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DEVELOPMENT OF THE CoCrAlY/ZrO_2–8 % Y_2O_3 TYPE THERMAL BARRIER COATING BY SURFACE DOPING OF THE METAL LAYER WITH ALUMINIUM

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ABSTRACT

The diffusion processes occurring at aluminium enrichment of the CoCrAlY overlayer during vacuum annealing from the slurry suspension applied to its surface and their influence on the structure, chemical composition and properties of CoCrAlY/ZrO_2–8 % Y_2O_3 coatings electron beam evaporated on nickel-based superalloy samples were studied. It is shown that the diffusion layer formed on the surface of the CoCrAlY alloy, enriched in aluminium, has a heterogeneous thickness and contains two microstructural zones with different aluminium content (external zone with aluminium up to 31 % and inner with aluminium up to 19 %). It was found that during vacuum heat treatment, cobalt and chromium diffuse into the slurry layer. As a result, microhardness increases up to 9 GPa and microcracks that propagate into the CoCrAlY layer are formed. The parameters of low-temperature heat treatment, which provides the formation of a defect-free diffusion zone in CoCrAlY, are established. The obtained results allowed us to optimize the technology of CoCrAlY layer thermodiffusional alumization from the slurry for CoCrAlY/ZrO_2–8 % Y_2O_3 coatings in order to increase the operating temperature of the turbine blades made of CM-88U and CM-93 superalloys.

KEYWORDS: electron beam physical vapor deposition, condensation in vacuum, thermal barrier coatings, nickel-based superalloy, CoCrAlY metal bond coat, thermodiffusional alumization, aluminium, slurry, thermally grown Al_2O_3 oxide (TGO), ZrO_2–8 % Y_2O_3 ceramic layer, diffusion of elements

INTRODUCTION

Alloys of MCrAlY type (M–Ni, Co or their combination) are used as coatings or bond coat in MCrAlY/ZrO_2/ZrO_2–Y_2O_3 thermal barrier coatings for protection of blades of modern gas turbine engines (GTE) made of high-temperature alloys (HTA) from high-temperature oxidation and corrosion. Aluminium content in them is usually equal to 8–12 % (wt.% here and furtheron) and it provides formation of a surface layer of Al_2O_3-based scale (TGO — thermally grown oxide) at high temperature in operation [1, 2].

Improvement of the effectiveness of GTE operation is accompanied by increase of working temperature, which necessitates increase of oxidation resistance (high-temperature resistance) of MCrAlY metal. One of the possible directions of such an increase is saturation of the surface of metal layer from MCrAlY alloy by aluminium using various methods [2–6]. The simplest and most cost-effective of these methods is saturation by aluminium from the coatings or slurries by prior deposition on the metal layer surface of filler material in the form of a suspension, containing the required alloying elements, and performing further heat treatment [7, 8].

The objective of this study is optimization of the parameters of the process of thermodiffisional alumization of the condensed CoCrAlY layer from the slurry with further heat treatment and deposition of ZrO_2–8 % Y_2O_3 ceramic layer by the method of electron beam evaporation and condensation in vacuum.

MATERIALS AND INVESTIGATION PROCEDURE

Deposition of CoCrAlY/ZrO_2–8 % Y_2O_3 thermal barrier coatings was conducted by electron beam evaporation and condensation in vacuum on samples (segments of airfoil of blades made from high-temperature nickel alloys of CM-88U and CM-93 type) by the serial multistage technology which is used in State-Run Enterprise «Gas Turbine Research & Production Complex «Zorya»-«Mashproekt».

At the first stage of coating deposition a CoCAlY layer (composition of evaporation ingots in keeping with TU U 27.4-20113410.002–2001) was applied on the blades, which was followed by their vacuum heat treatment (HT).

