

# Oxidation behaviour of TiAlYN and CrAlYN nanocomposite coatings deposited on a $\gamma$ -TiAl based alloy Ti-45Al-8Nb

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## Abstract

The oxidation behaviour of TiAlYN and CrAlYN nanocomposite coatings deposited on  $\gamma$ -TiAl was investigated in the temperature range between 750 and 950°C conducting cyclic oxidation tests in air. The  $\sim 4$   $\mu\text{m}$  thick layers with YN mole fractions of 0, 2 and 8% were produced by unbalanced magnetron sputtering. Post-oxidation microstructural examination was carried out using scanning electron microscopy and energy-dispersive X-ray spectroscopy. TiAlYN thin films provided reasonable oxidation protection to  $\gamma$ -TiAl alloy at 750°C, but they degraded after short time periods at 850°C. Samples with CrAlYN coatings exhibited significantly lower mass gains in comparison to the bare substrate material when thermally cycled at 900°C. The oxidised coatings proved to be effective diffusion barrier, thus reducing oxidation of the substrate material. CrAlYN thin films exposed at 950°C exhibited good initial oxidation resistance, but oxidation proceeded with longer exposure time periods, resulting in scale growth and spallation. Beneath both TiAlYN and CrAlYN coatings without and with 2% YN titanium nitride layers formed which were not observed in the surface region of the substrate coated with thin films containing 8% YN.

## Introduction

Titanium aluminides based on  $\gamma$ -TiAl are attractive high temperature structural materials for aircraft and industrial gas turbines as well as automotive applications [1,2]. To exploit potential service temperatures up to 900°C, the oxidation behaviour being insufficient above 800°C has to be improved [3]. The use of protective coatings is a promising method to enhance the oxidation resistance unaffected by adjustments of the alloy composition to optimize mechanical properties. Hard nitride coatings are widely used on cutting tools for wear and oxidation protection [4]. The performance of TiN and CrN established industrial coatings in cutting and forming applications can be enhanced by alloying further elements [5,6]. The oxidation resistance of  $\text{Ti}_{1-x}\text{Al}_x\text{N}$  and  $\text{Cr}_{1-x}\text{Al}_x\text{N}$  improved with increasing Al content, and chromium nitrides exhibited a better oxidation behaviour than titanium nitride films [5] Yttrium additions were also found to increase the oxidation resistance of TiN films [7]. The effect was attributed to segregation of ions of this reactive element to scale grain boundaries. Diffusing outward the yttrium ions inhibit the outward and inward diffusion of cations and oxygen, respectively [7,8]. Similarly, hardness and oxidation behaviour of TiAlCrN coatings were improved by incorporating yttrium into the nitride layers [9]. The aim of the present work was to study the oxidation protection capability of TiAlYN and CrAlYN thin films deposited on  $\gamma$ -TiAl substrate material.

## Experimental

Disk-shaped specimens with 15 mm diameter and 1 mm thickness were machined from an extruded and annealed rod of a  $\gamma$ -TiAl based alloy with the nominal composition Ti-45Al-8Nb (in at.%). On polished surfaces, TiAlYN and CrAlYN layers were deposited using a laboratory scale unbalanced direct current magnetron sputtering system. The 3 - 4  $\mu\text{m}$  thick coatings were produced in an Ar + N<sub>2</sub> glow discharge sustained on powder metallurgically produced Ti(Cr)Al targets with different Y contents. The substrates were placed parallel above the target at a distance of 50 mm and subsequently coated on both face sides. The Y-free Ti<sub>0.45</sub>Al<sub>0.55</sub>N film and the (Ti<sub>1-x</sub>Al<sub>x</sub>)<sub>1-y</sub>Y<sub>y</sub>N film containing 2 at.% Y in the metallic sublattice crystallized in the cubic NaCl structure, whereas addition of 8 at.% Y resulted in a mixed NaCl/ZnS wurtzite microstructure [10]. The deposited (Cr<sub>1-x</sub>Al<sub>x</sub>)<sub>1-y</sub>Y<sub>y</sub>N coatings with Al/Cr ratios of  $\sim 1.2$  and YN mole fractions of 0, 2 and 8% exhibited a single phase NaCl-type crystal structure [11,12]. Cyclic oxidation tests were carried out at 750, 850, 900 and 950°C in laboratory air up to a maximum testing period of 1000 cycles. One cycle consisted of exposure at high and ambient temperatures for 1 h and 10 min, respectively. During room temperature storage the samples cooled down to about 60°C. After oxidation cross-sectional analyses of the samples were performed using scanning electron microscopy (SEM) equipped with an energy-dispersive X-ray spectroscopy (EDS) system.

