



## Environmental protection of $\gamma$ -TiAl based alloy Ti-45Al-8Nb by CrAlYN thin films and thermal barrier coatings

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### ABSTRACT

The oxidation behaviour of CrAlN + 2 mol.% YN thin films deposited on  $\gamma$ -TiAl based alloy Ti-45Al-8Nb (at.%) was investigated at 850 and 900 °C under cyclic oxidation conditions in air. At both temperatures the coated samples exhibited significantly reduced mass gains compared to the bare substrate material. Slow oxide growth rates were observed for up to 2000 cycles of 1-h dwell time at high temperature, indicating effective oxidation protection provided by the CrAlYN coating to the  $\gamma$ -TiAl alloy. Microstructural examinations of coated specimens after high temperature exposure revealed an outer mixed scale of chromia and alumina grown on the degraded nitride film. Beneath the coating, TiN and Ti<sub>2</sub>AlN layers formed. When thermally cycled at 900 °C in air, thermal barrier coatings of yttria partially stabilized zirconia deposited on  $\gamma$ -TiAl samples coated with CrAlN + 2 mol.% YN thin films exhibited lifetimes exceeding the maximum exposure time period of 1000 1-h cycles. No spallation of the thermal barrier coating system was observed. The zirconia topcoats produced by electron-beam physical vapour deposition were well adherent to the mixture of chromium and aluminium oxides formed on the nitride coating.

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### 1. Introduction

The application of protective overlay coatings is a suitable way to increase the service temperature range of high temperature structural materials exhibiting poor oxidation behaviour. Titanium aluminides based on  $\gamma$ -TiAl are promising candidates to be used in automotive and aero engines due to their low density, high stiffness and good creep properties [1–3]. However, the oxidation resistance is insufficient above 800 °C associated with the formation of mixed titanium and aluminium oxides instead of a slow-growing protective alumina scale [4]. Intermetallic coatings, such as aluminides produced by pack cementation and Ti–Al–Cr based intermetallic layers with two-phase microstructure, were found to provide effective oxidation protection to  $\gamma$ -TiAl alloys [5–10]. Because of the high brittleness of these alumina forming intermetallic phases, however, there is an inherent risk of cracking, particularly with increasing coating thickness. Recent investigations on the oxidation behaviour of thin nitride layers deposited on titanium aluminides revealed noticeable potential of Ti- and Cr-based nitride films as

protective coatings in the temperature range between 750 and 850 °C [11–14].

Transition metal nitrides, like TiN and CrN, are extensively used as hard coatings to increase the lifetimes of cutting and forming tools [15]. Aluminium added to the binary nitrides was found to improve their oxidation behaviour. Ternary Ti<sub>1-x</sub>Al<sub>x</sub>N and Cr<sub>1-x</sub>Al<sub>x</sub>N films exhibited higher oxidation resistance, increasing with increasing aluminium content [16,17]. The oxidation behaviour of the Cr-based nitrides was superior to that of the Ti-based counterparts. Cr<sub>1-x</sub>Al<sub>x</sub>N films have emerged as important hard protective coatings for industrial applications [17–19]. The enhanced oxidation resistance was associated with the formation of mixed aluminium and chromium oxide scales reducing the inward and outward diffusion of oxygen and metallic cations, respectively [18–20]. The oxidation behaviour of nitride coatings can be further improved by addition of yttrium, attributed to the so-called reactive element effect [21–23]. Yttrium segregating to the oxide scale grain boundaries was considered to block fast diffusion paths [24,25].

Thermal barrier coatings (TBCs) deposited on high temperature materials are widely used to increase the gas turbine efficiency [26,27]. Due to the thermal insulation provided by ceramic topcoats with low thermal conductivities, internally cooled components can operate at increased temperatures. TBC systems on  $\gamma$ -TiAl alloys

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exhibited promising performance when thermally cycled in air at temperatures between 850 and 1000 °C [9,28–34]. Failure observed was related to spallation of oxide scales formed on the substrate after degradation of the protective coatings. The thermal barrier coatings were well adherent to the thermally grown oxides. Thus, lifetime of the TBC systems on  $\gamma$ -TiAl significantly depended on effective oxidation protection of the bond coats. The aim of the present work was to study the oxidation resistance of yttrium-containing CrAlN thin films deposited on  $\gamma$ -TiAl. Furthermore, the nitride coating was also used as bond coat for zirconia topcoats, and the lifetime of this TBC system was determined in cyclic oxidation tests.

