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Isothermal Oxidation of Thermal Barrier Coatings Deposited Using LPPS, CVD, and PS-PVD Methods on MAR M247 Nickel Superalloy

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Abstract

The article presents the results of microstructural characterization of newly developed three-layer thermal barrier coating (TBC) after isothermal oxidation test. Bond coats were deposited by the overaluminizing of MCrAlY coating deposited by low-pressure plasma spraying (LPPS) process. The outer ceramic layer of yttria-stabilized zirconia was deposited by the plasma spray physical vapor deposition process. The TBCs with MCrAlY bond coat without aluminizing process was produced by LPPS as well. The isothermal oxidation test at 1,100°C for 1,000 h showed that the thickness of the thermally grown oxides alumina oxide layer on overaluminized bond coats was significantly thinner in comparison with conventional LPPS-sprayed MCrAlY bond coats. The possibility of the presence of NiAl and Ni3Al phases in the outer zone of overaluminized bond coat after the oxidation test was observed.

Keywords

thermal barrier coatings • overaluminizing • PS-PVD • LPPS • turbine blades • aluminizing process

1. Introduction

High demands made on modern gas turbines and aircraft turbine engines to determine the development of modern technologies, aiming to improve their efficiency and effectiveness. Increasing temperature in the hot section part of a turbine requires the use of advanced materials such as single-crystal nickel-base superalloys and protective coatings [1]. The current research focuses on developing more efficient thermal barrier coatings (TBCs), which will protect the turbine blade surface from high-temperature oxidation and hot corrosion [2]. Multilayer TBC is commonly used in industrial conditions, where individual layers play different roles [3]. The inner layer of metallic bond coating (MCrAlY-type) protects the material surface from corrosive factors, while the outer ceramic layer is a thermal insulator [4, 5]. In the case of first-stage turbine blades, diffusion aluminide coatings modified by the addition of platinum, hafnium, palladium, or zirconium are used. Characterized by lower thickness and roughness, the ceramic layer is formed by electron beam physical vapor deposition method (EB-PVD) [6, 7]. Diffusion aluminide coatings are used as a bond coat for ceramic layers deposited by EB-PVD. They contain mainly the β-NiAl phase. They are produced using pack cementation, out-of-pack, or chemical vapor deposition (CVD) methods [8–10]. The oxidation resistance of MCrAlY bond coats can be improved by the overaluminizing process and formation of β-NiAl phase on its surface [11, 12]. In fact, the new technology of columnar ceramic layer production in TBCs – plasma spray physical vapor deposition (PS-PVD) – was developed [13]. The concept of the overaluminized MCrAlY layer as a bond coat for that type of ceramic layer was proposed [14]. In three-layer TBCs, the MCrAlY bond coat was obtained using low-pressure plasma spraying (LPPS) method and aluminized in the CVD process. The ceramic coating with columnar structure was deposited using a newly developed PS-PVD process. In this article, the microstructural characterization of obtained coating on MAR M247 nickel superalloy was conducted after deposition and isothermal test.

2. Experimental Study

The samples made from MAR M247 nickel superalloy were washed and sandblasted with corundum before producing the coatings. The NiCoCrAlY-type bond coats were produced using an LPPS hybrid system (Oerlikon-Metco). The commercial powder AMDRY 365-1 (Oerlikon-Metco) and NiCoCrAlY-type powder were plasma-sprayed. Half of the samples set with MCrAlY bond coats were aluminized in the low-activity CVD process using the parameters described in the paper [14]. The aluminizing process was carried out using a Bernex BPX Pro 325S. The deposition of the ceramic coating was conducted by

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the PS-PVD method using an LPPS hybrid system (Oerlikon-Metco). A specifically designed, commercial powder for the PS-PVD process (Metco 6700), yttria-stabilized zirconia (YSZ), was used to produce the TBCs ceramic layer. The isothermal oxidation resistance test was carried out at 1,100°C in static laboratory air for 1,000 h using Carbolite CWF 1300 furnace. For this test, cylinder-shaped samples with a diameter 14 mm and height 4 mm were used and put in an aluminum oxide bed. Cross-sections of the samples have been prepared, and the coating was analyzed using a scanning electron microscope (SEM) Hitachi S-3400.

3. Results

3.1. Microstructure of as-deposited two-layer TBC

On the surface of the coating, the upper side of the columns was visible (Figure 1A). The microscopic examination showed that the thickness of MCrAlY bond coat and outer columnar ceramic layer was about 50 and 200 μm, respectively (Figure 1B).