## Results and discussion

Figure 1 shows results of cyclic oxidation tests at 750°C for bare  $\gamma$ -TiAl and specimens with TiAlYN nanocomposite coatings containing 0, 2 and 8 mole% YN. The lowest mass gain was observed for the coating without yttrium. The yttrium containing coatings exhibited rapid initial oxidation increasing with higher yttrium nitride content. However, after the first 20 cycles, the further growth rate was slow, in particular for the nanocomposite layer containing 8% YN.

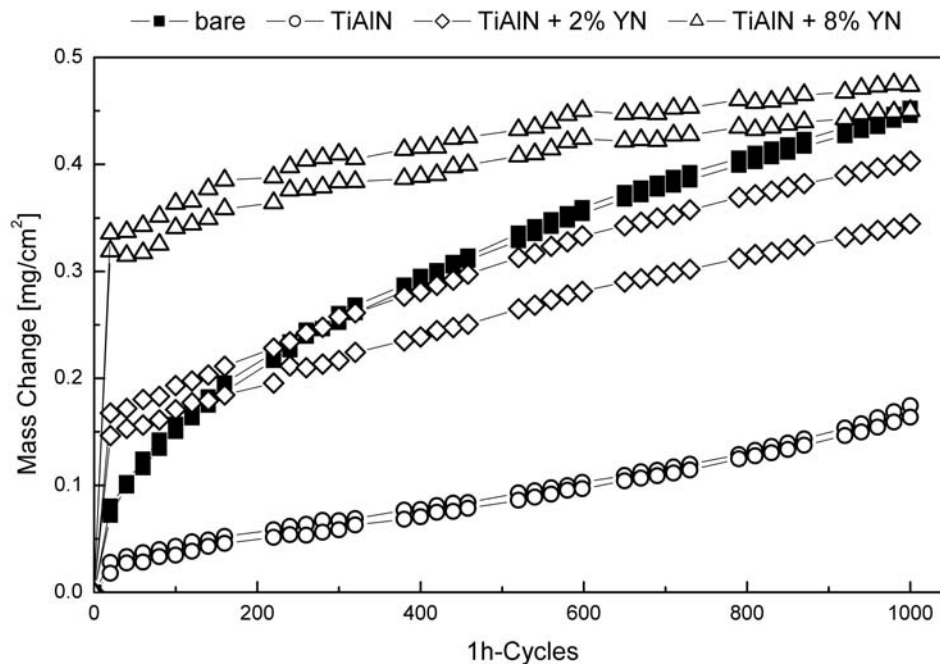


Figure 1: Mass change vs number of cycles of  $\gamma$ -TiAl specimens uncoated and coated with TiAlYN containing different amounts of YN which were thermally cycled at 750°C in air.

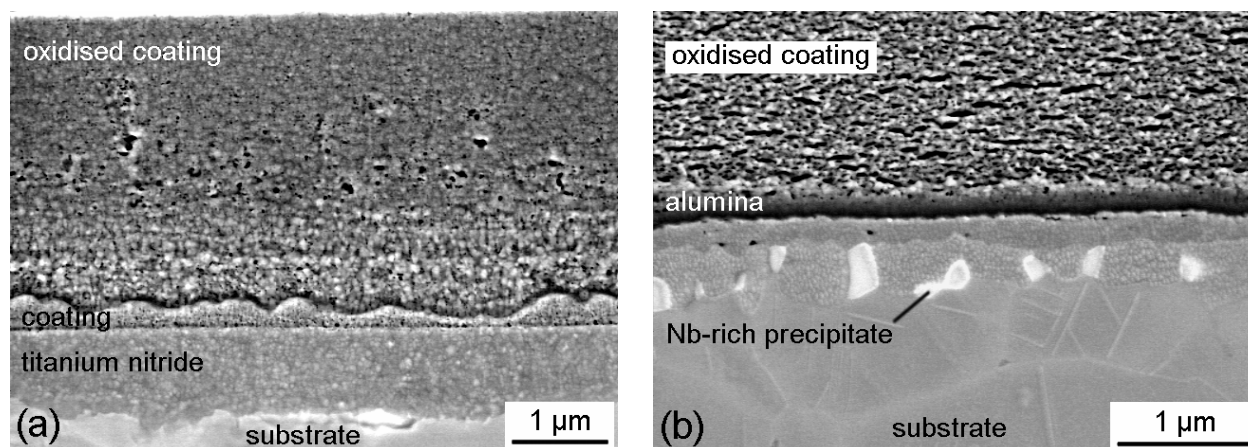


Figure 2: SEM micrographs of  $\gamma$ -TiAl samples coated with TiAlN containing (a) 2% and (b) 8% YN, which were exposed to air at 750°C for 1000 cycles