## 2. Experimental

The material used was an extruded and annealed rod of the  $\gamma$ -TiAl based alloy Ti-45Al-8Nb-0.2C (in at.%), supplied by g-t alloys, Nuremberg, Germany. From the rod, disk-shaped specimens with 15 mm diameter and 1 mm thickness were machined using spark erosion. The samples had a small pin for handling during the coating processes. Their surfaces were ground and polished. Prior to coating, the specimens were etched in argon plasma. CrAlN thin films with and without 2 mol.% YN at an Al/Cr ratio of  $\sim 1.2$  were deposited using a laboratory scale unbalanced direct current magnetron sputtering system. The approximately 4  $\mu\text{m}$  thick nitride coatings with single phase NaCl-type crystal structure were produced in an Ar + N<sub>2</sub> glow discharge sustained on powder metallurgically manufactured CrAl compound target with and without 2 at.% Y [23,35]. Some of the samples had a thin intermediate TiN base-layer ( $\sim 300$  nm thickness). The disk-shaped substrates were placed parallel above the target at a distance of 50 mm and subsequently coated all-sided. More details of the deposition conditions used can be found in Refs. [23,35].

On samples coated with CrAlN + 2 mol.% YN thin films and with and without a TiN base-layer, thermal barrier coatings of 7 wt% yttria partially stabilized zirconia (YSZ) were deposited using electron-beam physical vapour deposition (EB-PVD). The substrate temperature was  $\sim 900$  °C. The thickness of the YSZ topcoat was approximately 150  $\mu\text{m}$ . Before TBC deposition, the samples with CrAlN films were exposed to laboratory air at 750 °C for 100 h to form a thin oxide scale imparting TBC adhesion. The TBC was well adherent to the coatings after deposition.

Cyclic oxidation tests were carried out in laboratory air at 850 and 900 °C using automated rigs. One cycle consisted of 1 h exposure at high temperature and 10 min at ambient temperature during which the samples cooled down to about 70 °C. Prior to oxidation testing, the sample holder pins were removed, leaving a small unprotected area of bare substrate material. The specimens were weighed at certain intervals. Post-oxidation analysis of the coating systems was performed using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). Metallographically prepared cross-sections of oxidised samples were etched in argon plasma and subsequently coated with a very thin platinum film.

## 3. Results

Fig. 1 shows the mass change versus the number of cycles of  $\gamma$ -TiAl specimens uncoated and coated with CrAlN and CrAlN + 2% YN thin films. CrAlN coatings with and without yttrium nitride exhibited significantly reduced mass gain compared to the bare substrate material. Whereas the weight change of the yttrium containing nitride layer was slightly higher during the initial stages of oxidation in comparison to the CrAlN coating, it was lower for the samples coated with CrAlN + 2% YN after approximately 700 cycles.

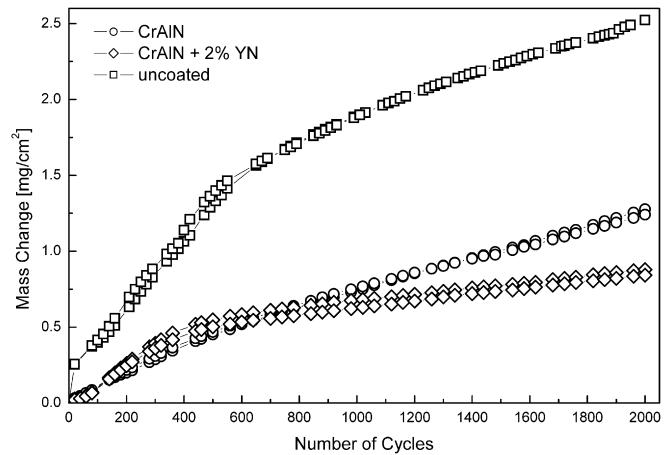


Fig. 1. Mass change vs. number of cycles of Ti-45Al-8Nb specimens uncoated and coated with CrAlN and CrAlN + 2% YN thin films which were thermally cycled at 850 °C in air. Two samples were tested for each condition.