The results of chemical composition analysis of the outer ceramic layer showed mainly the presence of oxygen, zirconium, and yttrium (areas 1 and 2 in Figure 1B, Table 1). The other elements, such as Hf, Cr, Fe, and Co, were also detected in those areas. In bond coat, MCrAlY, the presence of the following elements was detected (at.%): Al – 12 ¸ 20%, Cr – 9 ¸ 13%, Co – 10 ¸ 17%, and Ni – 37 ¸ 59% (areas 3 and 4 in Figure 1B, Table 1).

3.2. Microstructure of as-deposited three-layer TBC with overaluminized bond coat

On the surface of TBC, the topside of outer ceramic layer columns was observed (Figure 2). The microscopic investigation of TBC cross-section showed its multilayer structure. The thickness of outer ceramic layer was about 100 μm (Figure 3A). In the bond coat, the presence of outer aluminide zone was detected.

The chemical composition analysis of the outer zone of bond coat (areas 1–3 in Figure 3A, Table 2) showed that Ni and Al are the main components. The concentration of Cr and Co in this area was detected as well. This result suggests the formation of β-NiAl phase during the overaluminizing process of MCrAlY bond coat. In the middle zone of bond coat, the high porosity was observed. In this area, the lower concentration of Al (31.8 at.%) and the higher concentration of Cr (11.8 at.%) were detected (area 4 in Figure 3A, Table 2). In the inner

a) b)

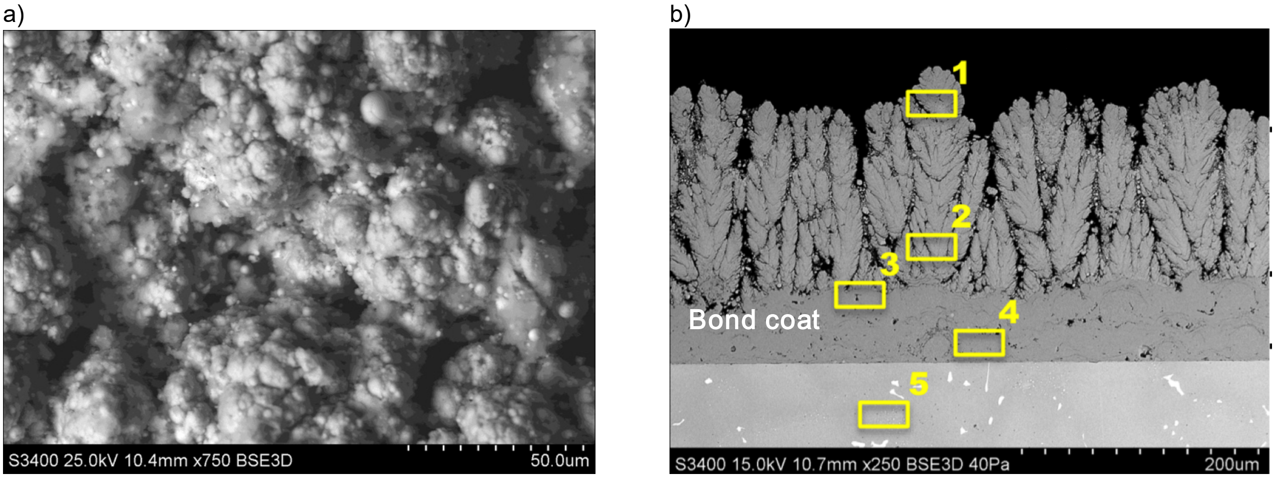

Figure 1. Surface morphology **(A)** and microstructure **(B)** of the as-deposited two-layer TBC.

Table 1. Results of chemical composition analysis of areas 1–5 presented in Figure 1B

Areas	Element content (at.%)									
	O	Al	Ti	Cr	Fe	Co	Ni	Y	Zr	Mo	Hf
1	63.5	0.5		0.6	0.1	0.8	2.2	2.2	29.6		0.5
2	60.5	0.6	0.2	1.4	0.1	1.4	5.2	1.9	28.78		
3	11.4	16.7		13.5	0.1	14.9	37.5	0.4	5.5		
4	4.3	20.2		15.2	0.2	17.0	41.0		2.1		
5	4.1	12.7	0.8	9.3		10.9	59.5		2.1	0.6	

zone (area 5 in Figure 3A, Table 2) of bond coat, the lower concentration of Al (26.5 at.%) and the higher concentration of Cr (13.3 at.%) and Co (16 at.%) were detected. In the outer ceramic layer, the high content of oxygen and zirconium was measured (areas 6–8 in Figure 3B). The presence of Al, Cr, Co, Ni, Y, and Hf in this area was noted as well.

