Rapid Communication

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The new concept of thermal barrier coatings with Pt + Pd/Zr/Hf-modified aluminide bond coat and ceramic layer formed by PS-PVD method

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Abstract: Thermal barrier coatings (TBCs) are widely used for protection of gas turbine parts from high temperature and corrosion. In the present study, the new concept of TBCs with three-element-modified aluminide coatings was presented. In the first stage, the Pt and Pd were electroplated on MAR M247 nickel superalloy. In the next stage, the low-activity CVD aluminizing process with Zr or Hf doping was conducted. The ceramic layer containing yttria-stabilized zirconia was obtained by the plasma spray physical vapour deposition (PS-PVD) method. The microscopic examination showed the formation of aluminide coating containing up to 5 at% of Pt and 10 at% of Pd in (Ni, Pt, Pd)Al solid solution. The small concentration of Hf and Zr in diffusion zone of aluminide bond coat was noted as well. The outer ceramic layer was characterized by columnar structure typically formed during the PS-PVD process. The obtained results showed that the new concept of TBCs formed using new processes might be an attractive alternative to conventional coatings produced using the expensive electron beam physical vapour deposition (EB-PVD) method.

Keywords: PS-PVD, aluminide coatings, TBCs, CVD

1 Introduction

The platinum modification of aluminide coatings is still state-of-art technology for oxidation resistance, improving at high temperature of nickel superalloys used for turbine blade production. Shirvani et al. [1] showed that low-Pt-modified aluminide coating did not improve the kinetics of scale formation, but improves its adhesion, inhibiting the formation of unstable oxides like TiO_2 . The Pt-modified aluminide coatings are usually produced using the Pt-electroplating process and by diffusion aluminizing using out of pack [2] or chemical vapour deposition (CVD) methods [3]. As an alternative, Swadzba et al. used the Pt and Pd combination for aluminide coating modification [4]. The presence of precious metals (Pt, Pd, etc.) can increase the hot-corrosion resistance especially with the presence of Hf [5]. The addition of Hf can also improve the oxidation resistance of simple aluminide coating as well [6]. Mohazabie and Nogorani [7] showed that addition of Zr to aluminide coating produced by the pack cementation process could be developed. Filip et al. [8] developed the Zr-doping process using gas phase and CVD aluminizing methods. The multiple-element modifications of aluminide coatings can improve their oxidation resistance. Adharapurapu et al. [9] showed that increasing the lifetime of aluminide coatings at 1,150°C is possible by Hf and Pd doping. Pytel et al. [10] proposed the modification of Pt-aluminide coating by Zr doping during the CVD process. The modified aluminide coatings are widely used as bond coats for thermal barrier coatings (TBCs) produced by the EB-PVD method [11]. Actually, an alternative to EB-PVD method of columnar ceramic layer formation called plasma spray physical vapour deposition (PS-PVD) was developed [12]. In our previous works, two different types of bond coats for PS-PVD TBCs were investigated: simple aluminide [13] and overaluminized MCrAlY coatings [14]. Actually, we investigated the possibility of formation of Pt/Pd/Hf/Zr-modified aluminide coatings in different

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element combinations [15]. In the present article, as a next step of investigation on selected modified aluminide coatings, we deposited the ceramic topcoat using the PS-PVD method.

2 Experimental

The MAR M247 nickel superalloy was used as a base material. Cylindrical samples with a diameter of 14 mm and a height of 4 mm were cut from a cast rod. Samples were grinded, sandblasted, and degreased in isopropanol. The samples were not heat-treated. The palladium and platinum were electroplated at Silesian University of Technology based on methodology developed in refs. [2,10]. After electroplating process, the low-activity aluminizing process based on parameters described in ref. [16] was conducted. The doping by Hf and Zr was conducted during aluminizing process using methodology described in ref. [15]. The Bernex BPX Pro 325 S CVD system was used for all aluminizing processes. The following three types of aluminide bond coats were prepared: (1) Pt + Pd electroplating and low-activity aluminizing with Hf doping, (2) Pt + Pd electroplating and simple low-activity aluminizing, and (3) Pt + Pd electroplating and low-activity aluminizing with Zr doping. The columnar ceramic layer was produced using LPPS-Hybrid system by the PS-PVD method based on parameters selected in ref. [14]: pressure 150 Pa, power current 2,200 A, spray distance 950 mm, plasma gasses flow Ar/He: 35/60 NLPM (normal litres per minute), and powder feed rate $2 \text{ g} \cdot \text{min}^{-1}$. Cross sections of the samples were prepared, and then the