Fig. 2 presents SEM micrographs of a sample coated with CrAlN which was exposed to air at 850 °C for 2000 cycles. The CrAlN coating was entirely decomposed forming a two-phase oxide mixture. Underneath the oxide scale a thick TiN layer was observed. At the oxide scale/titanium nitride layer interface lumps of metallic chromium precipitated. Adjacent to the TiN layer a continuous zone formed being rich in aluminium and niobium. Its chemical

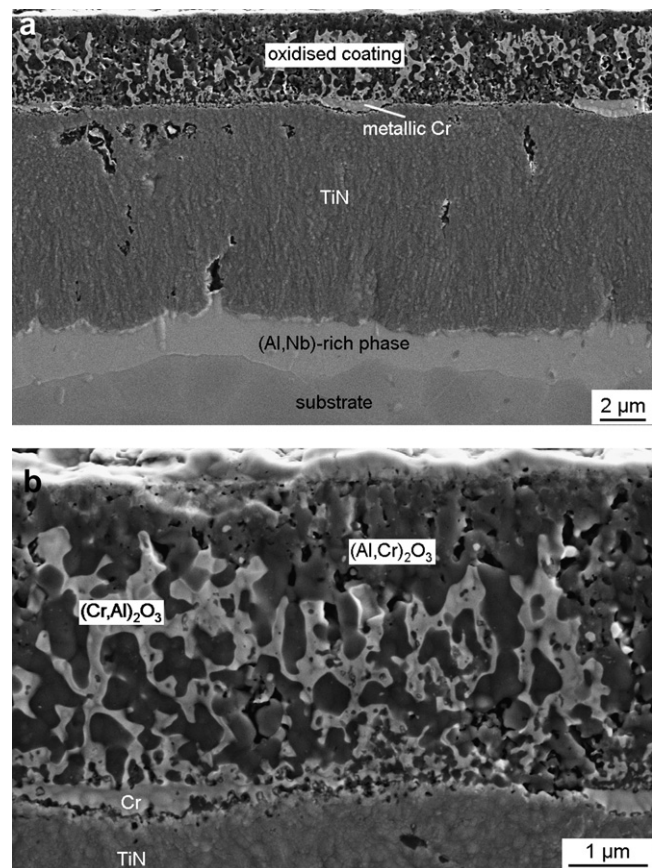


Fig. 2. Scanning electron micrographs of a  $\gamma$ -TiAl sample coated with CrAlN which was exposed to air at 850 °C for 2000 cycles, showing (a) the reaction zone between coating and substrate and (b) the oxidised coating.

composition measured by EDS analysis was 69.5Al–26.5Nb–4.0Ti (at.%), suggesting that the phase was probably Al<sub>3</sub>Nb. This phase was also found in cross-sections of  $\gamma$ -TiAl samples with CrAlYN/CrN nanoscale multilayer coatings exposed to high temperatures [14,36]. The formation of titanium nitrides depleted the substrate in titanium resulting in precipitation of phases rich in aluminium and niobium. Niobium was reported to be dissolved up to 27.5 at.%, in  $\gamma$ -TiAl, substituting Ti in the Ti-sublattice [37,38]. The oxide scale grown on the decomposed CrAlN coating consisted of two phases with the chemical compositions of 29.5Al–4.3Cr–0.2Ti–66.0O and 30.1Cr–20.9Al–0.9Ti–48.1O (at.%), as determined by EDS analysis (Fig. 2b). The former phase (dark) was predominantly alumina containing low amount of Cr<sub>2</sub>O<sub>3</sub>, whereas high concentrations of both chromium and aluminium were detected in the latter phase (bright). Due to the small size of the phases, their precise chemical compositions could not be determined by EDS analysis using SEM. The oxide scale exhibited a noticeable porosity. A thin chromia-rich layer formed on top.

Cross-sectional SEM examination of samples coated with CrAlN + 2% YN also revealed decomposition of the protective film after 2000 cycles of exposure at 850 °C, but to a considerably lesser extent as compared to the Y-free CrAlN film (Fig. 3). The upper part of the yttrium containing coating was entirely oxidised to a dense mixed oxide scale of alumina and chromia, whereas approximately 20 at.% nitrogen were still detected in the lower part (Table 1). An yttrium concentration of 1.1–1.2 at.% was measured throughout the coating. The partially oxidised film retained a columnar structure.