SEM micrographs of the cross-section of a sample coated with TiAlN which was exposed to air at 750°C for 1000 cycles revealed different oxidation attack on both face sides which might be associated with the subsequent deposition of the nitride coatings. On one side, the TiAlN coating was partly oxidized, and a porous mixed  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  scale grew with a rather dense outer layer. Nitrogen was not detected in the scale. About half of the TiAlN coating was still present, containing small pores. Its chemical composition was measured to 25.3Ti-23.7Al-0.3Nb-50.6N (at.%). Beneath the coating, in the surface region of the substrate, a titanium nitride layer formed. On the other side of the sample, a layered oxide scale grew on the substrate. The TiAlN + 2%YN coating was nearly entirely oxidized after 1000 cycles of exposure (Figure 2a). Again, a titanium nitride layer formed beneath the coating. A thin layer of the remaining TiAlYN coating was observed at the coating/titanium nitride layer interface. The sample coated with TiAlN + 8%YN exhibited a porous oxide scale consisting of Ti-, Al-, and Y-oxides (Figure 2b). In the transition region between the oxidised coating and substrate a dense thin layer of predominantly alumina was found followed by a fine grained layer of a titanium-rich phase with Nb-rich precipitates (bright phase) embedded. In contrast to the TiAlN coating without and with 2% YN, a titanium nitride layer did not form below the coating containing 8% YN.

Mass change data of  $\gamma$ -TiAl specimens bare and coated with TiAlYN thin films which were thermally cycled at 850°C are plotted in Figure 3. The Y-free coating exhibited rapid initial oxidation but the subsequent scale growth rate was very slow. After about 500 cycles the mass gain was lower than that of the bare substrate. Samples coated with TiAlN + 2% YN exhibited a low mass gain during initial stages of thermal cycling. However, pronounced increase in weight change was observed after about 200 cycles, indicating severe degradation of this coating. Specimens coated with TiAlN + 8% YN revealed a high mass gain after 20 cycles, probably caused by rapid oxidation of the coating, followed by a continuous scale growth.

SEM examinations of the samples coated with TiAlN which were exposed at 850°C for 100 and 1000 cycles revealed similar oxide scales. Dense nodules of  $\text{TiO}_2$  formed on top of a rather compact layer of alumina containing slight amounts of rutile (Figure 4a). The transition region between the porous titania layer and substrate consisted of a thin nitride zone and an  $\alpha_2$ - $\text{Ti}_3\text{Al}$  layer with alumina particles and Nb-rich precipitates embedded. The slow scale growth of the samples with TiAlN coatings was probably related to the thick outer alumina scale being an effective barrier to oxygen inward diffusion.

