

Oxidation Resistance of Modified Aluminide Coatings

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Abstract. The application of protective aluminide coatings is an effective way to increase the oxidation resistance of the treated parts and prolongs their lifetime. The addition of small amount of noble metals (platinum or palladium) or reactive elements such as: hafnium, zirconium, yttrium and cerium has a beneficial effect on oxidation behavior. This beneficial effect includes an improvement of adhesion of alumina scales and reduction of oxide scale growth rate. Platinum and hafnium or zirconium modified aluminide coating were deposited on pure nickel using the electroplating and CVD methods. The coatings consisted of two layers: an outer, β -NiAl phase and the interdiffusion γ' -Ni₃Al phase. Palladium dissolved in the whole coating, whereas hafnium and zirconium formed inclusions on the border of the layers. Samples were subjected to cyclic oxidation test at 1100 °C for 200h. Oxidation resistance of the palladium, Hf+Pd and Zr+Pd modified coatings deposited on pure nickel does not differ significantly, but is better than the oxidation resistance of the non-modified one.

1. INTRODUCTION

Protective aluminide coatings, characterized by low density, high melting point and oxidation resistance, are deposited on superalloys as bond coats in thermal barrier coatings (TBC) [1]. Aluminum in the coatings reacts with oxygen from the atmosphere forming α -Al₂O₃ at the surface, which protects the substrate from oxidation and hot corrosion [2]. Oxidation of coatings degrades them through internal weakening and deformation. Slowing down the oxide scale growth as well as improvement of their adherence to the substrate will improve oxidation resistance. That has been achieved by alloying them with small amount of noble metals (platinum [3], palladium [4]) or reactive elements (hafnium [5], zirconium [6]).

Palladium addition to these coatings are effective in reducing the oxide growth rate and scale adherence [4,7]. Yavorska et al. [8] proved, that palladium modified aluminide coatings on Inconel 713 LC and CMSX 4 superalloys contain mainly the (Ni,Pt)Al, and (Ni,Pd)Al phases. Higher total content of alloying elements such as molybdenum, tungsten chromium, titanium, tantalum and rhenium in CMSX 4, as compared to Inconel 713 LC, favoured formation of thinner alumina coatings. However, hafnium is the most efficient dopant in reducing the oxide scale growth rate [6]. Hafnium segregates to the alloy-scale interface and grain boundaries. Hafnium forms nanoparticles in aluminide coatings on pure nickel [9]. Its out-diffusion along oxide grain boundaries to the oxide scale surface is slowed down by the large atomic radii. This slow diffusion stands against the aluminum

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outward diffusion and oxygen inward diffusion [10,11]. This way the scale adhesion is improved and the growth rate of the scale is reduced.

Small Zr addition (about 0.1 at.%) [12] improves coatings' oxidation resistance, because of the diminishing of the scale spalling. Zirconium forms nanoparticles in aluminide coatings on pure nickel [13]. After oxidation, it is homogeneously distributed within the scale, delays spallation and improves adhesion [14].

“Co-doping” - the idea of using more than one dopant is a promising way for improvement of oxidation resistance of coatings [11,15]. Many pairs of dopants were analyzed, for instance: Y+La, Dy+Hf, Y+Hf, Pt+Pd, , La+Hf, , Hf+Zr, or Y+La [16,17]. Oxidation resistance of co-doped coatings is better than the respective single-doped ones. However, the Pd+Hf and Pd+Zr co-doping has not been investigated yet.

Therefore, this paper presents analysis of oxidation resistance of the Pd+Hf and Pd+Zr co-doped aluminide coatings deposited on pure nickel.

2. EXPERIMENTAL

Palladium layers were deposited on nickel (of technical purity) by the electrochemical method. The precise procedure of the electrodeposition process is presented in reference [18]. Then, the aluminide coatings were deposited by the CVD method [19, 20].

Chemical and phase composition of coatings was analyzed by SEM and EDS methods. The oxidation resistance was analyzed by placing samples in the furnace, than heating them up to 1100 °C and maintaining it at this temperature for 20 hours. Than samples were cooling to the room temperature with the furnace. After each cycle samples were weighed and inspected.