The elemental map of a cross-section of the overaluminized MCrAlY bond coat showed the presence of a thin aluminum oxide layer between NiAl outer and porous middle zones (Figure 4A,B,E). Within the inner zone of bond coat, a large number of Co and Cr-rich precipitations were also detected (Figure 4A,C,D).

3.3. Microstructure of two-layer TBC after isothermal oxidation test

In two-layer TBC, the formation of thick thermally grown oxides (TGO) layer with a large number of cracks and pores after isothermal oxidation test was observed (Figure 5A,B). The chemical composition analysis showed different contents of elements in selected areas (Figure 5A,B, Table 3):

- microarea 1 – presence of Zr, O, and Y – elements forming the YSZ columnar ceramic layer,
- microarea 2 – high content of Al and presence of O – which probably forms of Al_2O_3 in TGO layer,
- microarea 3 – near outer ceramic layer – presence of Al, Ni, and O,
- microarea 4 – nearest bond coat – high content of Al and O – probably formation of Al_2O_3,
- microareas 1 ¸ 4 – presence of Ti (up to 0.5 at.%), Cr (0.3 ¸ 2.1 at.%), and Co (0.4 ¸ 2 at.%),
- microareas 5 ¸ 8 – concentration of Al – 8¸11 at.%, Cr – 14 ¸ 15 at.%, Co – 13 ¸ 14 at.%, Ni – 57 at.%, and Ti – 0.8 ¸ 1.4 at.% and presence of Zr, Mo, and W.

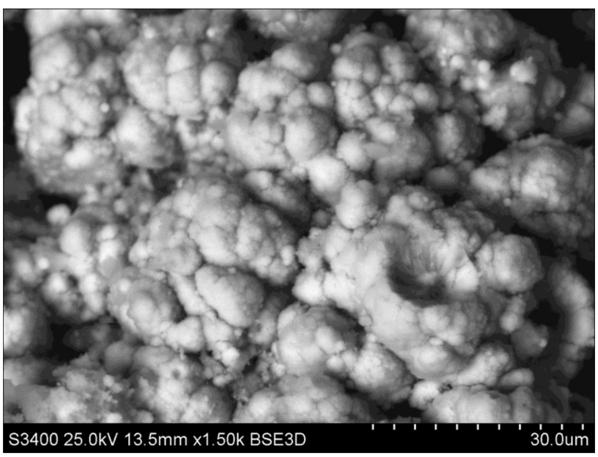

Figure 2. Surface morphology of the as-deposited three-layer TBC.

Table 2. Results of chemical composition analysis of areas presented in Figure 3A,B

Areas	Element content (at.%)								
	Al	OS	Cr	Fe	Co	Ni	Y	Zr	Hf
1	43.1		2.4	1.3	10.7	39.1		3.4	
2	34.6		6.5	0.7	12.8	43.1		2.3	
3	35.9		5.8	0.7	12.7	42.5		2.4	
4	31.8		11.8		12.9	41.6		1.9	
5	26.5		13.3		16.0	42.5		1.7	
6	0.7	65.1	0.5		1.0	2.5	2.1	27.7	0.4
7	1.1	64.5	1.0		1.0	4.1	1.5	26.5	0.3
8	1.7	63.4	1.1		1.1	5.3	1.4	25.7	0.3

a)

b)

