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### Authors

Hou, Peggy Y.  
Tolpygo, V.K.

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## **Examination of the platinum effect on the oxidation behavior of nickel-aluminide coatings**

P. Y. Hou<sup>1</sup> and V. K. Tolpygo<sup>2\*</sup>

<sup>1</sup>Lawrence Berkeley National Laboratory, Materials Sciences Division, Berkeley, CA 94720

<sup>2</sup>Materials Department, University of California, Santa Barbara, CA 93106

### **Abstract**

Oxidation resistant nickel-aluminide coatings are designed to develop a protective alumina scale during high temperature exposure. It is well established that platinum additions, typically about 6-8 at%, provide substantial improvements in oxidation resistance of such coatings, yet the nature of the platinum effect is still not fully understood. In this work, the oxidation behavior of two commercial NiAl and NiPtAl coatings deposited on the same Ni-base single crystal alloy CMSX-4 was analyzed. Cyclic and isothermal oxidation tests were conducted at 1150°C in air. Microstructure development and alumina/coating interface chemistry were studied as a function of oxidation time. Numerous voids developed at the Al<sub>2</sub>O<sub>3</sub>/NiAl interface, and sulfur was found to segregate at the void surfaces and at the contact interface, leading to spallation of the scale over the convex areas along ridges on the coating surface. The presence of platinum prevented sulfur segregation and void formation at the Al<sub>2</sub>O<sub>3</sub>/NiPtAl interface. As a result, the Al<sub>2</sub>O<sub>3</sub> scale on the NiPtAl coating remained adherent and virtually no spallation was observed even after prolonged cyclic oxidation.

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\* Present address: Honeywell Aerospace, 111 S. 34<sup>th</sup> St., M/S 503-118, Phoenix, AZ 85034

## Introduction

It is well known that platinum additions to  $\beta$ -NiAl significantly improve the adherence of alumina scales during high temperature oxidation [1-3]. For this reason, the platinum-modified aluminide coatings are commonly used for oxidation protection of Ni-base superalloys in the hot sections of gas turbines. Although the beneficial effect of platinum has long been established and implemented in various coating systems, the actual mechanism by which Pt improves alumina adhesion remains uncertain. One apparent role of platinum is to reduce the amount of interfacial voids [2,4], although it is not clear whether this effect can fully account for the improved adhesion of the scale.

In binary NiAl alloys, it has been found that ~2 at.% sulfur could segregate to the oxide-alloy interface during oxidation, and its presence greatly reduced the interfacial strength [5]. Although scale adhesion on nickel-aluminide coatings has been reported to improve with decreasing the amount of sulfur in the underlying alloy [2], no chemical information was obtained from the scale/coating interface. Recently, the effect of Pt on sulfur segregation has been evaluated using Auger spectroscopy. Platinum was found to reduce sulfur segregation to NiAl surfaces under vacuum [4,6], and it prevented sulfur segregation at an  $\text{Al}_2\text{O}_3$ /Ni-40Al-10Pt alloy interface [6]. In contrast, recent studies of a  $\beta$ -NiPtAl coating [7] showed that Pt did not prevent interfacial sulfur segregation, which resulted in a poorly adherent  $\text{Al}_2\text{O}_3$  scale.

In order to better understand the role of platinum in oxide adhesion, the chemistry of the oxide-metal interface on both Pt-modified and Pt-free coatings should be examined. The purpose of this work is to perform such study and to relate this

information to the adherence and microstructure of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> oxide scales formed on typical NiAl and NiPtAl diffusion coatings.

## Experimental

NiAl and NiPtAl coatings were deposited by Howmet Castings (Whitehall, MI) on coupons from the same bar of single crystal superalloy CMSX-4 (composition given in Table 1). The Pt-modified coating was produced by platinum electroplating followed by low-activity CVD aluminizing [8], whereas the NiAl coating was deposited using a similar CVD process directly onto the alloy surface.

Analysis of the as-deposited NiAl and NiPtAl coatings shows that both have similar microstructures consisting of an outer single-phase aluminide layer and an inner multi-phase diffusion zone. Concentrations of aluminum across the as-deposited coatings vary from approximately 44-45 at.% on the surface to 12-13 at.% in the alloy. In the Pt-modified coating, the platinum concentration changes from about 5 at.% on the surface to 8 at.% in the mid section of the outer NiPtAl layer and then decreases to zero at the coating-alloy interface. The outer layer of both coatings also contains small amounts of Co, Cr, Ti and Re, and the inner layer is slightly enriched with W and Ta. The coating surfaces exhibit a distinct network of grain-boundary ridges, similar to other outward-growing CVD nickel aluminides [2,3,9], and the surface roughness was about  $R_q \sim 1 \mu\text{m}$ .

The samples, without any surface grinding or polishing, were ultrasonically cleaned in acetone and ethanol prior to oxidation. Oxidation experiments were carried out in laboratory air at 1150°C. Isothermal and cyclic tests, with 10 min hot time per cycle, were conducted. Heating and cooling rates for both were approximately 200°C/min.

