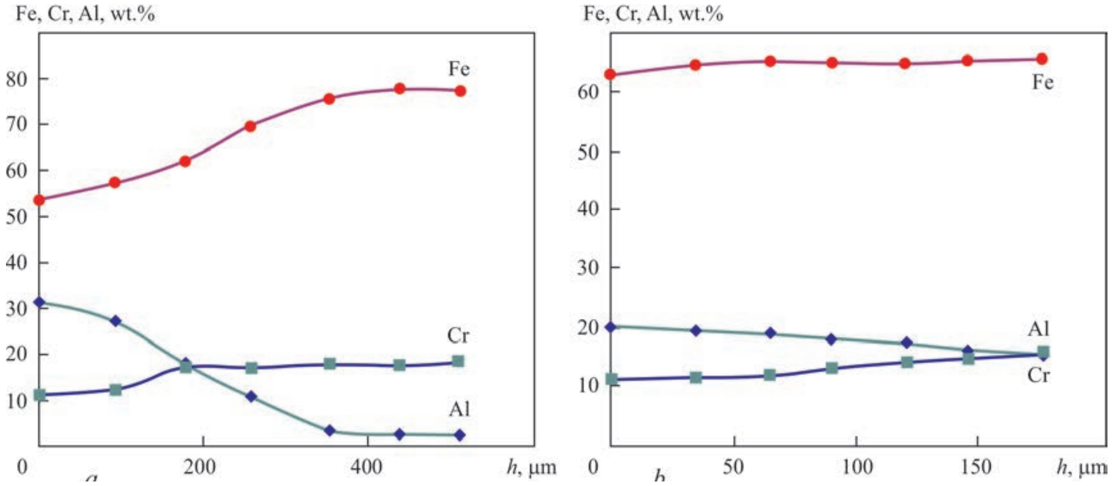

Figure 6. Distribution of elements in depth of diffusion layers of chromoaluminized steel 08Cr17Ti in the initial state (*a*) and after oxidation in air at a temperature of 1000 °C during 5 h (*b*)

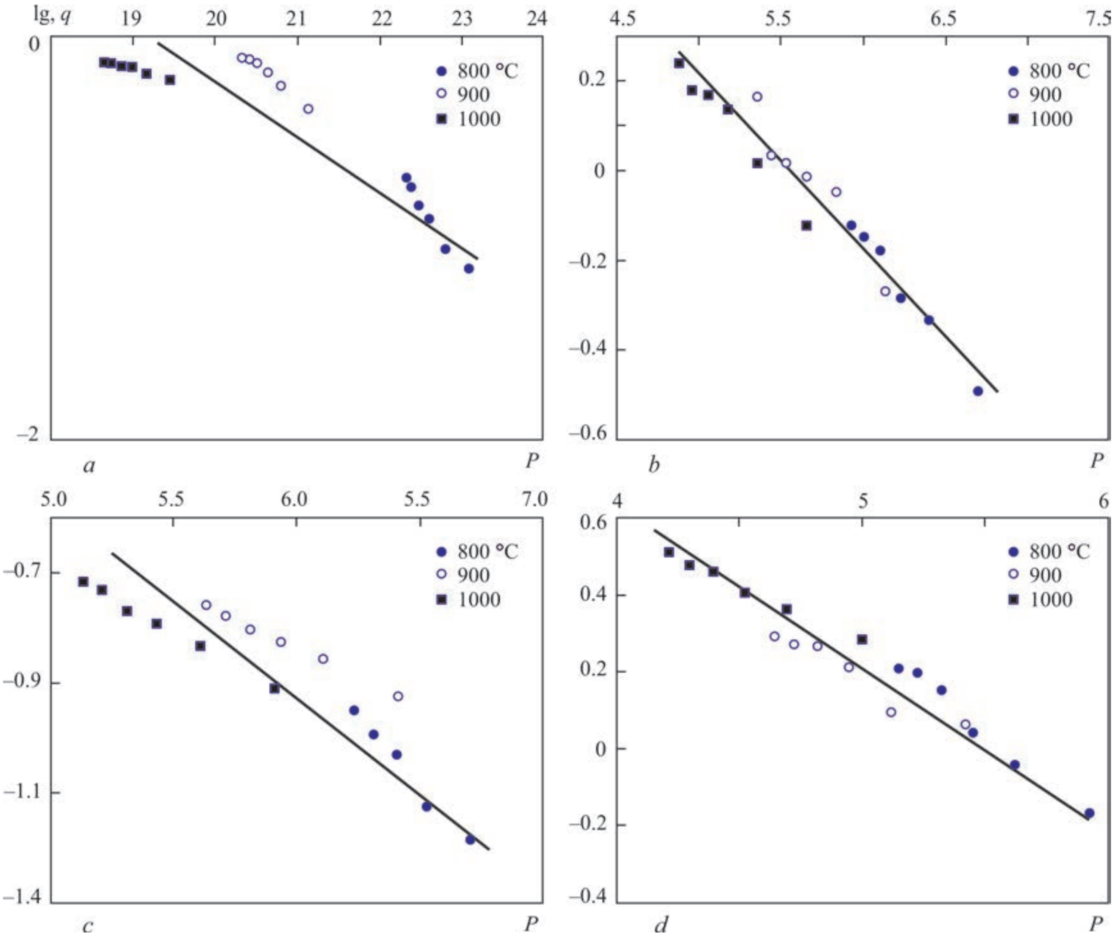

Figure 7. Parametric diagrams of thermal shock resistance for aluminized (*a*, *b*) and chromoaluminized (*c*, *d*) steel 08Cr17Ti (*a*, *c*) and steel 45 (*b*, *d*) according to the results of tests on thermal shock resistance at a temperature of 1000 °C during 5 h