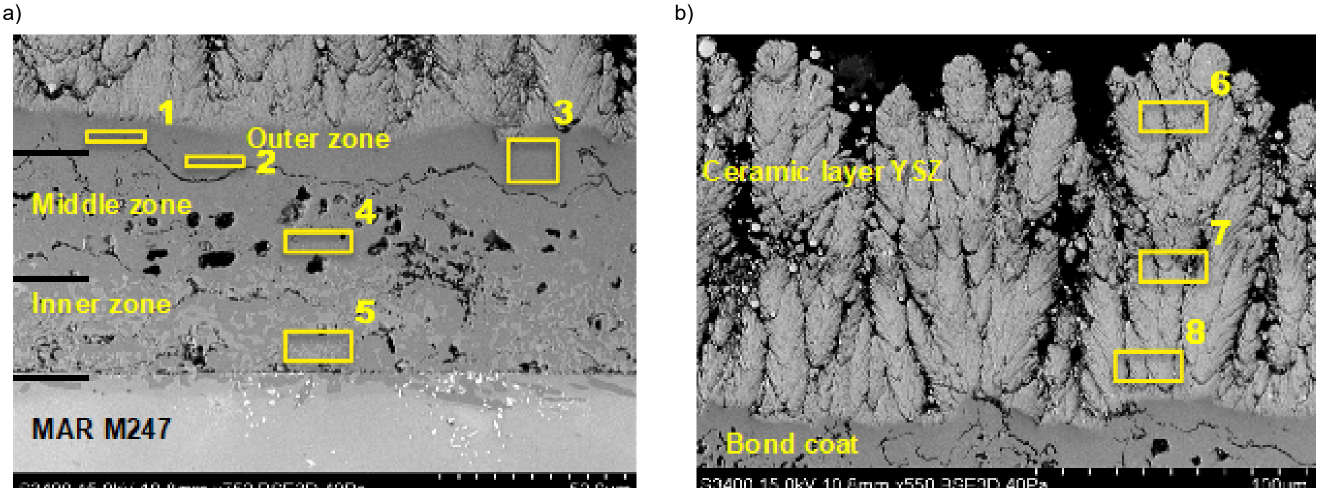

Figure 3. The microstructure of as-deposited three-layer TBC with marked areas of chemical composition analysis: **(A)** bond coat and **(B)** ceramic layer.

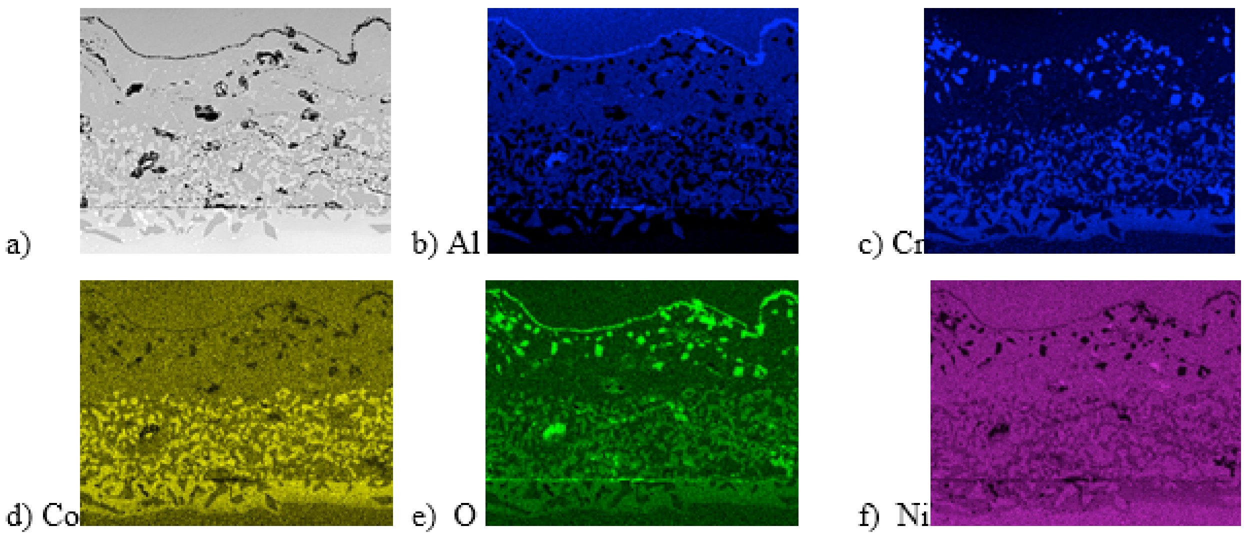

Figure 4. Microstructure **(A)** and elemental map: **(B)** Al, **(C)** Cr, **(D)** Co, **(E)** O, and **(F)** Ni.

