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# Microstructure degradation of simple, Pt- and Pt + Pd-modified aluminide coatings on CMSX-4 superalloy under cyclic oxidation conditions

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### ABSTRACT

The paper presents results of simple, Pt/Pd- and Pt-modified aluminide coatings' cyclic oxidation-induced degradation analysis. The coatings were deposited by Pt and Pt + Pd electroplating, followed by vapor phase aluminizing at 1050 °C. Cyclic oxidation tests were performed at 1100 °C in 23 h cycles. Microstructural and phase analysis conducted using XRD, SEM, EDS and EBSD methods revealed that the oxide layers that formed on the coatings were composed of three distinctive types of oxides growing according to a specific pattern which is described. The oxide layer that formed on the simple aluminide coating exhibited low adhesion in comparison to Pt- and Pt,Pd-modified aluminide coatings which managed to maintain an adherent oxide layer that contained higher amount of desirable  $\alpha$ -alumina. The Al-depleted  $\beta$ NiAl grains remained much larger in the modified aluminide coatings, even after failure. What is more, stripes characteristic for martensitic transformation were discovered in the  $\beta$  phase grains in all coatings.

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## 1. Introduction

Diffusion aluminide coatings are applied on jet engine turbine blades in order to provide high temperature oxidation and corrosion resistance. Incorporation of Pt to aluminide coatings makes it possible to apply them as bond coatings for thermal barrier coating (TBC) systems on blades and vanes operating under the most severe conditions [1–4]. Since the performance of the whole TBC system relies directly on the durability of the bond coat, its degradation mechanisms are widely studied in the literature.

Reversible transformation from a  $\beta$  phase (B2) to a tetragonally distorted martensitic phase (L1<sub>0</sub>) was observed in single-phase NiAl and (Ni,Pt)Al bond coats during quenching from high temperature both in isothermal and cyclic oxidation tests by many researchers [5–7]. This phenomena occurs once Al concentration in the  $\beta$  phase drops to 32–38 at.% and when the cooling rate is high enough to suppress the  $\beta$ –> $\chi'$  transformation, as well as due to interdiffusion with the substrate alloy and alloying elements present in the coating, such as Pt, Cr and Co [6–8]. Chen et al. [6,9] have concluded that the strain produced by martensitic transformation during each cycle is 0.7% which is comparable to the thermal strain caused by the coefficient of thermal expansion (CTE) mismatch. This may lead to elastic stresses in the surface layer, destruction of the heat resistant oxide film and

intensification of diffusion processes at high temperatures [10]. Zhang suggested that the volume changes probably contribute to the early stage of surface roughening [5].

Another type of transformation occurring in the  $\beta$ -NiAl coatings during oxidation is the alumina transformation studied in a number of articles [11,12]. While  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> provides protective properties because of its thermodynamic stability and slow growth rate, other types such as  $\theta$  and  $\chi$ -Al<sub>2</sub>O<sub>3</sub> exhibit low adhesion, porosity and volumetric changes with exposure time, hence they are not desirable [13.14]. The amount of  $\alpha$ -alumina in the oxide layer during oxidation increases with exposure time and temperature and leads to reduction of parabolic rate constant by one order of magnitude [15]. Modifying aluminide coatings with Pt significantly improves the formation rate and stability of  $\alpha$ -alumina, both in single and double phase PtAl coatings [16-18]. Other beneficial effect attributed to Pt is improvement of oxide scale adherence during cyclic and isothermal oxidation tests as well as mitigating the detrimental effects of sulfur impurities on scale adherence and inhibition of void growth at the scale-metal interface [19]. Li et al. [20,21] examined the influence of Pd on the transformations occurring in the oxide during high temperature exposure. Apart from the fact that palladium itself facilitates the  $\theta$  to  $\alpha$  transformation, it has been shown that it enhances the outward diffusion of Ti from the substrate to the coating surface which in turn forms TiO<sub>2</sub> that accelerates the transformation from  $\theta$  to  $\alpha$ -alumina.

Oxide layer that forms during high temperature oxidation is also susceptible to degradation due to void formation along the

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metal-oxide interface which has been studied in a number of papers [18,19,22,23]. This phenomenon is attributed to nonuniform Al/Ni diffusion, vacancy formation and/or Kirkendall effect [17]. Angenete et al. [23] proposed a void formation mechanism associated with volumetric changes accompanying the  $\beta$ -> $\chi'$  phase transformation. Other studies [22] suggest that pores and voids tend to collapse during cyclic oxidation tests due to thermal stresses, while they coalesce during long-term oxidation. Incorporation of Pt significantly retards the formation of voids due to enhanced Al diffusion which leads to a twofold advantage: it levels the Al/Ni diffusivity and promotes

 $Al_2O_3$  formation filling the voids and increasing the contact area between the oxide and the metal [17,18].

Surface roughening during high temperature cyclic oxidation, referred to as rumpling, has been observed both in Pt-modified and simple aluminide coatings on Ni-based superalloys and extensively studied by Tolpygo et al. [22,24–26]. It is also considered as a significant degradation form since it leads to initiation of cracking and eventual separation between the TBC and the superalloy.

Alperine et al. [27,28] studied high temperature performance of palladium modified aluminide coatings obtained applying various

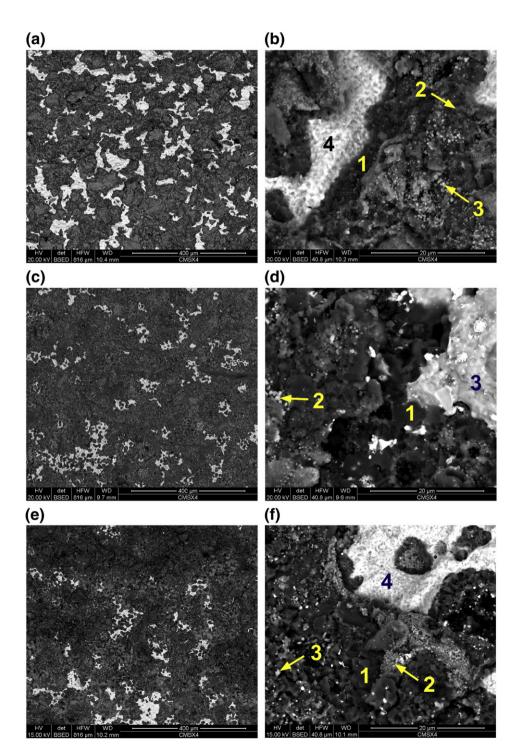


Fig. 1. Surface microstructure of aluminide coatings after cyclic oxidation test: (a and b) simple aluminide coating, (c and d) Pt-modified aluminide coating, and (e and f) Pt/Pd-modified aluminide coating.

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