Defects in diffusion coatings of this kind arise in connection with occurrence of residual stresses, the value and sign of which depend on chemical and phase composition of diffusion layer, which in this case is significantly different (see Figure 2, Table 1). As for the effect of such kind of cracks on thermal shock resistance of protective coatings, it is far from unique. The fact is that to provide endurance of coatings operating at high temperatures, thermal shock resistance is an equally important characteristic, on

Table 3. Results of calculation of parameters of thermal shock resistance of chromoaluminized steel 45

Temperature, K	$10^3/T$	Oxidation time, h	lg *t*	Specific increment of mass, mg/cm^2	lg *q*	$\frac{Q \lg e}{RT}$	Parameter of thermal shock resistance *P*
1073	0.932	1	0	0.32	–0.49	6.71	6.709746
		2	0.301	0.467	–0.33		6.408746
		3	0.477	0.52	–0.28		6.232746
		4	0.602	0.66	–0.176		6.107746
		5	0.699	0.72	–0.143		6.010746
		6	0.778	0.75	–0.12		5.931746
1173	0.852	1	0	0.54	–0.267	6.138	6.137731
		2	0.301	0.9	–0.046		5.836731
		3	0.477	0.97	–0.012		5.660731
		4	0.602	1.04	0.018		5.535731
		5	0.699	1.08	0.03		5.438731
		6	0.778	1.457	0.16		5.359731
1273	0.785	1	0	0.75	–0.122	5.65	5.655584
		2	0.301	1.04	0.0185		5.354584
		3	0.477	1.36	0.136		5.178584
		4	0.602	1.47	0.168		5.053584
		5	0.699	1.51	0.179		4.956584
		6	0.778	1.727	0.237		4.877584
Q = 33025.5							

which preservation or delamination of protective layer in the process of tests depends. One of the ways to increase thermal shock resistance is to reduce the effective elasticity modulus of the protective layer by creating deformation structure [7]. This can be achieved due to preservation of a significant residual porosity or creation of microcracks in an artificial way, oriented perpendicularly to the surface of a coating interface with the base [8]. As was shown by the investigations, in this work the presence of cracks in coatings did not impact the nature of their oxidation, which is evidenced by kinetic dependencies of oxidation of diffusion coatings, presented in Figure 3.

The carried out investigations allowed evaluating endurance of protective parts for any temperatures up to 1000 °C by plotting parametric diagrams of thermal shock resistance (Figure 7).

The methodology of plotting parametric diagrams of thermal shock resistance is described in detail in [4], and in Table 3 as an example, the results of calculating parameter of thermal shock resistance of chromoaluminized steel 45 are presented according to the results of this work.

Conclusions

As a result of carried out investigations, it was found that aluminizing increases thermal shock resistance of steel 45 by 2 times, steel 08Cr17Ti — by more than 7 times, and chromoaluminizing of steel 45 — by 3.5 times. The highest thermal shock resistance in the range of 800–1000 °**C** belongs to the chromoaluminized steel 08Cr17Ti, which exceeds the resistance of unprotected steel at 1000 °**C** by more than 25 times. Comparison of results of this work with previous investigations [1] showed that diffusion coatings (aluminizing and chromoaluminizing) are able to protect steel 08Cr17Ti and steel 45 from oxidation to higher temperatures (up to 1000 °C) as compared to AM- and EM-coatings produced of a composite powder FeAlCr — CeO_2 (up to 800 °C). However, it should be borne in mind that as compared with diffusion methods, the methods of thermal spraying are characterized by such advantages as ability to protect large-sized parts and producing large thicknesses of a protective layer.

At present time, prototype specimens of inner secondary emitters of recuperators of steel 08Cr17Ti and steel 45 with diffusion and thermal sprayed coatings were made for long-term tests by using the main workbench of the Gas Institute of the NASU during 2019–2020.

1. Borisov, Yu.S., Borisova, A.L., Tsymbalista, T.V. et al. (2019) Heat-resistant thermal coatings based on intermetallics with CeO_2 additives. *The Paton Welding J.*, **9**, 23–29.
2. Appen, A.A. (1976) *Temperature-resistant inorganic coatings*. 2nd ed. Leningrad, Khimiya [in Russian].
3. Borisenyuk, G.V., Vasiliev, L.A., Voroshnin, L.G. et al. (1981) *Chemical and heat treatment of metals and alloys*: Refer. Book. Moscow, Metallurgiya [in Russian].
4. Lygdenov, B.D., Guriev, A.M., Mosorov, V.I., Butukharov, V.A. (2015) Perspective diffusion coatings. *Int. J. of Experimental Education*, 12(**4**), 1, 572–573.
5. Muboyadzhyan, S.A., Galoyan, A.G. (2012) Diffusion aluminium coatings for protection of surface of inner sealing band of turbine blades. *Metally*, **5**, 4–13 [in Russian].
6. Burnyshev, I.N., Poryvaev, D.A. (2015) Aluminizing of steels in dynamic saturation medium. *Khimicheskaya Fizika i Mezoskopiya*, 17(**3**), 364–371 [in Russian].
7. Grot, A.S., Mortin, I.K. (1981) Behavior of plasma-sprayed ceramic thermal-barrier coating for gas turbine applications. *Amer. Ceram. Soc. Bull.*, **60**, 807–811.
8. Borisova, A.L., Adeeva, L.I., Tunik, A.Yu. (1994) Influence of characteristics of initial material and conditions of spraying on structure and properties of thermal coatings. Kyiv, PWI [in Russian].

Received 24.07.2019