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Oxidation performance of nano-scale multilayer coatings on \( \gamma \)-TiAl

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Abstract. There is a major drive to introduce \( \gamma \)-TiAl into gas turbine engines in order to reduce weight. However, this will require the development of coatings that protect against oxidation at high temperature, but do not adversely affect the mechanical properties. This work reports the high temperature degradation mechanisms of a nanoscale CrAlYN/CrN multilayer coating deposited on \( \gamma \)-TiAl(8Nb) by a combined high power impulse magnetron sputtering / unbalanced magnetron sputtering. Detailed TEM/STEM of FIB prepared specimens from isothermal static oxidation tests at 850\( ^\circ \)C for up to 1030 hours is presented. The evolution of the complex oxide structure and the implications for future coating development is discussed.

1. Introduction
A reduction in the weight of rotating and oscillating components for automotive and aerospace engine applications is currently seen as an effective way to reduce fuel consumption and subsequently lower the production of harmful emissions. Titanium aluminide alloys based on the intermetallic \( \gamma \)-TiAl phase meet many of these criteria for such applications however they possess limited immunity against environmental impact of oxidation, erosion and wear. Therefore, to fully utilize the potential of such light weight materials there is a need to develop new effective high temperature protective coating strategies. One such strategy is that based on the development of super-hard nanostructured thin films. Accordingly, we consider the oxidation performance at 850\( ^\circ \)C of a nanoscale CrAlYN/CrN multilayer coating deposited on \( \gamma \)-TiAl(8Nb) by a combined high power impulse magnetron sputtering / unbalanced magnetron sputtering. Because of the heterogeneous nature of the oxidation, focused ion beam was used to prepare site specific TEM specimens. The results reveal the evolution of a complex microstructure; not only at the coating surface but also at the interface between the coating and \( \gamma \)-TiAl substrate.

2. Experimental methods
\( \gamma \)-TiAl samples of composition Ti (45%), Al (47%), Nb (8%), were coated with a nanoscale CrAlYN/CrN multilayer coating using a combined high power impulse magnetron sputtering (HIPIMS)/ unbalanced magnetron sputtering at Sheffield Hallam University using the conditions detailed elsewhere [1]. Following either \( \gamma ^{-} \) or \( \gamma ^{+} \) ion etching of the intermetallic surface, a base layer
of CrAlN was applied followed by the multilayer coating, comprising alternating CrAlYN and CrN layers. The total coating thickness was ~5µm. Samples coated on all faces were suspended in a furnace at 850°C for times up to 1030h.

Phase analysis of the coating as a function of time was performed using Bragg-Brentano and glancing angle X-ray diffraction. Site specific focused ion beam microscopy was performed on a FEI Quanta 3D with Omicron in-situ sample TEM lift out. TEM and STEM were performed using a JEOL 2010F field emission gun instrument operating at 200kV. Compositional mapping was performed by energy dispersive spectroscopy using an Oxford Instruments ISIS system.

3. Results

Fig. 1a gives a bright field TEM image of a cross section of the outer region of the coating showing the columnar growth. Fig. 1b gives an annular dark field STEM image showing the regular multilayer structure, with a multilayer wavelength of ~4nm. The brighter layers are CrN.

The coating gave a 3 fold reduction in oxidation rate compared to the unprotected intermetallic at 850°C. However, oxidation was heterogeneous, with the growth of distinctive oxide crystals occurring preferentially in parallel lines through equally spaced cracks in the coating, Fig. 2a. However, a simple comparison of the area coverage of these crystals with the mass loss measurements indicates that oxidation must have occurred elsewhere- i.e. the remainder of the coating that in the SEM appeared morphologically similar to the starting coating must have oxidized.

In order to investigate the relative proportions of oxidation through the cracks and over the general surface, and to compare the mechanisms, FIB sections were removed from across one of these regions of preferential oxidation, incorporating an adjacent region, which did not exhibit preferential oxidation. Fig. 2b gives an ion induced secondary electron (ISE) image from the resultant cross-section. This shows 5 different features, in the order from the outside inwards: 1) Outer crystals with a faceted surface (centre of the image); 2) A uniform outer layer within the coating exhibiting regions of brighter contrast; 3) A crack through the coating, penetrated by oxide; 4) A region of significant porosity at the base of the crack in the coating; 5) A layer of significant microstructural change at the interface between the coating and the substrate.