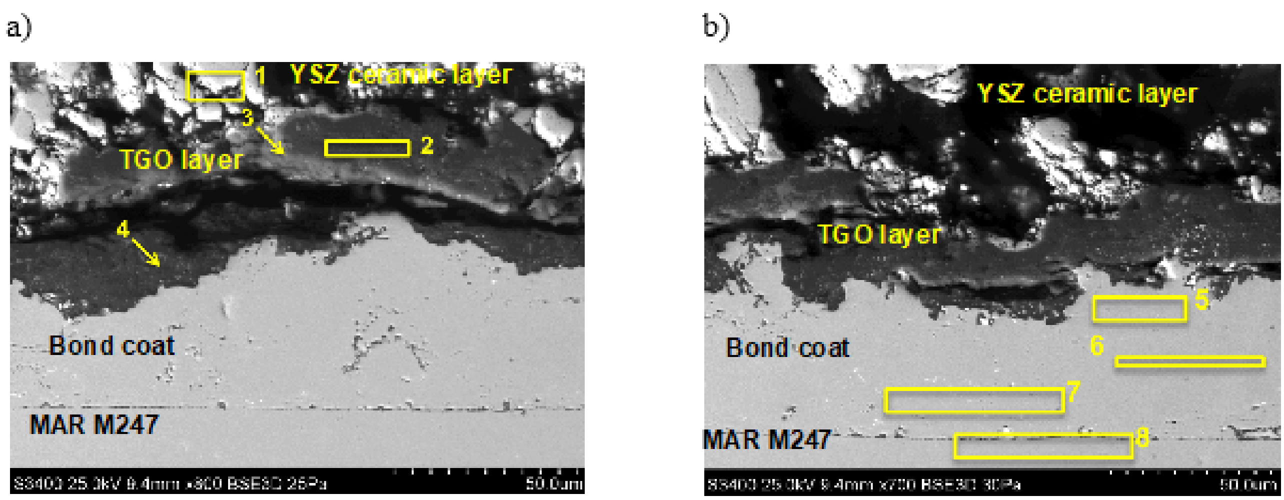

Figure 5. The microstructure of two-layer TBC after isothermal oxidation test 1,100°C/1,000 h with marked areas of chemical composition analysis.

Table 3. Results of chemical composition analysis of areas presented in Figure 5A,B

Areas	Element content (at.%)									
	OS	Al	Ti	Cr	Co	Ni	Y	Zr	Hf	Mo	W
1	65.3	1.3		0.5	0.4	1.9	2.3	28.0	0.3		
2	60.0	37.1	0.2	0.3	0.3	1.2	0.2	0.7			
3	58.7	25.5	0.3	2.1	2.0	9.0		2.4			
4	59.9	36.4	0.5	0.3	0.4	1.5	0.3	0.5	0.2		
5		10.7	0.8	14.7	13.9	56.0	0.1	1.1		0.5	2.2
6		8.9	0.7	15.0	14.5	57.3	0.2	0.9		0.4	2.1
7		8.6	1.4	14.7	14.3	57.3		0.9		0.4	2.4
8		8.3	1.2	14.9	14.3	57.6		0.8		0.5	2.4

3.4. Microstructure of three-layer TBC with overaluminized bond coat after isothermal oxidation test

The microscopic examination of three-layer TBC after isothermal oxidation test 1,100°C/1,000 h showed the formation of a thin TGO layer without any cracks or pores (Figure 6A,B). The chemical composition analysis of TGO layer demonstrated the presence of aluminum and oxygen (areas 1–3 in Figure 6A, Table 4). It could be concluded that the TGO layer containing Al_2O_3 was formed during isothermal oxidation. In this area, the presence of Cr, Ni, Y, Zr, and Hf was also detected.

In area 4 (Figure 6A), the concentration of the main components of YSZ ceramic layer was observed. In bond coat, two characteristic types of grains were observed. In the grains marked “6”, “8”, and “9” (Figure 6B), the concentration of Al was lower (~21.5 at.%) and the concentration of Ni was higher (~66.5 at.%). The presence of Ti, Hf, Zr, and W in these grains was also observed. In the grains marked “5” and “7” (Figure 6B), the higher concentration of Al and the lower concentration of Ni were measured (Table 4), and the presence of Ti, Hf, and Zr in these grains was also noted. In the inner area (marked “10” and “11”), the concentration of Al was low (below 17 at.%). In those areas, the content of nickel and chromium was measured high (Table 4).