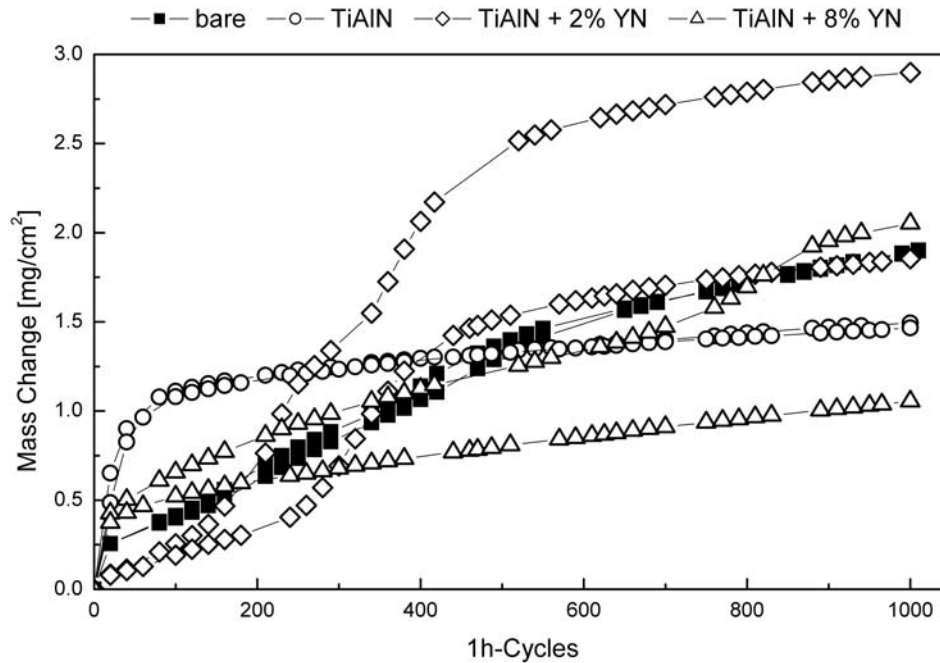


Figure 3: Mass change vs number of cycles of  $\gamma$ -TiAl specimens uncoated and coated with TiAlYN containing different amounts of YN which were thermally cycled at 850°C in air.

Figure 4b shows the cross-section of a sample coated with TiAlN + 2% YN oxidized for 100 cycles. On the coating a scale formed with an outer alumina and an inner titania rich layer. The chemical composition of the coating below the oxide scale was 19.7Ti-24.4Al-0.9Y-54.4N (at.%), as determined by EDS analysis. In surface region of the substrate a titanium nitride layer formed again. Between the TiN layer and the coating a porous zone was observed which might be related to decomposition of the lower part of the TiAlN +2% YN coating. The chemical composition of this zone was 40.1Ti-6.6Al-0.8Y-1.0Nb-51.4N. Because of the high measured Ti-concentration, TiAlN probably decomposed to  $Ti_2N$  and AlN. The released nitrogen reacted with titanium in the  $\gamma$ -TiAl phase. After 1000 cycles of oxidation, coating and titanium nitride layer were entirely oxidized, and a thick oxide scale formed on the substrate.

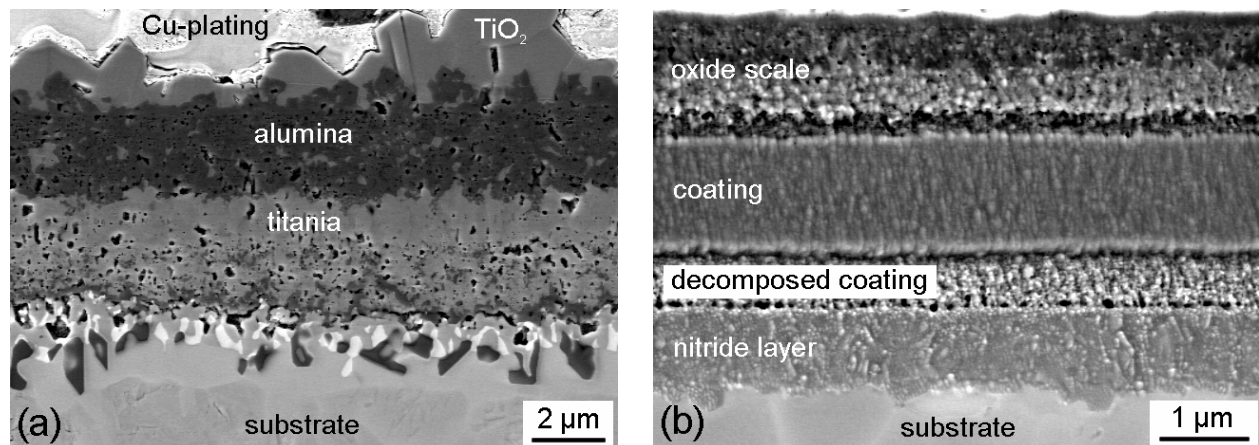


Figure 4: SEM micrographs of  $\gamma$ -TiAl samples coated with (a) CrAlN and (b) CrAlN + 2% YN which were exposed to air at 900°C for 100 cycles, showing thermally grown oxide scales