coatings were analysed using a Scanning Electron Microscope (SEM) type Hitachi S-3400.

3 Results

The TBC with platinum, palladium, and hafnium-modified aluminide bond coat was characterized by a two-zone structure (Figure 1a). The bond coat had a thickness of $47 \mu\text{m}$ (Figure 1b). It had a structure typical of the layers formed by the low-activity process as a result of nickel outward diffusion (Figure 1b). The ceramic coating had columnar structure formed by PS-PVD and the average thickness of $135.8 \mu\text{m}$. Vapourized powder particles were not observed. This indicates the correct formation of ceramic layer. In the diffusion zone, there were observed elements, which form characteristic precipitations: tungsten, hafnium, zirconium, cobalt, and titanium (areas 1–3 in Figure 1b and Table 1). The Al content in the diffusion zone was approx. 25 at%. The chemical composition analysis showed (Figure 1b and Table 1) that aluminium content in the outer zone was about 35 at% (areas 4–7 in Figure 1b and Table 1). Platinum concentration in the bond coat was in the range of 2–3 at%. The content of palladium in the outer zone was approx. 10 at%. Hafnium was not present in the outer zone, which pointed to difficulties of its introduction into the diffusion layer. In addition to the above-mentioned elements, presence of chromium, cobalt, and nickel from the substrate material in the outer zone was detected as well.

The second type of bond coat in the developed TBC was a diffusion aluminide coating modified by platinum

Figure 1: Microstructure of TBC with Pt, Pd, and Hf-modified aluminide bond coat deposited by CVD method and ceramic layer produced by PS-PVD method on MAR M247 nickel superalloy (a) with marked areas of EDS analysis (b).

Table 1: Results of EDS chemical composition analysis of TBCs on areas marked in Figure 1b

Area	Element concentration (at%)									
	Al	Ti	Cr	Co	Ni	Zr	Pd	Hf	W	Pt
1	23.2	2.0	7.9	8.9	42.1	6.7	3.7		5.4	
2	29.1	1.7	5.3	6.3	39.9	3.0	7.2	1.7	2.8	3.1
3	24.8	2.2	7.7	8.8	39.1	2.3	5.2	0.6	6.5	2.7
4	32.1	2.0	3.9	5.8	38.1	3.8	9.6	0.8	0.8	2.9
5	34.1		4.0	5.5	39.7	3.7	9.7			3.2
6	37.3		2.3	4.4	37.0	6.0	10.8			2.3
7	35.8		2.6	5.0	38.2	4.0	11.4			3.1

and palladium. Aluminizing of Pt and Pd electroplated coatings was performed by the CVD method in low-activity process. The measured average thickness was 58 μm (Figure 2b). The outer ceramic layer had a thickness of 75 μm and columnar structure (Figure 2a). Unmelted powder particles were not observed in the ceramic layer.

A small amount of hafnium was present only in the diffusion zone (>1 at%) (areas 1–3 in Figure 2b and Table 2). In the diffusion zone, the cobalt, chromium, and titanium were also presented. A small concentration of hafnium was detected only in the diffusion zone (>1 at%). In this area, the small concentration of platinum and palladium was measured (areas 1–3, Figure 2b). The platinum content in the outer zone of the bond coat was in the range of 2–3 at% and palladium about 6–8 at% (areas 4–7 in Figure 2b and Table 2). The aluminium content in the outer zone was approx. 37 at%. In the outer zone, the presence of cobalt, chromium, and titanium was also noted.