Given the complexity of this surface layer, further studies were undertaken on a TEM specimen removed from the area of Fig. 2b. Fig. 3 gives a bright field STEM image of this area, complete with X-ray maps generated from STEM imaging. Buckling of the sample during FIB milling to electron transparency, as a result of the inevitable residual stresses in such a sample, had resulted in loss of the surface to the right of the crack. The outer crystals visible in Fig. 2a were identified as Rutile-TiO₂ through a combination of XRD and the TEM investigation shown in Fig. 3, consistent with their

Fig. 1. Cross sectional bright-field TEM image from the CrAlYN/CrN coating: a) The outer region, showing the columnar growth. b) Annular Dark Field STEM image from this region showing the multilayer structure with ~4nm wavelength. The CrN gives the brighter contrast.
distinctive morphology. Immediately below these crystals was a mixed Cr/Al oxide layer, which extended across the surface of the entire coating. Such a surface layer is beneficial as it acts to reduce the rate of inward diffusion of the oxygen.

Fig. 2. a) SEM image of the sample exposed at 850°C for 1030h showing oxide crystals growing from cracks within the coating; b) ISE image of a FIB prepared cross-section taken from a region across the crack in the coating for the sample exposed for 168h. See text for description of microstructure.

The oxide within the crack was apparently a combination of phases, mainly Cr₂O₃, but also including TiO₂, and an additional Al containing phase, possibly Al₂TiO₅, but further work is required to positively identify the phase(s). Interestingly, the base of the crack was dominated by the formation of alumina, but with minority Ti and Nb oxides also present.

The interfacial layer, 1-2µm thick, between the coating and substrate, clearly visible in the ISE image in Fig. 2b, was not an oxide, rather a region where substantial diffusion had occurred. The structure of this region was established as polycrystalline TiN by electron diffraction and electron energy loss near edge structure analysis (Fig. 3g). In addition, a thin Al and Nb rich region was observed between the coating and the TiN layer.

4. Discussion
The cracking in the coating which occurs early in the thermal cycle, results from the mismatch stresses promoted by the difference in thermal expansivity between coating and substrate. The magnitude of these mismatch stresses are modified by the stresses in the coating that are dependent on the deposition condition, in particular, the bias voltage [1].

Once cracked, the Ti from the γ-TiAl is rapidly oxidized leading to the formation of Rutile. That this is the outer oxide indicates that the Ti diffuses the most rapidly towards the surface. This process is followed by the oxidation of the Al in the γ-TiAl at the base of the crack, with similar behaviour of the Nb (albeit giving much lower volume fractions consistent with the lower concentration of Nb). This has two important effects. Firstly, the local formation of aluminium oxide at the base of the crack forms a plug, which clearly acts as a barrier to the diffusion of oxygen, as shown by the absence of oxygen penetration further into the γ-TiAl or into the interface between coating and substrate or the base layer itself. Secondly, the diffusion of Al and Nb from the γ-TiAl to form the oxide leaves an area that is almost totally Al and Nb free. This region reacts with nitrogen to form TiN. The thickness of the TiN layer is substantial however, and retention of the original multilayer structure in the coating adjacent the crack, suggests that the nitrogen for this reaction came primarily from the air [3] whereas loss of nitrogen and an absence of the multilayer structure distant from the crack implies diffusion of nitrogen has also occurred from the coating.

The effect of the crack in the coating is clearly detrimental for oxidation resistance. However, the outer region of the coating did exhibit the expected behaviour, namely, preferential oxidation to form a Cr-rich mixed Cr/Al oxide layer, which acts as an effective diffusion barrier to further ingress of oxygen.
**Fig. 3.** BF-STEM image of FIB cross-section (168hrs at 850°C) (a), and corresponding X-ray maps, (b) oxygen Kα, (c) aluminium Kα, (d) chromium Kα, (e) titanium Kα, (f) niobium Kα and (g) ELNES at the N K-edge from the region labelled in (a) displays fingerprint for cubic TiN [2].

**5. Conclusions**
A new coating designed to offer high temperature oxidation resistance, based on CrAlYN/CrN, was successfully deposited onto γ-TiAl. Oxidation occurred via two main routes. Firstly, stable oxidation to a Cr-rich Cr/Al oxide occurred uniformly across the coating surface, which provided an effective barrier to the inward diffusion of oxygen. Secondly, cracking in the coating, resulting from thermal mismatch stresses, provided a short circuit for the oxidation of Ti from the γ-TiAl. Additionally, the availability of N₂ from the air and nitrogen diffusion from the coating facilitates the formation of a TiN layer at the surface of the γ-TiAl. Associated loss of Al and Nb from this region leads to the formation of aluminium and niobium oxides at the base of the crack arresting further oxidation.

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