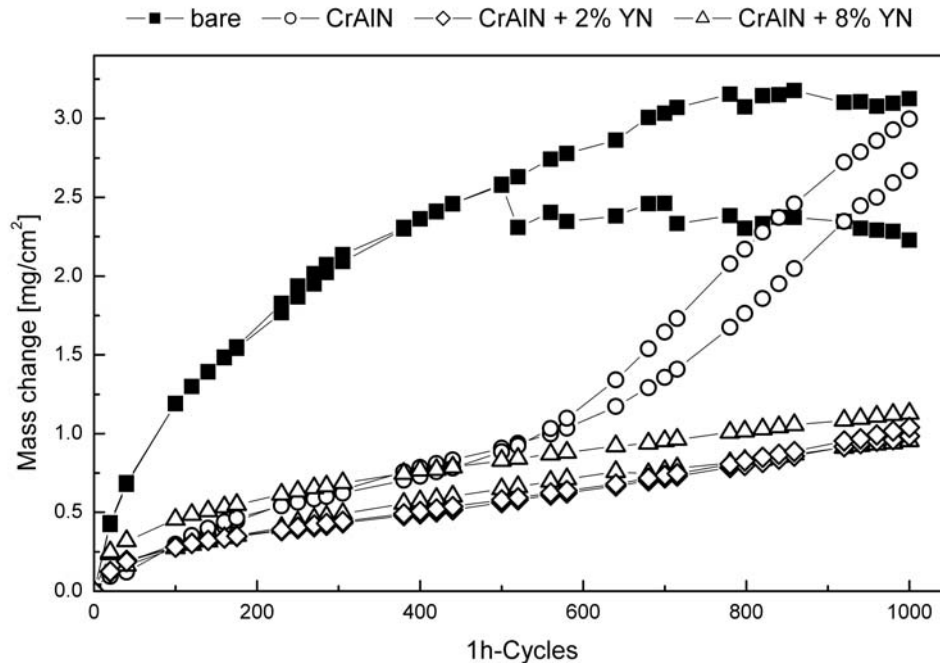


Figure 5: Mass change vs number of cycles of  $\gamma$ -TiAl specimens uncoated and coated with CrAlYN containing different amounts of YN which were thermally cycled at 900°C in air.

Figure 5 presents results of the cyclic oxidation tests at 900°C. Specimens uncoated and coated with CrAlN with various amount of YN were exposed to air up to 1000 1-h cycles. Compared to the bare TiAl material, samples coated with CrAlYN thin films exhibited a significant lower mass gain. For the Y-free CrAlN coating a pronounced increase in the mass change curve was observed after about 600 cycles. SEM micrographs of the latter specimens tested for 1000 cycles are shown in Figure 6. Different scales were observed on both face sides. On one side, the coating was still present; its chemical composition measured was 22.9Cr-27.0Al-0.8Ti-49.1N (at.%). On top of the CrAlN film a compact chromia layer formed. Again a titanium layer was observed beneath the coating consisting of TiN and Ti<sub>2</sub>AlN. On the other side, the coating and the titanium nitride layer were entirely oxidized, and a thick scale grew with an outer mixture of chromia and alumina (Figure 6b). Below a porous titania layer a mixed zone of Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> formed. Nb-rich precipitates and protrusions of alumina embedded in the  $\alpha_2$ -Ti<sub>3</sub>Al phase were found in the transition region to the substrate.

Figure 7 shows the cross-section and elemental profiles of a sample coated with CrAlN + 2% YN which was oxidized at 900°C for 1000 cycles. The coating oxidized to a dense mixture of chromia (bright) and alumina (dark) with a thin layer of alumina on top. Between coating and substrate layers of TiN and Ti<sub>2</sub>AlN formed. No chromium was detected in the titanium nitrides. The oxidized coating seemed to be an effective barrier to oxygen inward diffusion. The oxygen partial pressure at the coating/TiN interface was too low to oxidise titanium nitride. On the sample coated with CrAlN + 8% YN an outer porous alumina scale with flakes of chromia was observed (Figure 8a). At the lower part of the oxidised coating dense Cr<sub>2</sub>O<sub>3</sub>-rich oxides formed with an adjacent thin continuous layer of mainly alumina. The substrate below exhibited only slight oxidation with titanium nitride layers and alumina particles. The compact chromia and alumina rich layers probably reduced the ingress of oxygen. At some areas, however, a more proceeded oxidation of the substrate was observed (Figure 8b).