At the second stage a layer of slurry was deposited on the surface of CoCrAlY layer by the method of atomization of liquid suspension of PMS-Yu composition (analog of Sermetel W suspension), which was

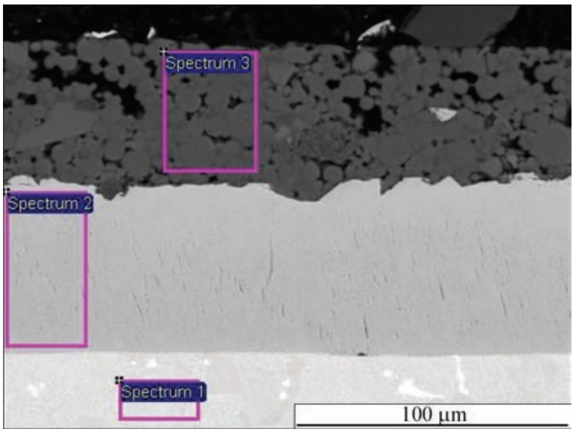

Figure 1. Microstructure and composition of CoCrAlY layer with PMS-Yu slurry on the surface after thermal setting

followed by thermal setting of the deposited slurry by drying at 350 °C.

At the third stage vacuum HT was performed for saturation of the surface of CoCrAlY layer by aluminium.

At the fourth stage air-abrasive treatment (AAT) by particles of abrasive from aluminium oxide was performed to remove the remains of slurry, and the outer ceramic layer of ZrO_2–8 % Y_2O_3(8YSZ) was deposited on the blade airfoil surface.

Part of the blades after the second stage were transferred to SC "ICEBT of the E.O. Paton Electric Welding Institute of NASU" for further investigations and deposition of an outer ceramic layer.

The thickness of individual coating layers was determined in PolivarMet optical microscope. Microstructural studies and determination of microhardness of the coatings were conducted on samples in as-delivered condition and after heat treatment.

The structure of coating layers was studied using scanning microscope Carl Zeiss Sigma 300. The chemical composition was further determined using X-ray microprobe energy-dispersive attachment XMAX 50 for electron microscope.

Microhardness measurement was performed on transverse sections of the coatings using Micro-Duromat 4000 E attachment for Polyvar-Met optical microscope by standard Vickers indenter at 200 N load and exposure time of 10 s.

Thermal cycle life of CoCrAlY/8YSZ coatings on segments of blade airfoils was studied by the method of furnace testing in air by the following mode: heating up to 1100 °C temperature for 6 min, soaking for 50 min at this temperature, fan cooling to the temperature of approximately 60–80 °C for 4 min. Segments were examined after every twenty cycles. Coating failure was assumed to be outer ceramic layer delamination from 20 % of airfoil segment surface.

INVESTIGATION RESULTS AND THEIR DISCUSSION

Figure 1 and Table 1 give the microstructure and chemical composition of CoCrAlY layer with a layer of PMS-Yu slurry after thermal setting (after stage 2).

CoCrAlY layer contains about 22 % Cr and 11 % Al and a low content of yttrium (0.1 %), which is detected only in individual regions of the layer.

The layer of aluminium-based slurry has a porous microstructure, which contains predominantly spherical-like particles of 4–15 µm dia.

Thickness of CoCrAlY layer is equal to 55–65 µm, microhardness is on the level of 5.8 GPa, thickness of the deposited slurry layer varies in the range of 30–50 µm, and its microhardness is not higher than 0.7 GPa.

Further high-temperature HT in vacuum in the temperature range of 950–1100 °C for 0.5–1.0 h leads to formation of an aluminium-saturated diffusion layer on CoCrAlY surface (Figure 2, Table 2). This formed diffusion layer is of a heterogeneous thickness (20–40 µm) and it contains two zones with the characteristic microstructure and different aluminium content. Outer zone has grain structure, the size of globular particles of intermetallics of Co–(26–31) % Al–(9–14) % Cr composition is equal to 25–35 µm. It was found to contain numerous microcracks and pores, and its microhardness reaches 8.0–8.2 GPa. The inner zone contains 15–19 % aluminium, its microhardness is equal to approximately 6 GPa.

With increase of the duration of vacuum HT at 1100 °C up to 4 h, the total thickness of this diffusion layer increases by 15–20 µm (Figure 2, *a*–*j*). Aluminium content in the outer zone decreases from 31 to 25 %, and the globular particles of CoAlCr intermetallics do not significantly change their composition or dimensions. The inner zone, alongside an increase of its thickness to 10–15 µm, is saturated by aluminium due to its diffusion from the slurry and the outer zone, its content rising from 14.7 to 17.5 %. Here a decrease of total aluminium content in the volume of CoCrALY layer (from 11 to 10 %) is also observed

Table 1. Chemical composition of CoCrAlY layer with PMS-Yu slurry on the surface after thermal setting, wt.%

