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Cyclic oxidation-induced cracking of platinum-modified nickel-aluminide coatings

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Short cracks, extending to the interdiffusion zone, have been observed in platinum-modified nickel-aluminide diffusion coatings on single-crystal CMSX-4 superalloys after these have been subject to short (10 min) rapid thermal cycles. The cracks were revealed after removing the thermally grown oxide formed during cycling on the coating surfaces. Cracking was observed for coatings subject to thermal cycling between 1150 and 1050 °C, with and without an applied compressive stress, as well as on thermal cycling between 1150 °C and room temperature.

Keywords: Aluminide coating; Rumpling; Grain structure; Cyclic oxidation testing; Compressive stress

Platinum-modified nickel-aluminide coatings are now widely used in the gas turbine industry to provide combined oxidation and corrosion resistance to superalloys in the hottest sections of turbines, as well as to provide an oxidation-resistant bond-coat for thermal barrier top-coats [1–3]. At high temperatures in air the aluminide forms a fine-grained α-alumina oxide that is under both a compressive growth stress and, on cooling, an additional compressive stress due to thermal expansion mismatch with the superalloy [2]. Extensive investigations have been made of the morphological stability of aluminide coatings under thermal cycling conditions [4–9] as well as the relationship to their oxidation resistance and the life of thermal barrier coatings [10,11]. Amongst these is the "rumpling" instability of aluminide coating [4–8]. Despite these studies, little is known about how the behavior of the coating under thermal cycling oxidative conditions is related to the long-term thermomechanical fatigue (TMF) of the underlying superalloy. One recent paper in the open literature shows an image of a coated superalloy after thermomechanical fatigue with many parallel cracks in the aluminide and only a few propagating into the superalloy [12]. There are several rather basic issues that need to be resolved to understand these observations and the role of the coating in TMF. These include whether, and under what combination of oxidation and thermomechanical conditions, incipient cracks form in the aluminide coating and how somem but not allm then extend into the superalloy. Multiple small cracks have been observed to form in the thermally grown oxide (TGO) under thermal cycling, both at the crests and troughs of the rumples, as shown in Figure 19 of Ref. [8]. However, images formed by sectioning with a focused ion beam (FIB) indicate that these cracks are sheathed by oxide and do not extend deep into the aluminide. However, in quantifying the rumpling displacements, under cyclic conditions that produce the maximum extent of rumpling, subsurface cracks have been revealed after removing the surface of the coating, including the TGO. These observations are reported here.

Samples from three types of cyclic oxidation tests have been examined. Two of the tests were on standard 1 in. diameter coupons subject to two different thermal cycles, and one of the tests was on rectangular bars of the same material thermal cycled with a superimposed compressive stress. The coatings, platinum-modified nickel-aluminide coatings produced by in-diffusion of 1 in. coupons of platinum-coated CMSX-4 single-crystal superalloys, were provided by Howmet Corporation. The aluminide coating produced has been characterized in detail elsewhere [6]. It consists of an outer, single-phase β-NiAl layer, approximately 35 μm thick, and an inner, microstructurally complex interdiffusion zone

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of similar thickness. The composition of the outer layer is approximately $Ni_{43}Al_{43}Pt_5$ with the balance being Cr, Co and Pt. Prior to cyclic oxidation, the aluminide coating surface was polished with 1200 grit SiC paper to remove the ridges formed on top of the bond-coat grain boundaries during the coating process. A number of the disk coupons were thermally cycled between 1150 and 1050 °C, with a hold of 10 min at each temperature. This was achieved by moving the coupons from one furnace at 1150 °C to another furnace at 1050 °C. After cycling, coupons were cooled down to room temperature at a rate of approximately $200\,°C\,min^{-1}$. This rapid, small temperature excursion thermal cycling test has previously been shown to lead to extensive rumpling [13]. For comparison, one of these coupons was cooled more slowly, at $\sim 5\,°C\,min^{-1}$ after the rapid cycling. The second thermal cycling regime was one in which the coupons were cycled between 1150 °C and room temperature to assess the effect of cooling the specimen below the estimated ductile-to-brittle transition temperature (DBTT) of the β phase in the coating. This temperature is not known with any precision for the coatings investigated but has been estimated to be ~760 °C for a $Ni_{35}Al_{52}Cr_8Ti_2$ alloy [14] and ~600 °C for a $Ni_{37}Al_{43}Cr_4Pt_{12}Co_4$ diffusion aluminide alloy [15]. The number of thermal cycles was varied from 20 to 500. In the third test, rectangular bar specimens ($10 \times 5 \times 3\,mm^3$) were machined from coupons with their long dimension parallel to the [001] axis of the CMSX-4 superalloy. After grinding to remove the grain boundary ridges, these bars were first oxidized for 1 h at 1150 °C to form a thin α-alumina scale. Then, a 80 MPa compressive stress was applied to the specimens along the [001] superalloy axis and the temperature cycled between 10 min at 1050 °C followed by 10 min at 1150 °C. Details of the experimental set-up are given elsewhere [17].