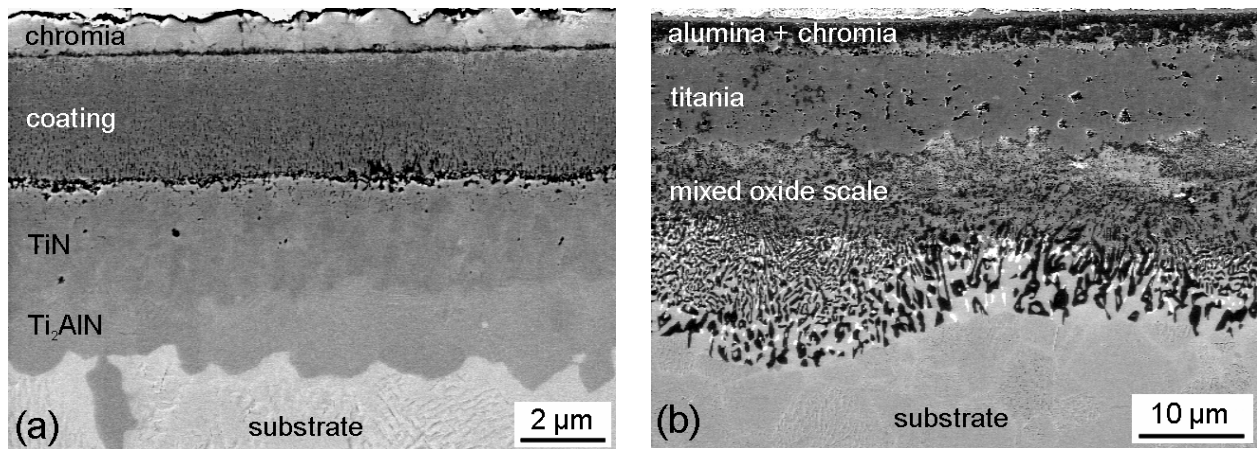


Figure 6: SEM micrographs of a  $\gamma$ -TiAl sample coated with CrAlN which was exposed to air at 900°C for 1000 cycles, showing thermally grown oxide scales on different face surfaces

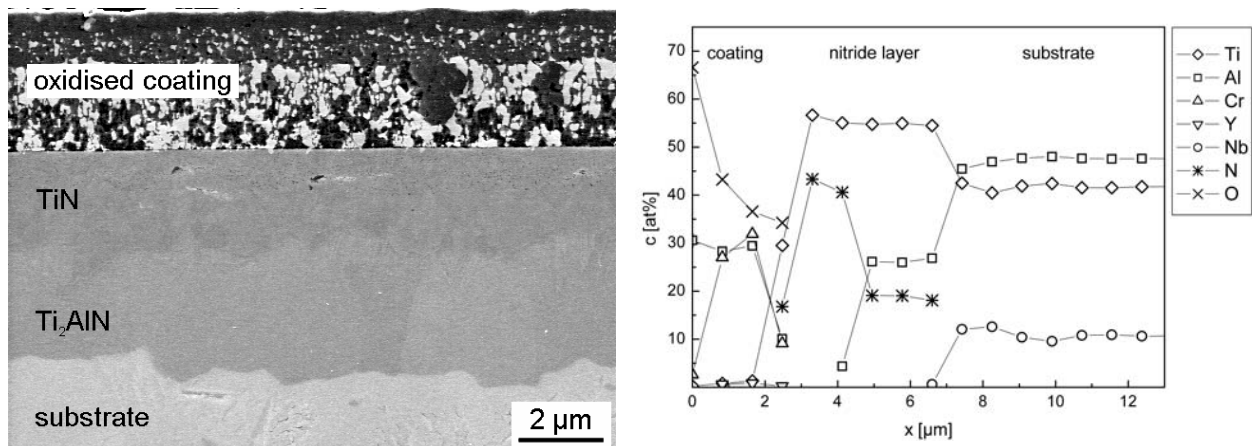


Figure 7: SEM micrograph and EDS analysis of a cross-section of a  $\gamma$ -TiAl sample coated with CrAlN + 2% YN which was exposed to air at 900°C for 1000 cycles