Spectrum	O	Mg	Al	Si	P	Ti	Cr	Co	Ni	Y	Mo	W	Re
1	–	–	2.6	1.0	–	4.7	14.1	7.8	63.0	–	1.0	3.6	2.5
2	–	–	11.1	–	–	–	22.0	66.9	–	0.1	–	–	–
3	14.0	1.6	71.5	4.0	6.1	–	2.8	–	–	–	–	–	–

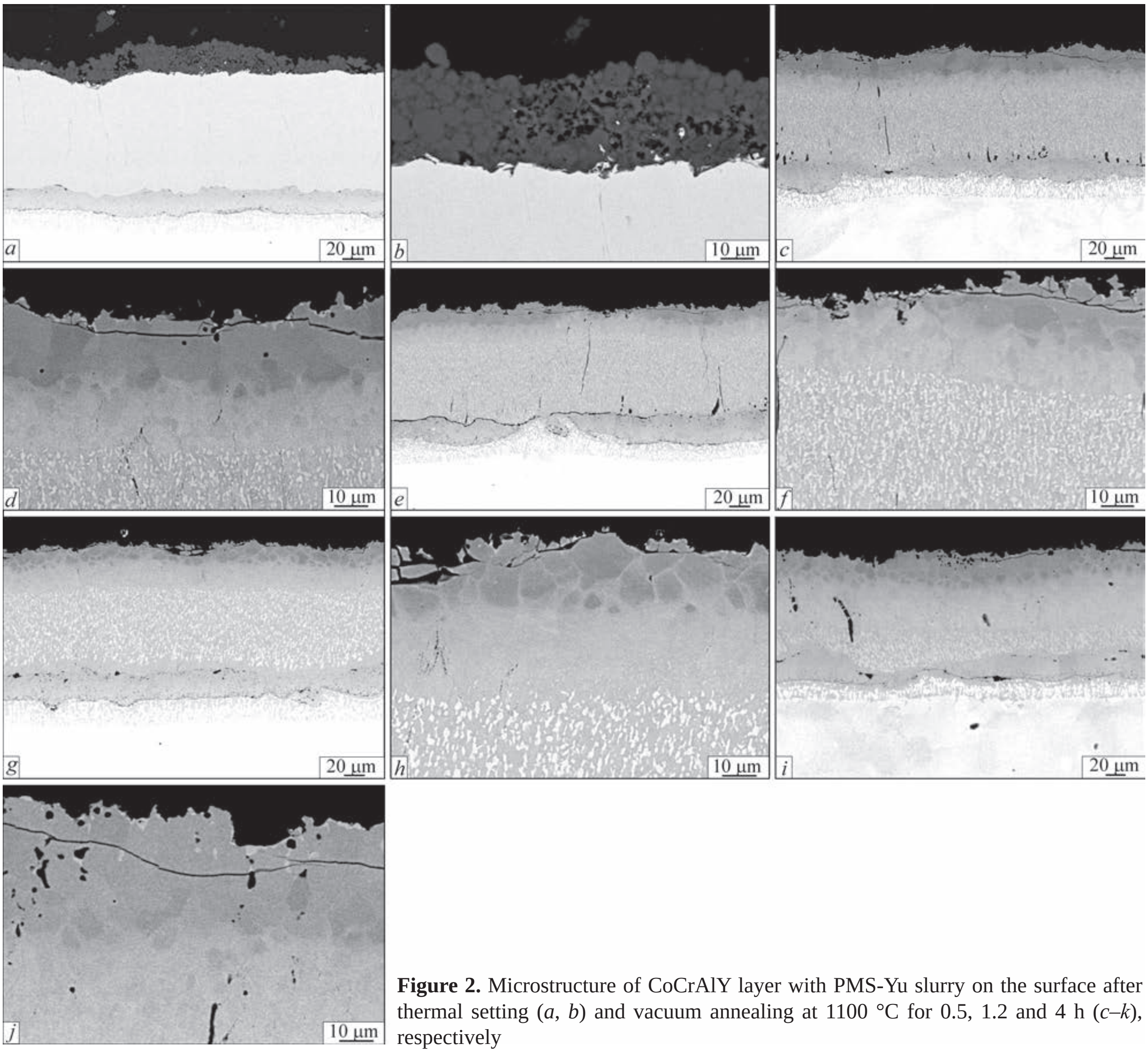

Figure 2. Microstructure of CoCrAlY layer with PMS-Yu slurry on the surface after thermal setting (*a*, *b*) and vacuum annealing at 1100 °C for 0.5, 1.2 and 4 h (*c*–*k*), respectively

that is attributable to its diffusion into the high-temperature alloy.