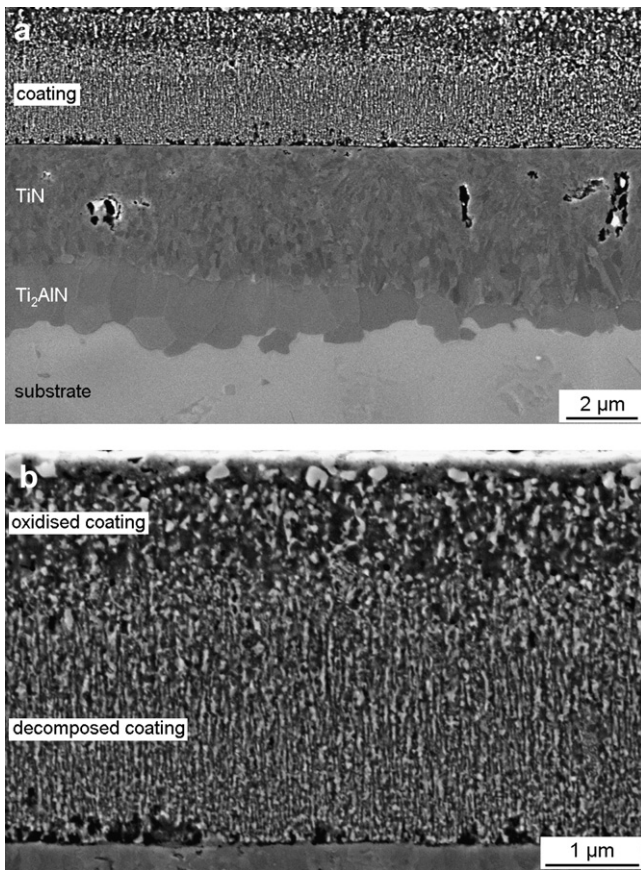


Fig. 3. Scanning electron micrographs of a  $\gamma$ -TiAl sample coated with CrAlN + 2% YN which was exposed to air at 850 °C for 2000 cycles, showing (a) the reaction zone between nitride coating and substrate and (b) oxidised and decomposed parts of the coating.

Table 1

Chemical compositions of different zones of the CrAlN + 2 mol.% YN coating and phases found in the subsurface region of the substrate after exposure to air at 850 °C for 2000 cycles (Fig. 3). Concentrations are given in at.%.

	Ti	Al	Cr	Y	Nb	N	O
Oxidised coating	0.2	27.0	15.9	1.1			55.9
Decomposed coating	0.5	29.2	21.2	1.2		20.3	27.6
TiN	44.6	1.0			1.0	53.4	
Ti <sub>2</sub> AlN	51.3	25.1			0.5	23.1	

Below the decomposed coating, a thick titanium nitride layer formed consisting of TiN and Ti<sub>2</sub>AlN adjacent to the coating and the substrate, respectively (Fig. 3a). In the region below the titanium nitride layer, the substrate was enriched in niobium and aluminium (Fig. 4). In contrast to the sample coated with CrAlN, a continuous Al<sub>3</sub>Nb zone did not form in the samples with yttrium containing thin films. For some regions, precipitation of a (Nb,Al)-rich phase was observed, being probably the  $\sigma$ -(Nb,Ti)<sub>2</sub>Al phase, as found in the subscale region of oxidised  $\gamma$ -TiAl alloys with high niobium content [29,32,34]. Obviously, the alumina/chromia scale was an effective barrier to oxygen diffusion, preventing oxidation of the substrate material. The oxygen partial pressure at the coating/nitride layer interface was too low to oxidise TiN to TiO<sub>2</sub>, usually occurring during oxidation of bare  $\gamma$ -TiAl alloys [29,32,39].

Fig. 5 shows the oxidation kinetics of  $\gamma$ -TiAl specimens bare and coated with CrAlN + 2% YN which were thermally cycled at 900 °C.