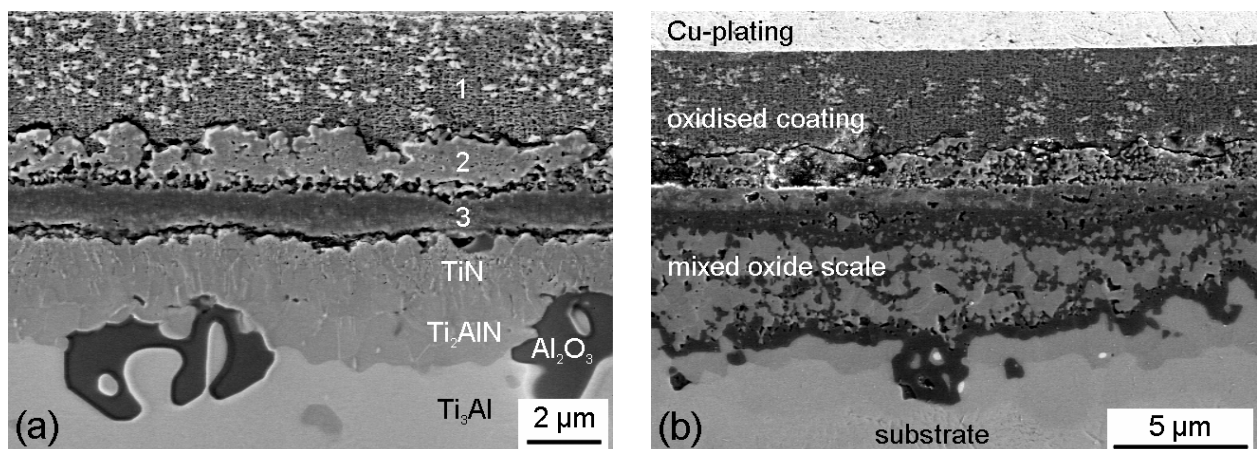


Figure 8: SEM micrographs of a  $\gamma$ -TiAl sample coated with CrAlN + 8% YN which was exposed to air at 900°C for 1000 cycles, showing thermally grown oxide scales (1- porous alumina rich layer, 2-dense chromia and alumina rich layer, 3-alumina layer)

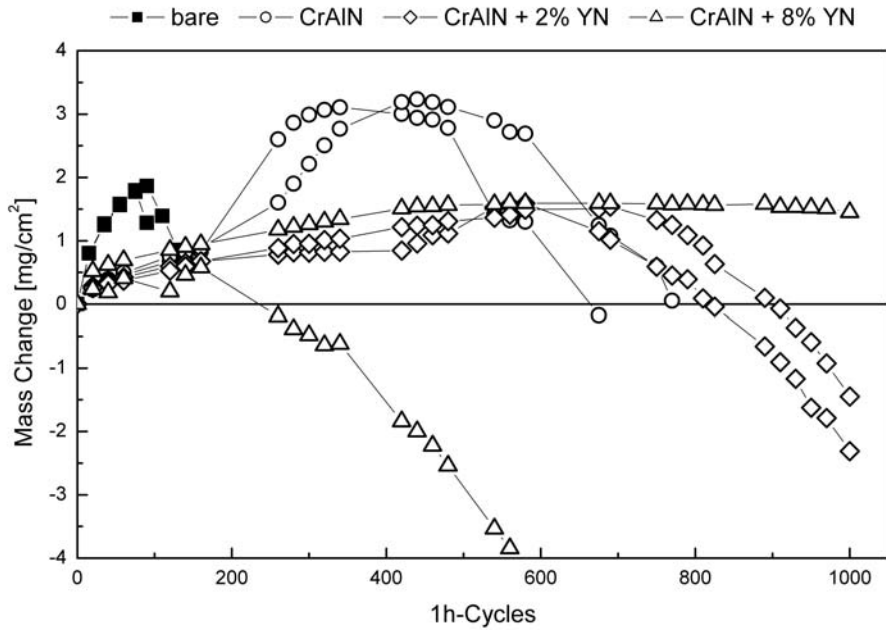


Figure 9: Mass change vs number of cycles of  $\gamma$ -TiAl specimens uncoated and coated with CrAlYN containing different amounts of YN which were thermally cycled at 950°C in air.

When thermally cycled at 950°C, bare  $\gamma$ -TiAl specimens failed after 100 cycles by scale spallation, whereas oxides thermally grown on the coated samples spalled off after longer exposure periods (Figure 9). Scanning electron microscopy revealed thick oxide scales being similar for specimens coated with CrAlN and CrAlN + 2% YN (Figure 10a). One sample coated with CrAlN + 8% YN exhibited a rather low mass gain being  $\leq 1.6 \text{ mg/cm}^2$  during 1000 cycles of exposure. Cross-sectional examinations of this sample revealed quite severe oxidation of the substrate on one face side, but on the other side a dense mixed oxide layer consisting of mainly alumina with small amounts of chromia and titania was observed beneath the oxidised coating followed by a thin continuous alumina scale (Figure 10b). Adjacent to the thin alumina layer, protrusions of alumina were found embedded in titanium depleted phases ( $\alpha_2$ -Ti<sub>3</sub>Al).