Lowering of vacuum HT temperature to 950 °C did not affect the forming defects. Microcracks form in the outer zone of CoCrAlY layer, which, as a rule, propagate parallel to the substrate (Figure 3).

The probable cause for microcrack appearance can be sintering of the slurry suspension during the process of high-temperature HT, resulting in increase of slurry layer microhardness to the level of 9 GPa. This is also promoted by cobalt (close to 41 %) and chromium (close to 8 %) diffusion into the slurry from CoCrAlY layer (Figure 3, Table 3). On the contact boundary of the slurry, containing up to 50 % aluminium, and the surface of CoCrAlY layer, enriched in aluminium up to 30 %, stresses develop during cooling after HT, which lead to slurry cracking and crack propagation into the aluminium-enriched metal layer.

Attempts to remove the defective surface layer by intensive air-abrasive treatment before deposition of the outer ceramic layer did not yield the desirable result, either, and appearance of microcracks was observed on metal-ceramics interface (Figure 4).

As the thickness of the applied slurry suspension (it is applied in a layer of minimum possible thickness) cannot be reduced, it is rational to lower HT

Table 2. Composition (wt.%) and microhardness of CoCrAlY layer (GPa), depending on annealing time at 1100 °C

Zone of Al-saturated CoCrAlY layer	Initial		0.5 h		1 h		2 h		4 h	
	H_μ	Al	H_μ	Al	H_μ	Al	H_μ	Al	H_μ	Al
Outer	–	–	8.8	31.2	8.2	31.0	7.6	28.2	6.5	25.5
Inner	–	–	6.4	14.7	6.2	16.3	7.0	16.0	6.9	17.5
Layer	6.0	12.0	5.3	10.7	5.7	11.5	6.1	10.6	6.5	9.9

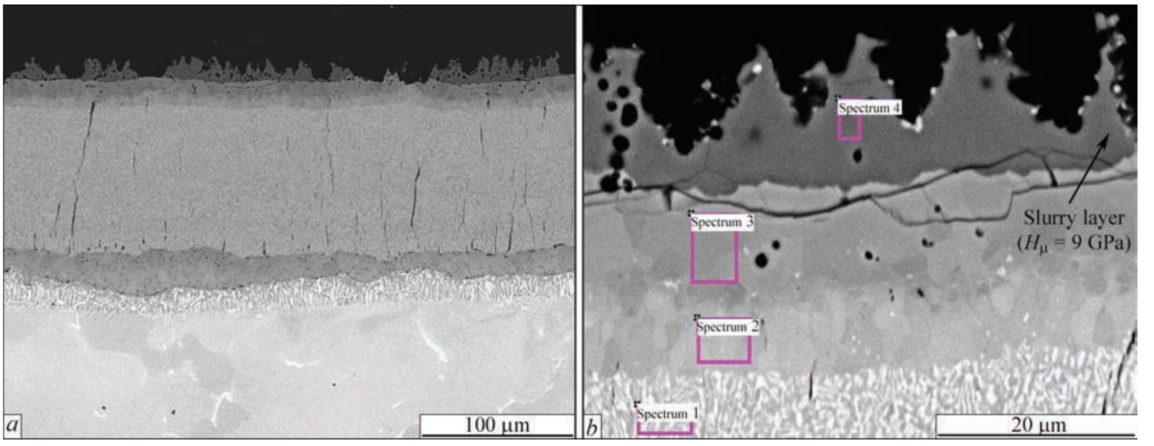

Figure 3. Microstructure (*a* — ×300; *b* — ×1800) of CoCrAlY layer after slurry deposition (H_μ = 9 GPa) and vacuum HT at 950 °C, 1 h

temperature at stage 3 of coating deposition process so as to slow down both the diffusion processes of CoCrAlY layer saturation by aluminium, and the processes of sintering of the slurry layer. Here, diffusion interaction in slurry CoCrAlY layer system would occur only in a limited volume of the slurry, adjacent to the metal surface. It would allow lowering the aluminium content in the diffusion layer, the thickness of this layer and reducing the microhardness of sintered slurry (preventing microcrack initiation in it). After that, when performed further AAT, part of the slurry, which has not reacted and remained, will be removed for the surface of aluminium-saturated diffusion zone in CoCrAlY layer that will prevent its further saturation by aluminium.