Oxidized samples were examined using SEM, and chemistry of the  $\text{Al}_2\text{O}_3$ /coating interface was studied after 10h, 100h and 250 h isothermal oxidation using a scanning Auger probe. The interface was exposed by scratching the oxidized samples in ultra-high vacuum [5-7]. The scratch plows through the scale into the metal, causing oxide spallation adjacent to the scratch mark. Auger analyses, with a probe size of 0.5-1  $\mu\text{m}$ , were made on many exposed areas, and occasionally within the scratch mark to determine the coating composition away from the interface.

## Results

Figure 1 illustrates the difference in cyclic oxidation behavior between the NiAl and NiPtAl coatings. While the NiPtAl sample displayed continuous weight gain throughout the 2000-cycle test, the NiAl started to show weight loss after 600 cycles. Visual observation revealed oxide spallation on the NiAl coating after ~200-300 cycles, but fully adherent scale on the NiPtAl coating even after 2000 cycles.

No spallation was observed on the NiAl coating after isothermal oxidation at 1150°C for 10h, but the scale could be easily scratched off. Examinations of these scratch-induced spalled areas revealed fine oxide imprints with no interfacial voids, as shown in Figure 2a. After longer isothermal exposures (100 and 250 hrs), extensive scale spallation occurred on the NiAl coating (Fig. 2b,c). These spalls took place almost exclusively along grain-boundary ridges, whether or not there were interfacial voids, which formed preferentially along these ridges.

Figure 3a shows the NiPtAl surface after 250h isothermal oxidation. Ridges similar to those found on the NiAl coating can be seen, but there was no scale spallation;

furthermore, the oxide scale was difficult to scratch off, indicating strong interface adhesion. Scratching only induced small areas of spalls (Fig. 3b as an example), which showed oxide imprints with no voids.

Significant roughening (rumpling) of both coatings occurred during cyclic oxidation (Figure 4), but it was less pronounced on the NiAl due to repeated scale spallation from ridges and peaks. Unlike under isothermal conditions, these spalled areas were free of interfacial voids. No spallation was observed on the NiPtAl coating after cyclic oxidation, even though cracks were often found in the alumina along the ridges (see inset of Fig. 4b).

Auger analysis clearly showed sulfur segregation everywhere at the  $\text{Al}_2\text{O}_3/\text{NiAl}$  interface regardless of its morphology (Fig. 5a); its surface concentration after 10h, 100h and 250h was  $0.9\pm 0.3$ ,  $1.1\pm 0.4$  and  $0.9\pm 0.3$  (at.%), respectively. These numbers indicate that the amount of interfacial sulfur has already reached a steady state level after 10 hrs. Most of the void surfaces were covered with a thin layer of oxide (due to spallation or cracking of the scale above them during cooling). Some voids that were found to be oxide-free during the AES measurements demonstrated significantly higher, up to 15 at.%, concentration of sulfur. Contrary to the NiAl coating, no sulfur was detected at the  $\text{Al}_2\text{O}_3/\text{NiPtAl}$  interface (Fig. 5b).

In addition to the major elements in the coatings (Ni, Al and Pt), both interfaces also had Cr, Co, Ti, N, O and C, as illustrated in Fig. 5. Whereas oxygen and carbon are usual UHV contaminants (their levels increased with exposure time in the AES chamber), Cr, Ti and Co were enriched at the interface relative to their concentrations in the bulk (determined by analyses made within the scratch track). On the  $\text{Al}_2\text{O}_3/\text{NiAl}$  interface, a

group of peaks (marked by the arrow in Fig. 5a) with energies close to that of Ta, W and Re are present. Closer examinations suggested that they might correspond to rhenium. Nano-sized Re [2] and Cr [2,7] particles at Al<sub>2</sub>O<sub>3</sub>/NiPtAl interfaces have been previously detected by TEM, but their effect on scale adhesion is unknown. Overlaps with low-energy Pt Auger signals prevented detection of these peaks on the NiPtAl, but high levels of Cr were found at some locations, which may be due to the presence of Cr-rich precipitates at the interface.

## **Discussion**

The difference in oxidation behavior of the NiAl and NiPtAl coatings, in terms of weight changes during cyclic oxidation and oxide spallation, is very similar to that reported by others [2,7]. The isothermal and cyclic oxidation experiments performed in this work demonstrate that Pt additions significantly improve Al<sub>2</sub>O<sub>3</sub> scale adhesion.

It has been suggested [2] that the improved scale adhesion on NiPtAl coatings is due to a reduction of the amount of interfacial voids; however our results indicate that voids are not necessary to cause spallation. For example, spallation during cyclic oxidation of the NiAl coating did not reveal any voids at the interface. Furthermore, the same degree of spallation was observed on regions with or without any voids on the NiAl after isothermal oxidation for 100h and 250h. The absence of interfacial voids during cyclic oxidation of the NiAl coating is quite intriguing. It suggests that some prolonged isothermal exposure is required for the voids to grow, at least the type observed here.