4. Conclusion

In this study, the microstructure of three-layer TBC was investigated. The outer columnar ceramic layer containing YSZ was deposited in PS-PVD process. In the outer zone of the bond coat, the β-NiAl layer was formed. Below it, the very

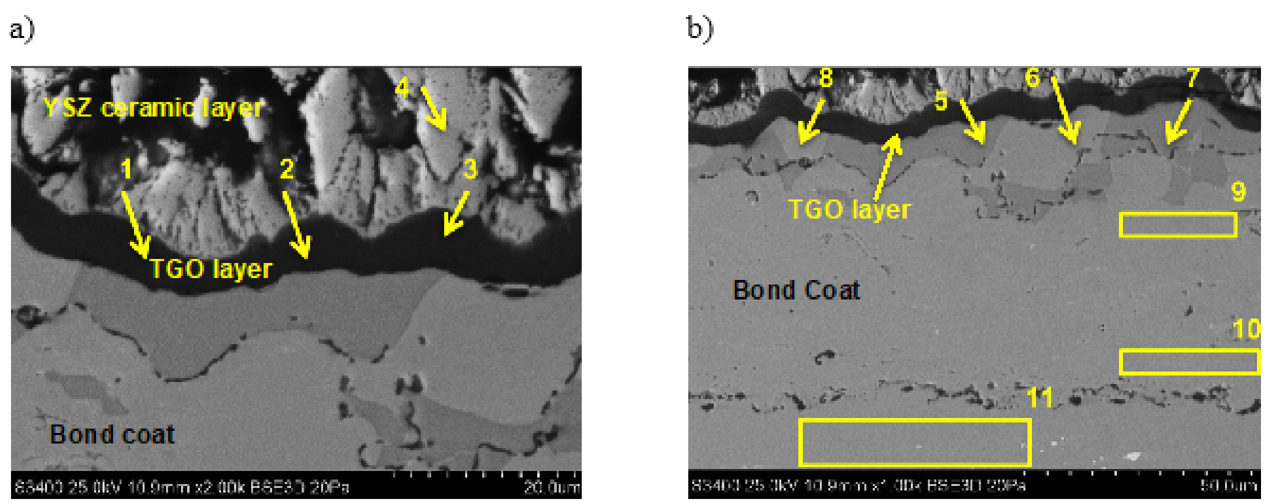

Figure 6. The microstructure of three-layer TBC after isothermal oxidation test 1,100°C/1,000 h with marked areas of chemical composition analysis.

Table 4. Results of chemical composition analysis of areas presented in Figure 6A,B

Areas	Element content (at.%)									
	OS	Al	Ti	Cr	Ni	Y	Zr	Hf	Mo	W
1	60.0	37.6		0.3	1.1	0.1	0.9			
2	60.0	37.2		0.2	1.2	0.2	1.2			
3	60.0	37.1	0.1	0.3	1.3	0.1	1.0	0.1		
4	65.5	0.8		0.4	1.6	2.4	28.9	0.4		
5		32.8	0.4	6.0	59.1		1.6	0.1		
6		21.5	1.2	6.8	66.3	0.2	1.8		0.2	2.0
7		33.4	0.4	5.9	58.6		1.6	0.1		
8		22.2	1.1	6.4	67.2		1.3			1.8
9		21.0	1.1	7.0	67.3	0.4	1.1	0.3		1.8
10		16.8	1.8	14.5	62.4	0.8	0.9	0.4		2.4
11		14.3	0.7	19.1	62.3	0.3	0.7	0.1		2.5

thin (<1 mm) alumina film appeared probably during plasma spraying, despite using Ar atmosphere at reduced pressure. In the middle area of bond coat, a large number of pores were observed. Reference [15] suggests that pores form as a result of the Kirkendall effect. The Al content in this zone was approximately 32 (at.%). In the inner zone of bond coat, the equiaxed grains were observed.

After 1,000 h of isothermal oxidation test at 1,100°C into two-layer TBC, the thick TGO layer with a large number of pores and horizontal cracks was formed. Based on the results of chemical composition analysis, it could be concluded that alumina oxide is the main component of TGO layer. In bond coat, the aluminum depletion (below 10 at.%) was observed. In the three-layer TBC, a thin TGO layer without any cracks or pores was formed during the isothermal oxidation test. The results of chemical composition analysis suggest that Al_2O_3 is the main component of TGO layer. In the bond coat of three-layer TBC, the two types of grains with different Al contents were observed. Probably, they were formed from NiAl or Ni_3Al phases. In comparison with two-layer TBC, the concentration of Al below TGO layer in three-layer TBC is higher. The results of conducted research showed that newly developed three-layer TBCs produced by advanced plasma-spraying processes (LPPS and PS-PVD) can improve the corrosion resistance of turbine blades [16]. The additional overaluminizing process enables the formation of thin alumina oxide into isothermal oxidation conditions.

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