In order to clarify the possibility of preventing such microcrack initiation in aluminium-saturated CoCrAlY layer, investigations were performed on the influence of temperature and time of heat treatment after slurry application (stage 3 – coating deposition).

Minimum HT temperature, at which no microcracks form during annealing in the range of 0.5–0.8 h, was established (not higher than 700–750 °C).

Figure 5 and in Table 4 give the microstructure and composition of CoCrAlY layer with deposited slurry after high-temperature HT for 6 h. On the surface of CoCrAlY layer after HT the slurry layer contains three zones: outer of approximately 30 μm thickness (slurry which did not react) with microhardness on the level of 0.65 GPa; middle of approximately 20 μm thickness (sintered slurry) with microhardness on the level of 3.9 GPa; and diffusion of approximately 8 μm thickness (microhardness is equal to 6.7 GPa), which is adjacent to the surface of CoCrAlY layer (microhardness of 6 GPa).

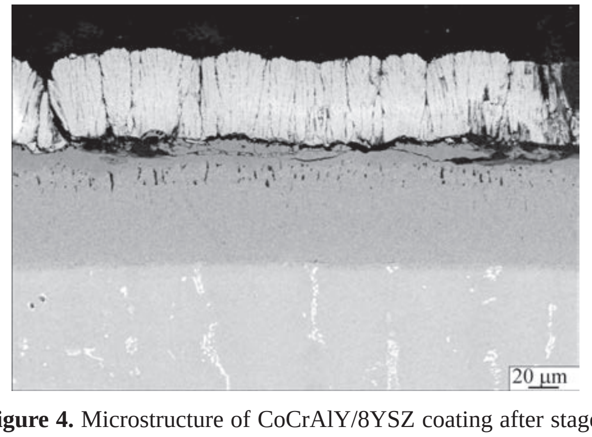

Figure 4. Microstructure of CoCrAlY/8YSZ coating after stages 1–4 of coating deposition (HT) in vacuum at the temperature of 950 °C for 1 h)

Aluminium content in the diffusion zone reaches 42.5 %. Here, no microcrack formation was detected in the sintered slurry layer and in the diffusion zone.

Lowering of the temperature of vacuum HT allows: ensuring formation of aluminium-saturated diffusion zone of a more homogeneous thickness in CoCrAlY, due to aluminium coming not from the entire volume of slurry layer of heterogeneous thickness, but just from the slurry zone which is in direct contact with CoCrAlY surface; controlling both the thickness and content of aluminium in the diffusion zone owing to a change of HT time.

Here, selection of AAT mode parameters, ensuring removal of remains of the slurry mass from the diffusion layer surface after HT, is important.

After performance of stage 4 (deposition of 8YSZ layer) the diffusion zone thickness increased up to 15 μm, Al content was close to 21 % and it gradually decreased to the level of 12 % in CoCrAlY layer, and a TGO interlayer of approximately 1 μm thickness was present between CoCrAlY layer and 8YSZ layer (Figure 6, Table 5).

Table 3. Composition of CoCrAlY layer with slurry after vacuum HT at 950 °C, 1 h

Spectrum	Al	Cr	Co	Y
1	11.3	21.4	67.2	–
2	17.5	15.9	66.4	0.15
3	30.6	6.8	62.1	0.4
4	50.5	8.2	41.3	–