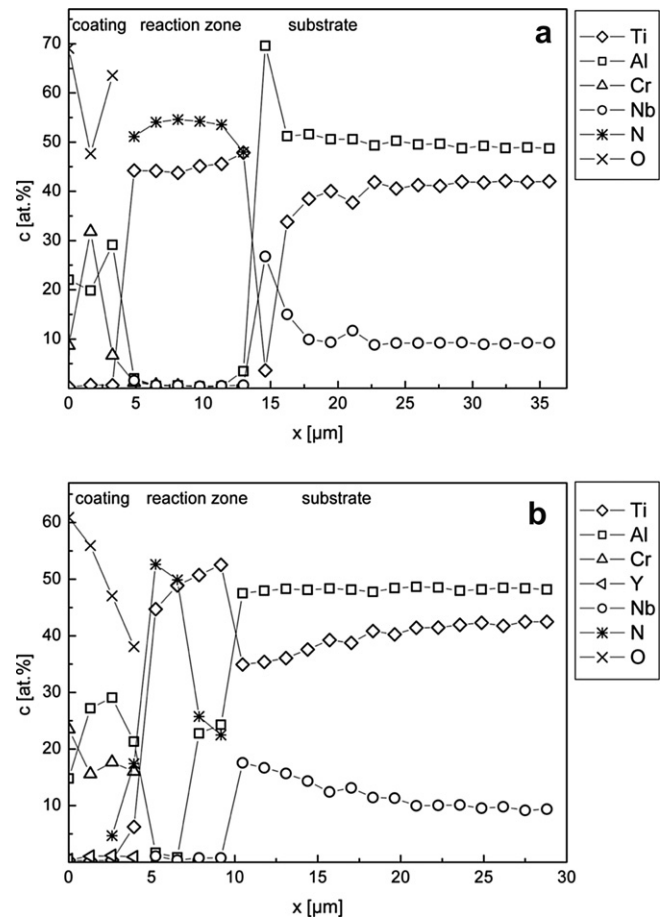


Fig. 4. EDS analyses of  $\gamma$ -TiAl specimens coated with (a) CrAlN and (b) CrAlN + 2% YN which were exposed to air at 850 °C for 2000 cycles (spectrum profiling across coating, reaction zone and substrate).

Slight oxide spallation occurred on one of the bare samples after 500 cycles. Compared to the bare substrate material the specimens coated with CrAlN + 2% YN thin films exhibited considerably reduced mass gains with slow growth rate after about 200 cycles. SEM cross-sectional analyses revealed a similar degradation process to that found at 850 °C (Fig. 6). The upper part of the coating was entirely oxidised forming a mixture of alumina and chromia, whereas ~12 at.% nitrogen was detected in the lower part (Fig. 6b). The degraded nitride film contained 1.0–1.1 at.% yttrium. Below the coating, again a TiN/Ti<sub>2</sub>AlN layer formed (Fig. 6c).

X-ray diffraction (XRD) pattern taken from the surface of an oxidised  $\gamma$ -TiAl specimen is given in Fig. 7. The sample coated with CrAlN + 2% YN was exposed to air at 900 °C for 1000 cycles. The XRD pattern indicated Al<sub>2</sub>O<sub>3</sub> and, less markedly Cr<sub>2</sub>O<sub>3</sub>. High diffraction peaks were recorded for bcc-chromium, resulting from decomposition of the CrAlYN thin film, whereas hcp-Cr<sub>2</sub>N and hcp-AlN were not definitely detected. XRD analysis also confirmed the presence of TiN, but no accurate evidence for the Ti<sub>2</sub>AlN phase was found. Due to the higher depth of the Ti<sub>2</sub>AlN layer in the scale intensities of the diffraction reflections were probably very weak. As reported in the literature, however, both TiN and Ti<sub>2</sub>AlN phases were identified by transmission electron microscopy formed at the oxide scale/substrate interface in a  $\gamma$ -TiAl sample which was oxidised at 900 °C in air [39,40].

Fig. 8 presents the results of cyclic oxidation tests of specimens with TBC systems which were exposed to air at 900 °C for up to 1000 cycles. The YSZ topcoats were deposited on  $\gamma$ -TiAl specimens coated with CrAlN + 2% YN thin films. Two of the coated specimens had a TiN base-layer. The TBC system on the bare  $\gamma$ -TiAl alloy failed after 700 cycles by severe spallation. The thermal barrier coatings deposited on samples with nitride thin films did not spall off during the maximum exposure length of 1000 cycles. Drops in the mass change curves observed for specimens with CrAlYN coatings after 700 cycles were related to spalled oxides at areas with missing TBC due to removal of the sample holder pin. The mass loss during the initial stages of exposure was associated with release of water vapour absorbed by the TBC from natural air humidity during the storage prior to testing. The open symbols in Fig. 8 present plots of mass gain data corrected with regard to oxide spallation on the unprotected spots and the evaporation of water during the first heating cycle.