Spallation of the oxide on NiAl after 200-300 cycles or after 100h and 250h isothermal oxidations occurred preferentially along grain boundary ridges (Fig. 3), where

local tensile stresses normal to the interface developed upon cooling due to the oxide-metal thermal expansion mismatch [10,11]. Notably, the scale was more adherent after 10h, because the normal stresses, which drive spallation, are smaller for a thinner oxide and on a surface with smaller curvature [10]. In addition, the local stresses normal to the interface should be compressive in the concave areas; therefore, the scale remained adherent between grain boundary ridges.

On the NiPtAl coating, the interface is significantly stronger; consequently, no spallation was observed even when extensive undulations developed after prolonged cyclic oxidation (Fig. 4b). AES analysis of the interface chemistry showed no segregation of sulfur (Fig. 5b). This absence of sulfur at the oxide-metal interface appears to be the major reason of strong scale adhesion on the NiPtAl coating, although the mechanism by which platinum prevents sulfur segregation is not determined in this study. Taking into account that both coatings were deposited on the same alloy, it can be argued that the amount of sulfur in the NiPtAl should not be any smaller than in the NiAl. Also, given that no Pt enrichment was observed at the oxide-metal interface, it is unlikely that the absence of sulfur is a result of site competition with platinum (unless there is a strong repulsive interaction between S and Pt). It is possible that the presence of Pt by itself strengthens the interface. However, previous study on a similar NiPtAl coating on a different substrate showed poor scale adhesion due to S co-segregation with Cr [7], indicating that any interface strengthening effect due to Pt must be suppressed by the presence of S at the interface.

Approximately 1 at.% S at the oxide-metal interface on the NiAl coating appears to be sufficient to weaken the interface and cause oxide spallation. This concentration is



similar to that found at the oxide-metal interface on a Ni-40Al alloy, where interface strength dropped rapidly with the first few percent of sulfur [5]. The amount of hafnium present in the CMSX-4 alloy (0.03 at.%) is apparently insufficient to mitigate the effect of sulfur in the NiAl coating. In this respect, oxidation behavior of NiAl coatings is different from that of NiAl alloys where similar Hf additions provided strong scale adherence [12].

Although Cr was also enriched at the interfaces studied here, no S and Cr co-segregation was detected, as that observed on a NiPtAl coating on a different alloy [7]. The difference may be due to a lack of any reactive element, such as Hf or Y, in the earlier alloy [7], or a lower S content in the present coating, since co-segregation depends not only on the interactive attraction between the segregants, but also on the bulk and surface concentrations of each segregating element [13]. Further study is needed to illustrate the interaction between segregating and alloying elements.

## **Conclusions**

Sulfur was found to segregate at the  $\text{Al}_2\text{O}_3$ /metal interface during oxidation of the NiAl diffusion coating. The amount of sulfur after 10, 100 and 250h isothermal exposure at 1150°C was at a near constant level of  $1.0 \pm 0.3$  at.%. No sulfur segregation was detected on the NiPtAl coating deposited on the same superalloy. The presence or absence of interfacial sulfur is believed to be the cause for the weak and strong oxide adhesion on NiAl and NiPtAl, respectively. Numerous interfacial voids developed on the NiAl coating, but only after prolonged isothermal oxidation. Scale spallation initiated by delamination along surface ridges, and the process appears to be unaffected by the

presence of interfacial voids. The presence of 0.03 at% hafnium in the superalloy did not provide sufficient spallation resistance of the alumina scale on the Pt-free NiAl coatings.

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**Table 1: Composition of alloy CMSX-4**

| <b>element</b> | <b>wt %</b> | <b>at %</b> |
|----------------|-------------|-------------|
| Ni             | 61          | 63.1        |
| Al             | 5.7         | 12.9        |
| Cr             | 6.3         | 7.4         |
| Co             | 9.5         | 9.8         |
| Ta             | 6.5         | 2.2         |
| W              | 6.3         | 2.1         |
| Mo             | 0.6         | 0.4         |
| Re             | 3           | 1           |
| Ti             | 1           | 1.3         |
| Hf             | 0.09        | 0.03        |
|                | <b>ppmw</b> | <b>ppma</b> |
| Y              | <1          | <1          |
| Zr             | 20          | 13          |
| S              | 2           | 4           |
| P              | 18          | 35          |
| C              | 29          | 101         |
| O              | 10          | 38          |

### Figure Captions:

Figure 1: Cyclic oxidation behavior of NiAl and NiPtAl coatings tested in air.

Figure 2: Surface of the NiAl coating after isothermal oxidation for 10h (a) and 250h (b),(c): after 10h, no voids are observed in the areas exposed by scratching; after 250h, spallation along grain boundary ridges exposes areas with (b) and without (c) interface voids. The insert in (b) shows a magnified view of the interface void.

Figure 3: NiPtAl surface showing no spallation after 250h (a) isothermal oxidation and oxide imprints on a scratch-induced spall (b).

Figure 4: Surface morphology of NiAl (a) and NiPtAl (b) coatings after 2000 10-min cycles at 1150°C. Magnified views are added as inserts showing the lack of interface voids in (a) and oxide cracking along surface ridges in (b).

Figure 5: Typical AES spectrum found on NiAl (a) and NiPtAl (b) after Al<sub>2</sub>O<sub>3</sub> scale removal in ultra high vacuum.