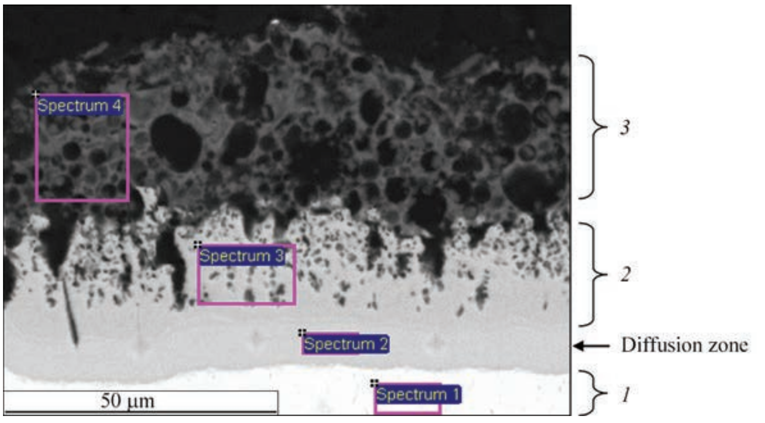

Figure 5. Microstructure and composition of CoCrAlY layer with PMS-Yu slurry on the surface after thermal setting and low-temperature HT for 6 h: *1* — CoCrAlY layer; *2* — sintered slurry layer; *3* — layer of slurry which did not react

Table 4. Chemical composition (wt.%) of CoCrAlY layer with PMS-Yu slurry on the surface after thermal setting and low-temperature HT for 6 h

Spectrum	O	Na	Mg	Al	Si	P	Cl	Ca	Cr	Co	Y
1	–	–	–	10.9	–	–	–	–	23.0	66.1	–
2	–	–	–	42.6	2.6	–	–	–	14.4	40.5	0.1
3	2.4	–	–	48.8	2.8	–	–	–	12.1	33.9	–
4	39.1	2.1	4.4	37.7	3.5	7.4	0.4	0.4	4.1	0.8	–

Changing HT time and temperature enables increasing the thickness of the diffusion zone, saturated by aluminium, to 40 μm, and reducing its aluminium content to 15–16 % (Figure 7, Table 6).

Performed thermal cycling testing of blade airfoil segments with CoCrAlY/8YSZ coating showed that slurry application improves the life by 25–30 %, due to a positive influence of aluminium-saturated diffusion zone, under the conditions of high-temperature cyclic testing (increase of high temperature resistance and prevention of spinel formation during growth of Al_2O_3 layer) [9].

Developed recommendations on improvement of the technology of thermodiffusional alumization of the surface of metal layer of CoCrAlY/8YSZ coatings (lowering of the temperature of vacuum heat treat-

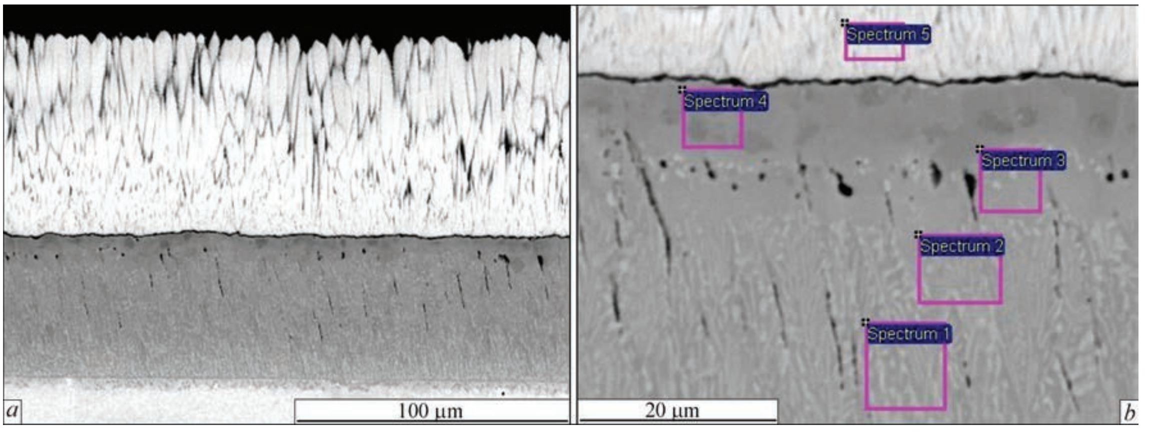

Figure 6. Microstructure (*a* — ×500; *b* — ×1800) and composition of CoCrAlY/8YSZ coating with predeposited PMS-Yu slurry after stages 1–4 (variant with low-temperature HT)

Table 5. Chemical composition (wt.%) of CoCrAlY/8YSZ layer with predeposited PMS-Yu slurry after stages 1–4 (variant with low-temperature HT)