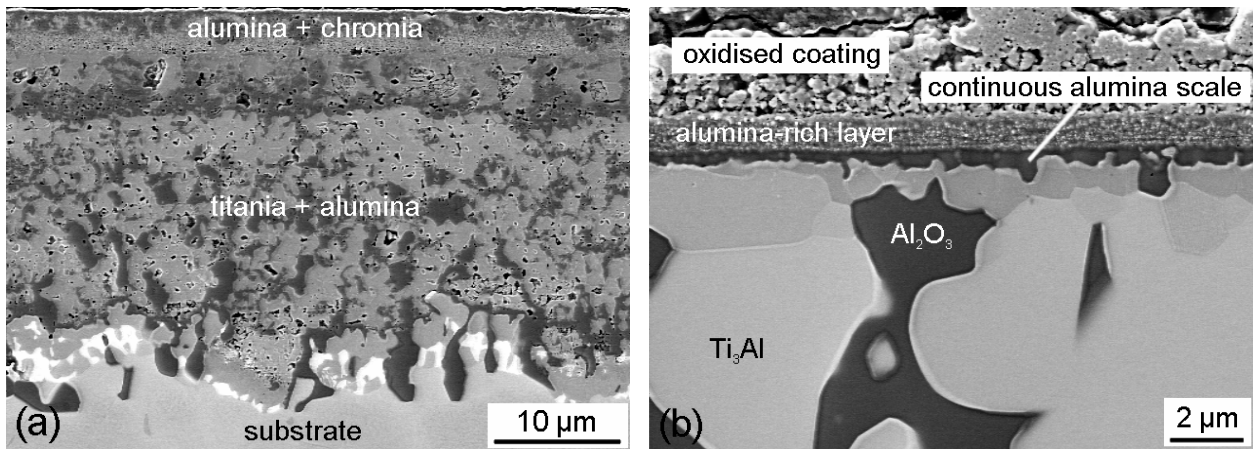


Figure 10: SEM micrographs of  $\gamma$ -TiAl samples coated with CrAlN containing (a) 2% and (b) 8% YN which were exposed to air at 950°C for 1000 cycles, showing (a) the thermally grown oxide scale and (b) the transition region between oxidized coating and substrate

## Conclusions

TiAlN coatings Y-free and with 2% and 8% YN provided reasonable oxidation protection to  $\gamma$ -TiAl alloy at 750°C. Although the yttrium containing layers exhibited high initial mass gain, which increased with increasing yttrium amount, the subsequent oxide growth rates were slower compared to that of uncoated titanium aluminide. The high initial mass change was probably associated with rapid oxidation of yttrium. As revealed by cross-sectional examinations, noticeable oxidation of the substrate did not occur beneath the coatings. The TiAlYN coatings did not withstand exposure at 850°C, but degraded at this temperature for prolonged time periods. In the surface region of the substrate, titanium nitride layers formed beneath TiAlN and TiAlN + 2% YN coatings, probably caused by decomposition of TiAlN. The rapid oxidation of TiAlN films containing 8% YN might prevent the formation of titanium nitride at the coating/substrate interface.

Cyclic oxidation tests at 900°C revealed significantly lower mass gains of samples with CrAlYN films in comparison to the bare substrate material. Whereas samples coated with CrAlN exhibited an increase in mass gain after about 550 cycles, the coatings containing 2 and 8% YN retained slow oxidation kinetics up to the maximum exposure length of 1000 1-h cycles. Compared to uncoated samples, oxidation of the substrate was considerably reduced beneath the entirely oxidised CrAlYN films, indicating that the dense oxide mixture of chromia and alumina presented an effective barrier to oxygen diffusion. Titanium nitride layers formed again in the surface region of  $\gamma$ -TiAl substrates coated with CrAlN and CrAlN + 2% YN films. When thermally cycled at 950°C, the CrAlN coatings with 2 and 8% YN exhibited moderate oxidation rates, but spallation occurred for longer exposure lengths.

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