Fig. 9 shows the cross-section of a sample coated with CrAlN + 2% YN and TBC which was exposed to air at 900 °C for 1000 cycles. The scale grown on the sample was similar to that observed

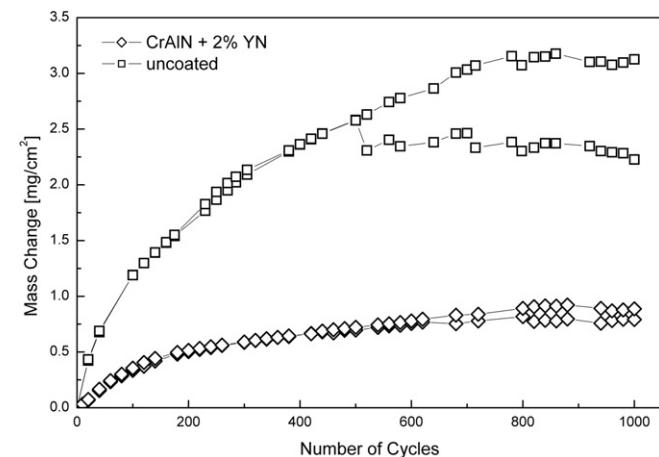


Fig. 5. Mass change vs. number of cycles of Ti-45Al-8Nb specimens uncoated and coated with CrAlN + 2% YN thin films which were thermally cycled at 900 °C in air. Two samples were tested for each condition.

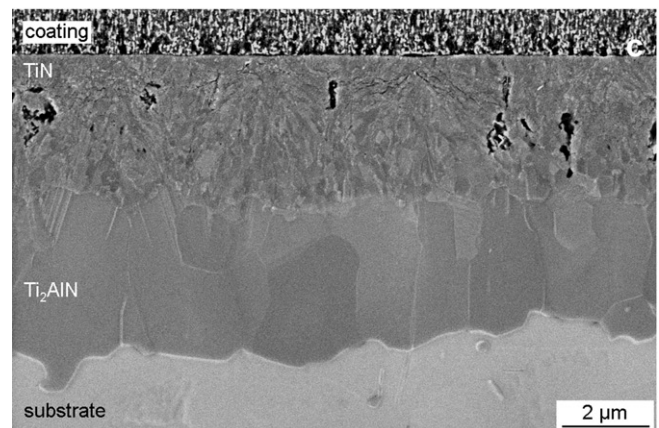
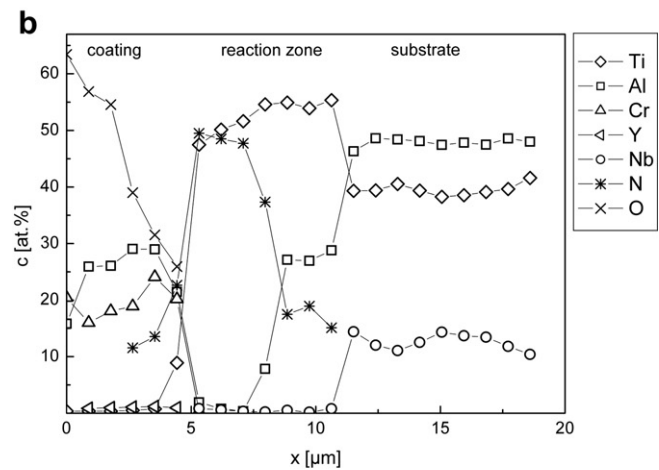
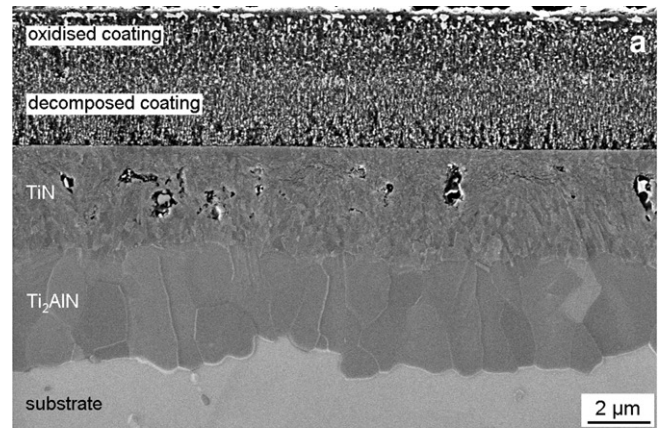