In order to observe and characterize the bond-coat microstructure after thermal cycling, the surface oxide scale was slowly polished away using a 6 μm diamond paste until the surface roughness associated with the rumpling was removed. The surface was then carefully polished with γ-alumina powder (Buehler) down to 0.05 μm. This resulted in a smooth, featureless surface. Then, to reveal the grain structure, the coupons were lightly etched with a mixture of one part of HCl + 5% HNO_3 diluted in nine parts of methanol. This solution is known to preferentially etch aluminum-rich phases in aluminide coatings.

Quite unexpectedly, the light etching revealed short cracks that were not observable after even the most careful polishing (Fig. 1). These cracks were observed after etching for all the specimens subject to cyclic oxidation with the exception of coupons that had only been cycled for two 5 min cycles from room temperature to 1150 °C and the coupon slowly cooled after rapidly cycling. Although some cracks were primarily along individual grain boundaries, most cracks extended into and across adjoining grains, as shown in Figures 1 and 2. Some specimens were polished again to make sure that the cracks were not due to an etching artifact. The cracks remained and did not appear to change. Micrographs such as these indicate that there may be a correlation between the cracks and the γ′ precipitates along the grain boundaries, but this could not be substantiated because the crack origins could not be unequivocally identified. However, it was noted that there were no cracks that were entirely intragranular. A further striking feature of many of the intragranular crack segments was their serrated appearance, as shown for instance in area A of Figure 2.

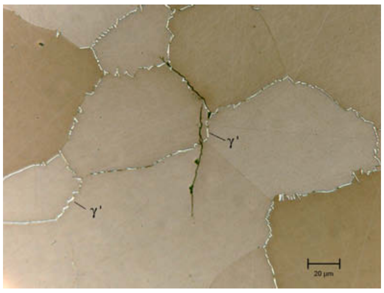

Figure 1. Crack in a nickel-aluminide coating revealed by polishing away the thermally grown oxide and light etching to reveal both the individual β-NiAl grains and the γ′ phase along portions of the β-NiAl grain boundaries. The γ′ phase appears as the bright phase. The coating was cycled 40 times between 1150 and 1050 °C with 10 min at each temperature. Optical micrograph.

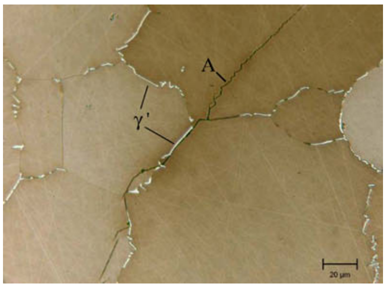

Figure 2. Top view of a crack in another nickel-aluminide coating, again after polishing away the thermally grown oxide. Specimen was cycled 40 times between 1150 and 1050 °C with 10 min at each temperature. Optical micrograph.