3. Results and discussion

3.1 Palladium modified aluminide coating on pure nickel

Palladium modified aluminide coating on pure nickel has a double-zone structure (Fig. 1, Table 1). In the first, additive zone, on the top of the coating, the proportion of Ni to Al corresponds to the β -NiAl phase (Table 1, Point 1). Moreover, some palladium (5.2-4.5 at. %) was identified (Fig. 1-2, Table 1-2). This indicates formation of the β -(Ni,Pd)Al phase. The thickness of this zone is ~52 μ m. The second, interdiffusion zone, situated below is much thinner (~5 μ m). Its chemical composition suggests formation of the palladium doped γ' -Ni₃Al phase (Table 2, Point 3). The nickel substrate/palladium doped γ' -Ni₃Al as well as the palladium doped γ' -Ni₃Al/ β -(Ni,Pd)Al interfaces were relatively flat (Fig. 2). Kirkendall-like porosity was observed within the β -(Ni,Pd)Al phase near palladium doped γ' -Ni₃Al phase (Fig. 2).

Table 1. Chemical composition on the cross-section of the palladium modified aluminide coating deposited on the nickel substrate (in at.%)

Spot	Chemical composition		
	Al	Ni	Pd
1	34.3	60.6	5.2
2	-	100	-

Table 2. Chemical composition on cross-section of additive/interdiffusion zone of palladium modified aluminide coating deposited on the nickel substrate (in at.%)

Spot	Chemical composition		
	Al	Ni	Pd
1	32.4	63.1	4.5
2	31.3	64.6	4.1
3	21.7	77.5	0.8
4	-	100	-

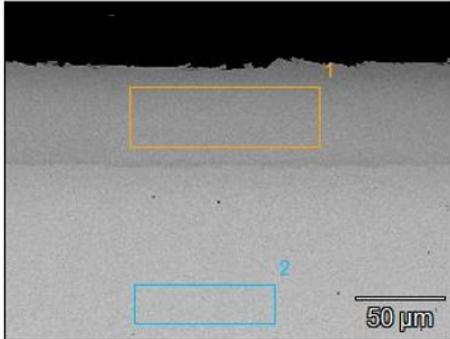


Figure 1. SEM microstructure on the cross-section of the palladium modified aluminide coating deposited on the nickel substrate.

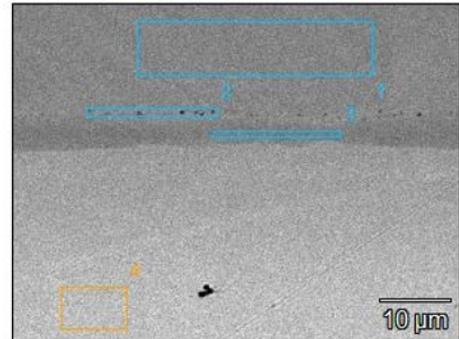


Figure 2. SEM microstructure on the cross-section of the additive/interdiffusion zone of the palladium modified aluminide coating deposited on the nickel substrate.

EDS analysis and concentration profiles of the cross-section of the palladium modified aluminide coating showed outward nickel diffusion from the substrate and the inward aluminum diffusion from the surface to the nickel substrate (Figure 3). It was found that palladium diffuses both outward from the surface to the additive zone and inward from the surface to the interdiffusion zone (Figure 3).

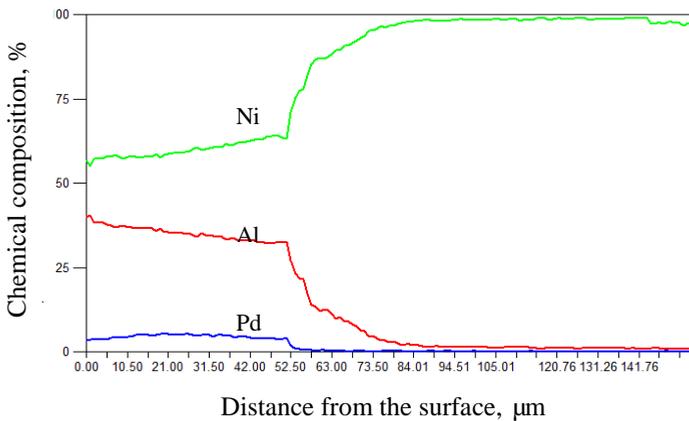


Figure 3. EDS analysis on the cross-section of the palladium modified aluminide coating deposited on the nickel substrate.