The last type of bond coat for developed TBCs was an aluminide coating modified with platinum, palladium,

Table 2: Results of EDS chemical composition analysis of TBCs on areas marked in Figure 2b

Area	Element concentration (at%)									
	Al	Ti	Cr	Co	Ni	Zr	Pd	Hf	W	Pt
1	23.1	2.0	10.8	9.4	41.0	2.7	2.8	0.3	6.7	1.2
2	25.5	2.0	11.1	7.6	38.9	3.1	4.2	0.8	4.9	1.8
3	25.3	2.3	9.0	8.2	41.3	3.0	4.0	0.5	4.6	1.8
4	34.7	1.4	4.5	5.4	40.4	1.2	7.8	0.2	0.4	3.9
5	39.1		1.8	4.3	39.4	5.5	7.8			2.1
6	37.8		2.9	5.3	39.0	3.9	8.9			2.2
7	29.9	2.3	7.4	6.5	40.2	7.5	6.1			

and zirconium. The aluminide coating was formed by electroplating of platinum and palladium. The Pt + Pd layers were subjected to the CVD aluminizing with zirconium doping. The bond coat, as assumed, had the structure characteristic for the low-activity process. Its average thickness was 55 μm (Figure 3a). The thickness of the outer ceramic layer was approx. 118 μm and had the structure typical of those formed by the PS-PVD method (Figure 3a).

In the diffusion zone presence of three-element-modified aluminide coating with electroplated platinum and palladium and co-doped zirconium during aluminizing presence of these elements was recorded (areas 1–3, Figure 3b, Table 3). Furthermore, in this area, tungsten and titanium were also observed. Chemical composition analysis showed that the coating contains no hafnium (Figure 3b, Table 3). Platinum content in the outer zone was approx. 3.5 at% and palladium approx. 8 at% (areas 4–7 in Figure 3b and Table 3). The zirconium content in this zone was >5 at%. Similar to the previously analysed

(a)

(b)

Figure 2: Microstructure of TBC with Pt and Pd-modified aluminide bond coat deposited by CVD method and ceramic layer produced by PS-PVD method on MAR M247 nickel superalloy (a) with marked areas of EDS analysis (b).

Figure 3: Microstructure of TBC with Pt, Pd, and Zr-modified aluminide bond coat deposited by the CVD method and ceramic layer produced

Table 3: Results of EDS chemical composition analysis of TBCs on areas marked in Figure 3b

Area	Element concentration (at%)								
	Al	Ti	Cr	Co	Ni	Zr	Pd	Hf	Pt
1	20.2	1.8	13.1	10.2	37.9	3.4	3.0		8.4
2	28.8	1.5	9.9	6.9	38.9	1.6	5.6		2.0
3	26.4	2.0	9.0	8.2	39.6	1.5	4.6	0.6	4.0
4	33.8		5.3	5.7	40.1	2.3	7.4		5.4
5	37.9		2.5	5.3	40.3	4.3	7.2		2.5
6	36.1		3.7	5.4	38.6	3.9	8.2		4.2
7	36.4		3.7	5.0	39.0	4.6	7.8		3.5

coatings, the presence of chromium and cobalt was detected as well. Aluminium content in the outer zone was approx. 36 at% (areas 4–7, Table 3), while in the diffusion zone from 20 to 29 at% (areas 1–3 in Figure 3b and Table 3).