Spectrum	O	Al	Si	Cr	Co	Y	Zr	Hf
1	–	11.3	–	22.8	65.9	–	–	–
2	–	11.6	–	22.9	65.5	–	–	–
3	–	14.9	0.4	21.3	63.4	–	–	–
4	–	21.7	0.8	13.4	64.0	–	–	–
5	25.1	–	–	–	0.6	7.6	64.6	2.2

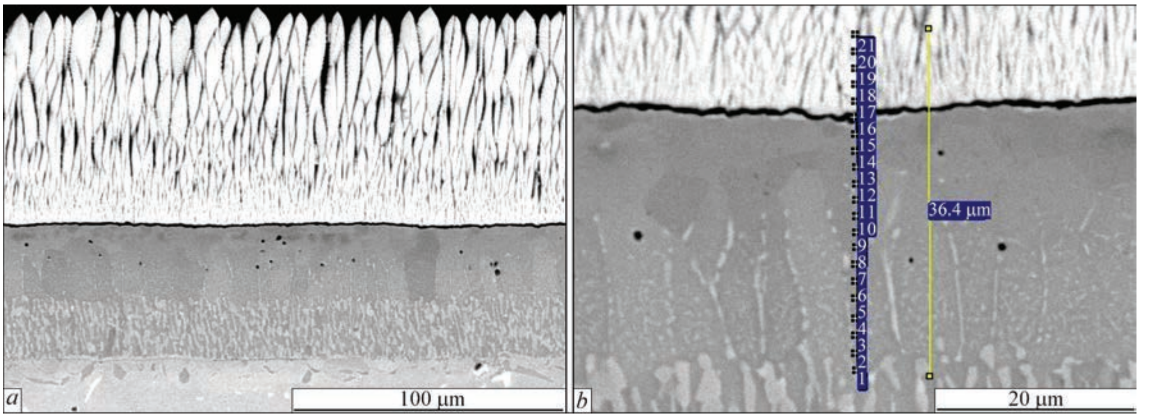

Figure 7. Microstructure (*a* — ×500; *b* — ×1800) of CoCrAlY/8YSZ coating and distribution of chemical elements in aluminium-saturated diffusion zone with predeposited PMS-Yu slurry after stages 1–4 (variant with low-temperature HT)

Table 6. Distribution of chemical elements (wt.%) in aluminium-saturated diffusion zone with predeposited PMS-Yu slurry after stages 1–4 (variant with low-temperature HT)

Spectrum	O	Al	Ti	Cr	Co	Ni	Y	Zr	Hf
1	–	12.7	0.8	23.9	54.4	8.3	–	–	–
2	–	14.0	0.7	18.4	56.4	10.4	–	–	–
3	–	14.9	0.8	19.4	56.2	8.8	–	–	–
4	–	10.5	0.5	21.8	60.0	7.3	–	–	–
5	–	14.9	–»–	17.9	59.5	7.2	–	–	–
6	–	15.6	–»–	18.0	59.8	6.1	–	–	–
7	–	13.0	–»–	20.9	59.6	6.0	–	–	–
8	–	15.4	0.4	18.5	61.1	4.6	–	–	–
9	–	15.3	0.2	18.6	61.7	4.3	–	–	–
10	–	–»–	0.1	18.2	62.4	4.0	–	–	–
11	–	14.8	0.3	20.6	61.4	2.9	–	–	–
12	–	–»–	0.1	18.5	63.9	2.6	–	–	–
13	–	16.4	0.2	17.2	63.8	2.4	0.1	–	–
14	–	15.8	–	16.3	65.6	2.3	–	–	–
15	–	15.6	–	16.9	64.6	–»–	–	0.7	–
16	31.8	19.3	–	5.4	9.6	0.2	2.9	29.7	1.2
17	24.6	1.2	–	0.5	0.8	–	6.9	63.4	2.6
18	–»–	–	–	–	–	–	7.7	65.7	2.1
19	24.0	–	–	–	–	–	7.6	66.6	1.7
20	24.8	–	–	–	–	–	7.9	65.5	1.9
21	25.1	–	–	–	–	–	7.3	64.5	3.1

ment to 700–750 °C at stage 3 and optimized parameters for AAT at stage 4) were transferred to end user.