3.2 Palladium and hafnium modified aluminide coating on pure nickel

Palladium and hafnium modified aluminide coating on pure nickel has a double-zone structure (Fig. 4, Table 3). In the first, additive zone, on the top of the coating, the proportion of Ni to Al corresponds to the β -NiAl phase (Table 3, Point 1). Moreover, some palladium (10.2 at. %) and hafnium (0.3 at. %)

was identified. This indicates formation of the hafnium doped β -(Ni,Pd)Al phase. The thickness of this zone is $\sim 45 \mu\text{m}$. The second, interdiffusion zone, situated below is much thinner ($\sim 3 \mu\text{m}$). Its chemical composition suggests formation of the palladium and hafnium doped γ' -Ni₃Al phase (Table 3, Point 4). Bright, hafnium rich precipitates were observed in the additive zone (Fig. 4-5). EDS spectrum of particle 1 and 2 shows presence of aluminum, nickel, palladium and hafnium peaks (Fig. 5 b, c). The nickel substrate/hafnium doped γ' -Ni₃Al as well as the hafnium doped γ' -Ni₃Al/hafnium doped β -(Ni,Pd)Al interfaces were relatively flat (Fig. 4). Kirkendall-like porosity was observed within the hafnium doped β -(Ni,Pd)Al phase near the hafnium doped γ' -Ni₃Al phase (Fig. 5).

Table 3. Chemical composition on the cross-section of the palladium and hafnium modified aluminide coating deposited on the nickel substrate (in at.%)

Spot	Chemical composition			
	Al	Ni	Pd	Hf
1	35.8	70.1	10.2	0.3
2	33.2	73.3	7.8	1.1
3	33.2	74.7	7.3	0.0
4	23.4	85.7	1.7	0.5
5	-	100.0	-	-

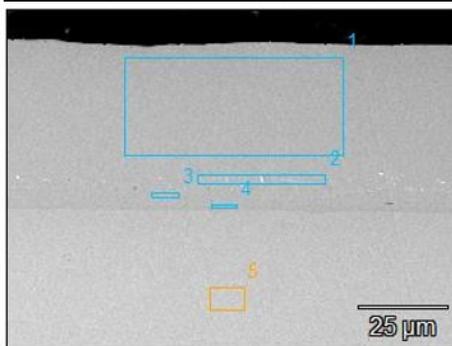


Figure 4. SEM microstructure on the cross-section of the palladium and hafnium modified aluminide coating deposited on the nickel substrate.

a)

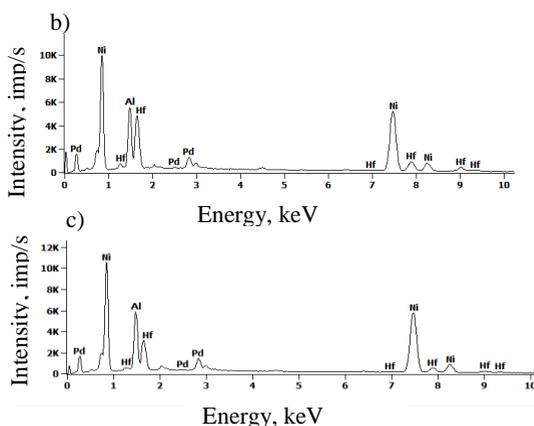
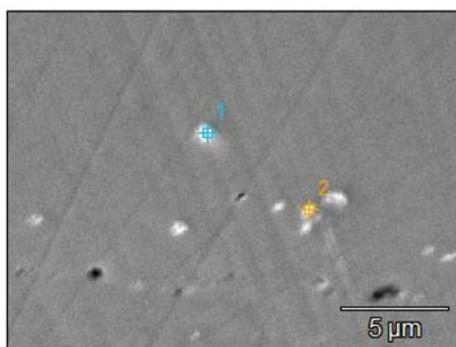


Figure 5. SEM microstructure of additive zone (a) with EDS spectrum of particle 1 (b) and particle 2 (c) of palladium and hafnium modified aluminide coating on the nickel substrate.

3.3 Palladium and zirconium modified aluminide coating on pure nickel

Palladium and zirconium modified aluminide coating on pure nickel has a double-zone structure (Fig. 6). In the first, additive zone, on the top of the coating, the proportion of Ni to Al corresponds to the β -

NiAl phase. Moreover, some palladium (3.7 at. %) was identified. This indicates formation of the β -(Ni,Pd)Al phase. The thickness of this zone is $\sim 52 \mu\text{m}$. The second, interdiffusion zone, situated below is much thinner ($\sim 6 \mu\text{m}$). Its chemical composition suggests formation of the palladium doped γ' -Ni₃Al phase. Bright, zirconium rich precipitates were observed in the additive zone (Fig. 6 a, b, c, e). EDS spectrum of points 1 - 4 show presence of aluminum, nickel, palladium and zirconium peaks (Fig. 6 b - e). Kirkendall-like porosity was observed within the β -(Ni,Pd)Al phase near the γ' -Ni₃Al phase (Fig. 6).