No correlation was observed between features of the rumpled surface and the cracks in the aluminide. The length scales are also different: the rumpling wavelength is typically smaller than the aluminide grain size, whereas the aluminide crack spacing was several times the grain size. No correlation was found either between the number of cracks and the number of thermal cycles the coupons had been subjected to. Many cracks were revealed, most of them intragranular, after only 20 cycles between 1050 and 1150 °C (Fig. 1). In contrast, few cracks were observed after 160 cycles and most of these were intergranular. The formation of cracks also seems independent of the lower temperature in the thermal cycles: the cracks' shapes and their density were difficult to estimate but looked very similar after either 40 cycles between 1150 °C and room temperature or after 40 cycles between 1150 and 1050 °C. The incidence of cracking is summarized in Table 1. It is pertinent to note that no martensitic microstructure was seen in any of the etched coupons until after 80 thermal cycles, corresponding to a hot-time above 1000 °C of 40 h. This

Table 1. Observed incidence of cracking.

No. of cycles	Temperature cycles	Applied stress	Cracking
1, 2	RT–1150 °C	None	No
20, 40, 80	RT–1150 °C	None	Yes
40, 160	1050–1150 °C	None	Yes
40, 60	1050–1150 °C	80 MPa	Yes

was consistent with our earlier observations of the same coatings after 1 h thermal cycles for similar times at temperature. It also suggests that cracking occurred well before the coating becomes sufficiently Ni-rich for martensite to form.

To assess the depth of the cracks, FIB cuts were made across a number of the surface cracks. In each case, the cracks extended deeper into the aluminide than the depth of the FIB cut, indicating that the cracks were at least several microns deep and were not sheathed with an oxide. Other coupons were cross-sectioned after their top surfaces were first polished down. Micrographs revealed the presence of cracks extending all the way through the thickness of the aluminide, stopping at the interdiffusion zone. Again, careful polishing was required to reveal the cracks in the cross-section. Cracks were also observed in the aluminide coating of the samples thermally cycled while under a 80 MPa compressive stress. Cracks were also observed after cycling 60 times between 1050 and 1150 °C and they were similar to the ones formed without the applied stress. Again the cracks were observed to go all the way through the coating and stop at the interdiffusion zone (Fig. 3). Also, although a preferential orientation of the thermal cycling induced rumpling perpendicular to the stress axis has been reported [17], no preferential orientation of the cracks was observed.

To the best of our knowledge, cracks have not previously been reported in aluminide coatings after cyclic oxidation. While many observations have been made of the oxidized surfaces, there have been relatively few of the cross-sections and none that we are aware of after polishing off the surface oxide and removing the rumples. One possible reason for the fact that they have not been reported previously is that the cracks are closed due to residual stress in the coating and it is only after the compressed oxide surface is removed that there is sufficient stress relief for them to open up. Another possible explanation is that the compressive stresses introduced by all but the finest polishing keep the cracks closed. One other possibility is that the cracks are nucleated by the light etching, perhaps by preferentially attacking the interface between the γ' phase at the β-NiAl grain boundaries. The etchant used was chosen to provide contrast between the β-NiAl grains since it preferentially etches β-NiAl rather than γ' or γ phases in nickel-aluminide. (This is the reason the γ' precipitates along the grain boundaries are so prominent in the optical micrographs.)

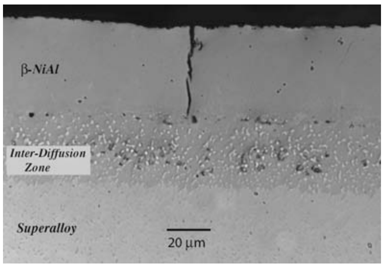

Figure 3. Cross-section of a coating cycled 60 times between 1150 and 1050 °C with a superimposed 80 MPa compressive stress. The crack extends through the thickness of the β-NiAl portion of the coating, stopping at the interdiffusion zone.

On the basis of the reported thermal expansion coefficients of the superalloy and nickel-aluminide, the coating can be expected to be under biaxial tension after rapid cooling [18]. However, one of the major complications inherent with studying the behavior of aluminide coatings on superalloys is that their composition and physical properties are continually changing during thermal cycling. This is a result of both interdiffusion between the aluminide and the superalloy on which it is formed as well as the depletion of Al that occurs as a result of the oxidation process to form the surface oxide. As has been extensively established, the aluminide coating becomes enriched in Ni and depleted in Al, and the initial single-phase β-NiAl composition becomes a two-phase $\beta-\gamma'$ mixture with the γ' phase forming preferentially along the grain boundaries. Concurrently, the interdiffusion leads to swelling of the aluminide [8]. Over a range of nickel concentration, the $L1_0$ face-centered tetragonal martensite forms on cooling below about ~530 °C and it is accompanied by a ~2% volume change [19]. Further complicating the picture is that as a result of the thermal cycling and associated plasticity, the stresses in the aluminide are not simply those associated with thermal expansion mismatch and are likely to converge through shakedown [20] to some, as yet undetermined, state. In addition, the β-NiAl phase is brittle at low temperatures, below about 500–750 °C, whereas the martensite is generally assumed to be soft [21] and have a low elastic modulus [21,22].