Fig. 6. Scanning electron micrographs (a,c) and EDS analysis (b) of a  $\gamma$ -TiAl sample coated with CrAlN + 2% YN which was exposed to air at 900 °C for 1000 cycles, showing (a) the reaction zone between nitride coating and substrate, (b) spectrum profiling across coating, reaction zone and substrate, and (c) titanium nitride layers below the coating.

for the samples without TBC. At some areas, the CrAlYN thin film was entirely oxidised. No nitrogen was detected there. Below the degraded coating, again a thick titanium nitride layer consisting of TiN and Ti<sub>2</sub>AlN formed. On top of the oxidised coating, a very thin oxide film was observed with bright particles embedded (Fig. 9b), which was also found on samples without TBC (Fig. 6a). Due to the small thickness (200–300 nm), the chemical composition of this oxide scale could not be determined by EDS analysis in the scanning electron microscope. The bright precipitates might be pure Cr<sub>2</sub>O<sub>3</sub>

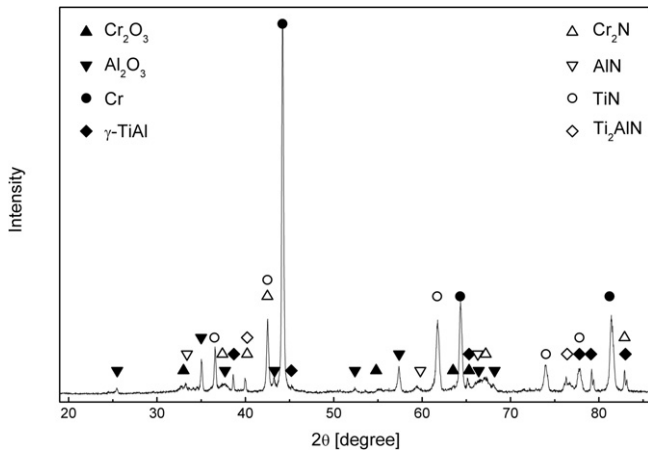


Fig. 7. X-ray diffraction pattern of a  $\gamma$ -TiAl sample coated with CrAlN + 2% YN which was exposed to air at 900 °C for 1000 cycles.

surrounded by a chromia-rich  $(\text{Cr,Al})_2\text{O}_3$  solid solution, as supported by small probe microanalysis using scanning transmission electron microscopy. The YSZ topcoat was well adherent to the thin oxide film and the mixture of alumina and chromia below. A similar scale formed on samples with a TiN base-layer between coating and substrate (Fig. 10). The intermediate layer of dense TiN, widely used as diffusion barrier in semiconductor technology [41], was deposited to inhibit outward diffusion of Ti cations. The separation of the CrAlYN coating from the  $\gamma$ -TiAl alloy by an intermediate TiN thin film was intended to prevent the reaction between titanium and nitrogen and retard the total N-loss from the coating into the substrate. After 1000 cycles of exposure to air at 900 °C the CrAlN + 2% YN film deposited on the TiN base-layer was not entirely oxidised, but nitrogen was still detected in the lower part of the coating. However, the intermediate base-layer did not impede the reaction between the CrAlYN film and the substrate, resulting in the formation of titanium nitride. The thicknesses of the TiN and  $\text{Ti}_2\text{AlN}$  layers were similar to those observed in the sub-coating region of samples without base-layer.

The SEM cross-sectional examination of samples with TBC revealed severe oxidation of the substrate in a few areas (Fig. 11a).

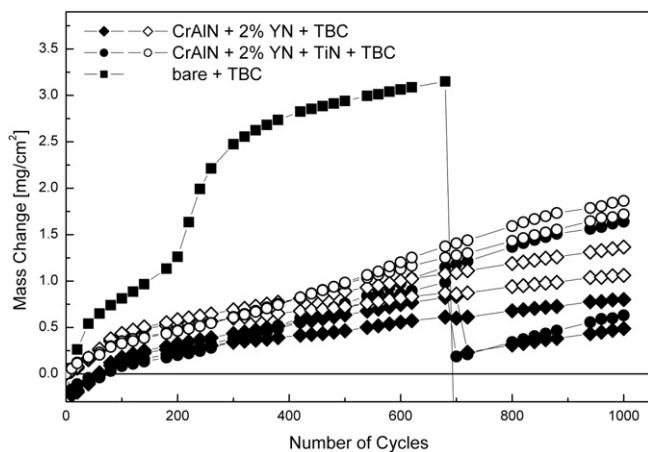


Fig. 8. Mass change vs. number of cycles of Ti-45Al-8Nb specimens with TBC systems which were thermally cycled at 900 °C in air. YSZ topcoats were deposited on samples bare and coated with CrAlN + 2% YN thin films with and without a TiN base-layer. The open symbols represent mass change data corrected regarding evaporation of water during first sample heating and spalled oxides from unprotected areas.