4 Discussion

In the present study, the three-element (Pt, Pd, Hf/Pd)-modified aluminide coating in low-activity high temperature (LAHT) was formed. The structure of outer additive zone is characterized by single-phase structure. Based on results of chemical composition analysis, it might be concluded that β -Ni(Al, Pt, Pd) solid solution is the main component of the outer zone. The concentration of both precious metals was relatively low (Pt up to 4.7 at%, Pd up to 11.4 at%). The aluminium content in this area did not exceed 40 at% in whole measured areas in all modified aluminide coatings. The lower concentration

of these elements might be connected with lower activity of aluminizing process as well as thinner Pt/Pd electroplated layers. The structure of all modified coatings was similar to that reported by Hong *et al.* [17] – the PtAl_2 phase precipitations were not observed in outer zone. The differences of Pt and Pd concentration on cross section of outer zone were low and did not exceed 2 at%. The gradient of this element concentration in modified aluminide coating was observed by Swadzba *et al.* [18]. However, the presence of Cr and Co (about 2–5 at%) in this zone reported by this author was observed in obtained coatings as well. The zirconium was observed in whole areas of obtained aluminide coatings regardless of its doping during aluminizing process [8]. It might be connected with some concentration of this element from base alloy. In our previous work [10], the formation of small precipitations containing Zr was observed in Pd/Zr-modified aluminide coatings. The highest concentration of hafnium was measured in diffusion zone in aluminide coating modified by Pd/Pd electroplating and Hf doping during aluminizing. There are a lot of difficulties in the analysis of this element's contribution in aluminide coating. The maximum concentration of Hf in the NiAl phase is very low and formation of any precipitations in Hf-doped aluminide coatings was not observed [5]. On the other hand, the MAR M247 contains hafnium and its presence in simple aluminide coating formed on similar alloy was observed [19]. The obtained ceramic layer was characterized by columnar structure typically formed during the PS-PVD process [12]. The layer thickness was in the range of 100–130 μm and typically for TBC applications. The morphology columnar grains were smooth characteristically for using Ar/He plasma gasses in the PS-PVD

process [13,14]. Further research should be conducted on isothermal and cyclic oxidation tests of obtained TBCs according to aerospace industry requirements at 1,100°C. The obtained results showed that combination of using modified aluminide coatings produced by CVD method and ceramic layer formation using PS-PVD is a promising technology for decreasing production costs of EB-PVD TBCs.

5 Conclusion

- (1) The developed three-element (Pt, Pd, Hf, Pd)-modified aluminide bond coats were characterized by structure typically for LAHT process with preferred outward nickel diffusion as a dominant coating formation mechanism.
- (2) The β -Ni(Al, Pt, Pd) solid solution is the main component of the developed modified aluminide bond coats.
- (3) The obtained TBCs with Pt/Pd/Zr/Hf-modified aluminide bond coats were produced by the CVD method, and ceramic layer formation using PS-PVD is a promising technology for decreasing production costs in comparison with EB-PVD TBCs.