The fact that no cracking was observed in the coatings that had only been exposed to two very short cycles to 1150 °C suggests that the cracking is not due to the rapid cooling rate alone or to the brittle behavior of the coating in its β-NiAl phase condition. The observation that cracking occurred after only 20 cycles and was associated with the presence of γ' precipitates along the β-NiAl grain boundaries suggests that the origin of the cracking is related to the change in the coating composition and properties during these first few cycles. As no martensite is seen after either 20 or 40 cycles (100 and 200 min at 1150 °C) it can be further concluded that the composition had not changed sufficiently to significantly change the properties of the NiAl grains themselves. Our interpretation of the cracking is that the coating is in a supercritical stress state as a result of the combination of shakedown and thermal mismatch stresses, and the fine polishing and etching nucleates cracking at the grain boundary γ' precipitates. Once nucleated, the cracks can propagate laterally, parallel to the coating, into the adjoining grains until the local strain energy is released. (The serrated appearance of the transgranular portions of the cracks suggests rapid fracture.) A related possibility is that crack nucleation occurs preferentially in the vicinity of the γ' precipitates because the stresses in the aluminide are locally modified by the difference in thermal expansion between γ′ and β phases, and these stresses are not relaxed on rapid cooling. Data for phases of the same composition as our coatings have not been reported, but measurements by Haynes et al. indicate that the thermal expansion of platinum-containing cast β-NiAl is larger at all temperatures than cast Ni_3Al containing 0.06 at.% Hf [18]. This would lead to the interfaces between the γ′ and β phases being under local tension on cooling, a requirement for preferential crack nucleation at the γ′ particles.

In addition to the fact that all the cracks were observed after removing the surface oxide, the other feature that all the samples had in common was the fact that they were all subject to rather rapid thermal cycling conditions. These short cycle tests, which are more representative of thermal cycling in high-performance aircraft turbines, not only lead to enhanced rumpling but are characterized by rapid heating and cooling between cycles. The greater rumpling implies extensive plastic deformation within the aluminide [23] and the rapid temperature changes limit the possibility for stress relaxation in the aluminide and TGO to anneal out at the high temperatures by creep. Further studies of coating cracking under longer cycle conditions are underway.

It is anticipated that the aluminide cracks we observe may well be related to the cracking pattern reported recently in a similarly coated superalloy that had been subjected to asymmetric counterclockwise diamond thermomechanical fatigue between 400 and 1100 °C, and from 0.7% to 1.0% strain [12]. The macroscopic strain–temperature cycle used in that report was much more complex than that used in this work but in both sets of tests the aluminide coating is subject to strain reversal and rapid thermal cycling. Contrary to this work, the grain boundary ridges formed on aluminizing were not removed prior to testing, nor did the samples spend as much time at the oxidation temperature. Nevertheless, the crack spacing they observe appears to be related to the aluminide grain size and so overall we are led to conclude that our observations capture an earlier stage of the crack formation but that the underlying mechanisms are likely to be similar.

In summary, we have observed subsurface cracking of a platinum-modified nickel-aluminide coating after rapid, brief thermal cycling oxidation conditions with and without a superimposed compressive stress. The cracks appear to be associated with the formation of γ′ precipitates along the grain boundaries of the β-NiAl phase aluminide grains. As cracking was also observed in coatings thermally cycled between 1050 and 1150 °C, it is concluded that the cracking is not directly related to the brittle–ductile transition in the aluminide but rather to mismatch stresses between the γ′ and the β-NiAl phases under rapid cooling.

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