CONCLUSIONS

1. It was found that vacuum heat treatment of CoCrAlY layer with aluminium-containing slurry applied on its surface, ensures formation of a surface diffusion layer of heterogeneous thickness in it (10–40 µm) at the temperature in the range of 950–1100 °C, which contains two microstructure zones with different aluminium content. The outer zone contains globular particles of up to 20 µm size from intermetallics with the composition of 60 % Co–31 % Al–9 % Cr. Numerous microcracks are observed in this zone, its microhardness reaching 8 GPa. The inner zone contains 15–19 % aluminium.

2. It was established that diffusion of cobalt and chromium from CoCrAlY layer into the slurry layer (40 and 9 %, respectively) results in the slurry layer microhardness increasing up to the level of 9 GPa. Numerous microcracks form in it, which propagate into CoCrAlY layer.

3. Mode of low-temperature vacuum heat treatment (not higher than 700–750 °C) was determined, when a defectfree surface diffusion layer approximately 8 µm thick with aluminium content of approximately 42 % forms in CoCrAlY. Here, the slurry contains two zones: outer zone of approximately 30 µm thickness (slurry which did not react) and inner one of approximately 20 µm thickness (sintered slurry, containing approximately 34 % Co and 12 % Cr).

4. Performed thermal cyclic testing of blade airfoil segments with CoCrAlY/8YSZ coating, in which the thickness of diffusion zone saturated by aluminium from the diffusion zone slurry was equal to 15 μm, and aluminium content was up to 21 %, showed that slurry application increases the life by 25–30 % due to increase of high-temperature resistance of the metal layer and ability to prevent spinel formation during growth of Al_2O_3 layer.

5. Recommendations were developed as to improvement of the technology of thermodiffusional alumization of the surface of metal layer of CoCrAlY/8YSZ coatings to ensure the operation of blades made from high-temperature alloys of CM-88U and CM-93 type at higher temperature.

REFERENCES

1. Darolia, R. (2013) Thermal barrier coatings technology: Critical review, progress update, remaining challenges and prospects. *Int. Mater. Rev*., **58**, 315–348. DOI: https://doi.org/10.1179/1743280413Y.0000000019
2. Pollock, T.M., Lipkin, D.V., Hemker, K.J. (2012) Multifunctional coating interlayers for thermal-barrier systems. *MRS Bulletin*, **37**, 923–931.
3. Movchan, B.A., Yakovchuk, K.Yu. (2004) Graded thermal barrier coatings, deposited by EB-PVD. *Surface & Coatings Technology*, **188–189**, 85–92.
4. Bababdani, S., Nogorani, F. (2014) Overaluminizing of a CoCrAlY coating by inward and outward diffusion treatments. *Metallurg. and Mater. Transact*., **A45**, 2116–2112.
5. Jiang, J., Zhao, H., Zhou, X. et al. (2013) Oxidation resistance of vacuum plasma sprayed CoNiCrAlY coating modified by filtered cathodic vacuum arc deposition aluminizing. *J. of Thermal Spray Technology*, **22**, 69–74.
6. Pillai, R., Jalowicka, A., Galiullin, T. et al. (2019) Simulating the effect of aluminizing on a CoNiCrAlY-coated Ni-base superalloy. *Calphad*, **65**, 340–345. DOI: https://doi.org/10.1016/j.calphad.2019.04.004
7. Boissonnet, G., Grégoire, B., Bonnet, G., Pedraza, F. (2019) Development of thermal barrier coating systems from Al microparticles. Pt I: Influence of processing conditions on the mechanisms of formation. *Surface and Coatings Technology*, **380**, 125085. https://doi.org/10.1016/j.surfcoat.2019.125085
8. Kashin, D.S., Dergacheva, P.E., Stekhov, P.A. (2018) Heat-resistant coatings deposited by slip method (Review). *Trudy VIAM*, 65(**5**), 64–75 [in Russian].
9. Jalowicka, A, Naumenko, D., Ernsberger, M. et al. (2018) Alumina formation and microstructural changes of aluminized CoNiCrAlY coating during high temperature exposure in the temperature range 925–1075 ºC. *Materials at High Temperatures*, 35(**1–3**), 66–77. DOI: https://doi.org/10.1080/09603409.2017.1392114

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CONFLICT OF INTEREST

The Authors declare no conflict of interest

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