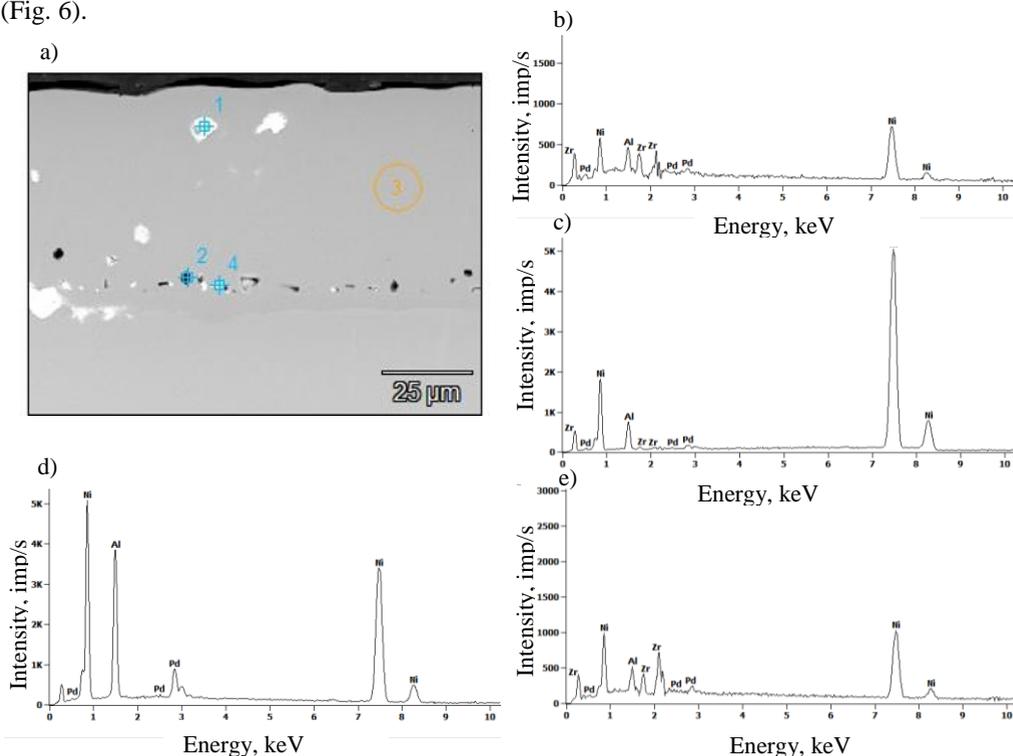


Figure 6. SEM microstructure on cross-section of palladium and zirconium modified aluminide coating deposited on the nickel substrate (a) with EDS spectrum of point 1-4 (b-e).

Palladium, palladium and hafnium and palladium and zirconium doped aluminide coatings show better oxidation resistance than the nonmodified ones (Fig. 7).

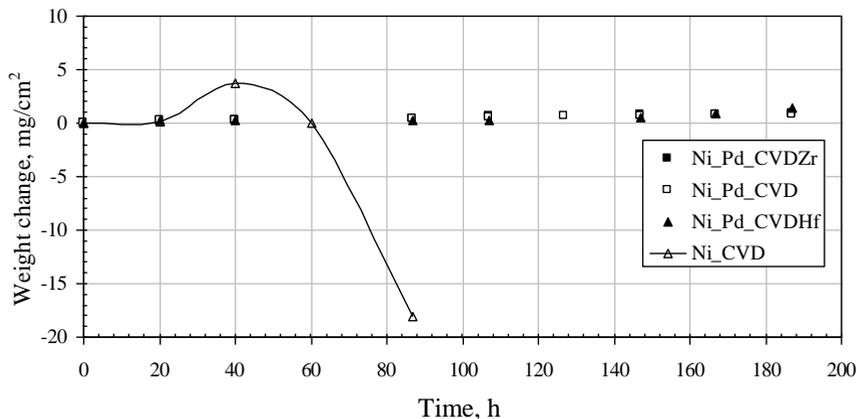


Figure 7. Weight change versus oxidation time coatings deposited on pure nickel.

4. Conclusions

The analyzed coatings consist of two zones, the additive and the interdiffusion ones. The additive zones in Pd modified and Pd+Zr modified coatings contain the the β -(Ni,Pd)Al phase, whereas in Pd+Hf modified one – the hafnium doped β -(Ni,Pd)Al phase The interdiffusion zone is formed by the palladium doped γ' -Ni₃Al or palladium and hafnium doped γ' -Ni₃Al phase phase. Palladium is distributed in whole coatings, whereas zirconium and hafnium is situated in precipitates in the additive zone. Oxidation resistance of co-doped Pd+Zr and Pd+Hf) coatings is significantly better than the single-doped (Pd) one. The sinegritic effect of two dopants is obserwed.

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