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References

- [1] Shirvani, K., S. Firouzi, and A. Rashidghamat. Microstructures and cyclic oxidation behavior of Pt-free and low-Pt NiAl coatings on Ni superalloy Rene-80. *Corrosion Science*, Vol. 55, 2012, pp. 378–384.
- [2] Swadzba, L., G. Nawrat, B. Mendala, and M. Goral. The influence of deposition process on structure of platinum-modified aluminide coatings on Ni-base superalloy. *Key Engineering Materials*, Vol. 465, 2011, pp. 247–250.
- [3] Warnes, M. Reactive element modified chemical vapor deposition low activity platinum aluminide coatings. *Surface and Coatings Technology*, Vol. 146–147, 2001, pp. 7–12.
- [4] Swadzba, R., M. Hetmanczyk, J. Wiederman, L. Swadzba, G. Moskal, B. Witala, et al. Microstructure degradation of simple, Pt- and Pt + Pd-modified aluminide coatings on CMSX-4 superalloy under cyclic oxidation conditions. *Surface and Coatings Technology*, Vol. 215, 2013, pp. 16–23.
- [5] Zagula-Yavorska, M., J. Morgiel, J. Romanowska, and J. Sieniawski. TEM analysis of hafnium-doped aluminide coating deposited on Inconel 100 superalloy. *Vacuum*, Vol. 116, 2015, pp. 115–120.
- [6] Leyens, C., B. A. Pint, and L. G. Wright. Effect of composition on the oxidation and hot corrosion resistance of NiAl doped with precious metals. *Surface and Coatings Technology*, Vol. 133–134, 2000, pp. 15–22.
- [7] Mohazabie, M. S. Z. and F. S. Nogorani. The addition of zirconium to aluminide coatings. The effect of the aluminide growth mode. *Surface and Coatings Technology*, Vol. 378, 2019, id. 125066.
- [8] Filip, R., A. Nowotnik, and M. Goral. Zirconia modified aluminide coatings deposited by VPA and CVD methods. *Solid State Phenomena*, Vol. 203–204, 2013, pp. 220–223.
- [9] Adharapurapu, R. R., J. Zhu, V. S. Dheeradhada, D. M. Lipkin, and T. M. Pollock. Effective Hf-Pd-doped B-NiAl(Cr) coatings for single-crystal superalloys. *Acta Materialia*, Vol. 76, 2014, pp. 449–462.
- [10] Pytel, M., M. Tokarski, M. Goral, and R. Filip. Structure of Pd-Zr and Pt-Zr modified aluminide coatings deposited by a CVD method on nickel superalloys. *Kovove Materialy*, Vol. 57, 2019, pp. 343–354. Doi: 10.4149/km20195343
- [11] Swadzba, R., J. Wiedermann, L. Swadzba, M. Hetmanczyk, B. Witala, U. Schultz, et al. High temperature oxidation of EB-PVD TBCs on Pt-diffused single crystal Ni superalloy. *Surface and Coatings Technology*, Vol. 260, 2014, pp. 2–8.
- [12] Deng, Z. Q., J. Mao, M. Liu, C. M. Deng, and J. T. Ma. Regional characteristic of 7YSZ coatings prepared by plasma spray-physical vapor deposition technique. *Rare Metals*, Vol. 40, 2021, pp. 3308–3315.
- [13] Góral, M., J. Sieniawski, S. Kotowski, M. Pytel, and M. Maślak. Influence of turbine blade geometry on thickness of TBCs deposited by VPA and PS-PVD methods. *Archives of Materials Science and Engineering*, Vol. 54, No. 1, 2012, pp. 22–28.
- [14] Góral, M., R. Swadzba, and T. Kubaszek. TEM investigations of TGO formation during cyclic oxidation in two- and three-layered thermal barrier coatings produced using LPPS, CVD

- and PS-PVD methods. *Surface and Coatings Technology*, Vol. 394, 2020, id. 125875.
- [15] Goral, M., M. Pytel, K. Ochal, M. Drązewicz, T. Kubaszek, W. Simka, et al. Microstructure of aluminide coatings modified by Pt, Pd, Zr and Hf formed in low-activity CVD process. *Coatings*, Vol. 11, No. 4, 2021, id. 421.
- [16] Nowotnik, A., M. Goral, M. Pytel, and K. Dychton. Influence of coatings deposition parameters on microstructure of aluminide coatings deposited by CVD method on Ni-superalloys. *Solid State Phenomena*, Vol. 197, 2013, pp. 95–100.
- [17] Hong, S. J., G. H. Hwang, W. K. K. Han, and S. G. Kang. Cyclic oxidation of Pt/Pd modified aluminide coating on a nickel-based superalloy at 1150°C. *Intermetallics*, Vol. 17, 2009, pp. 381–386.
- [18] Swadzba, R., M. Hetmanczyk, M. Sozanska, B. Witala, and L. Swadzba. Structure and cyclic oxidation resistance of Pt, Pt/Pd-modified and simple aluminide coatings on CMSX-4 superalloy. *Surface and Coatings Technology*, Vol. 206, 2011, pp. 1538–1544.
- [19] Filip, R., M. Góral, M. Zawadzki, A. Nowotnik, and M. Pytel. The influence of long-term heat treatment on microstructure of Zr-modified aluminide coating deposited by CVD method on MAR M200 + Hf nickel superalloy. *Key Engineering Materials*, Vol. 592–593, 2014, pp. 469–472.