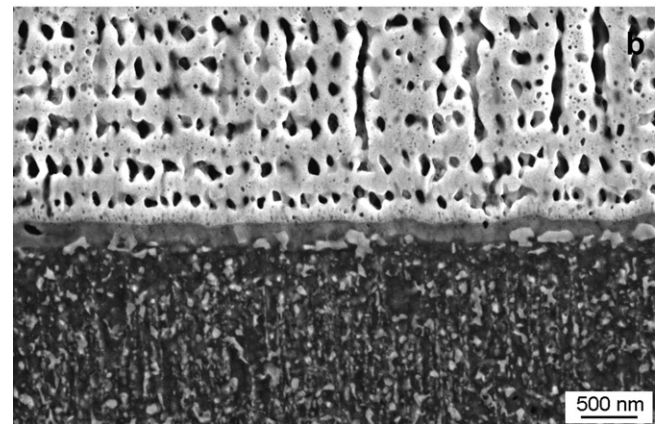


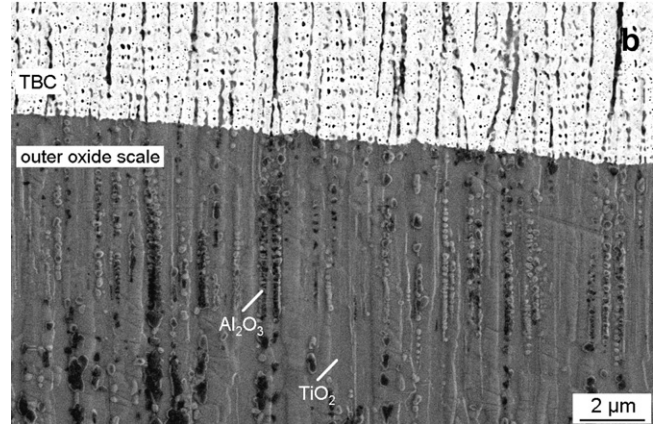
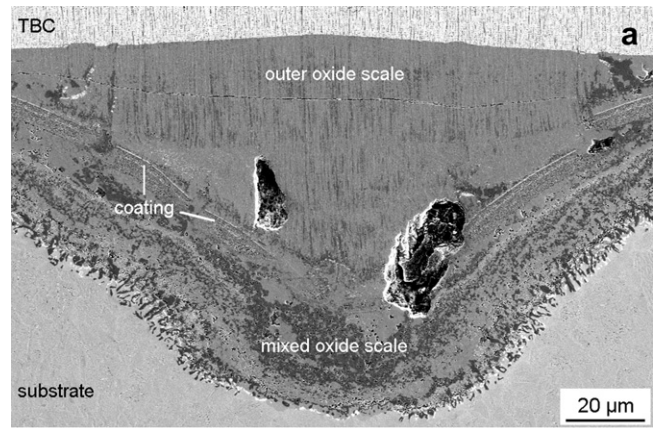
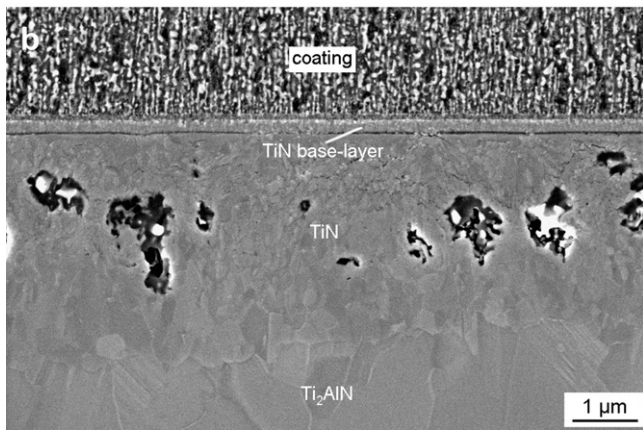
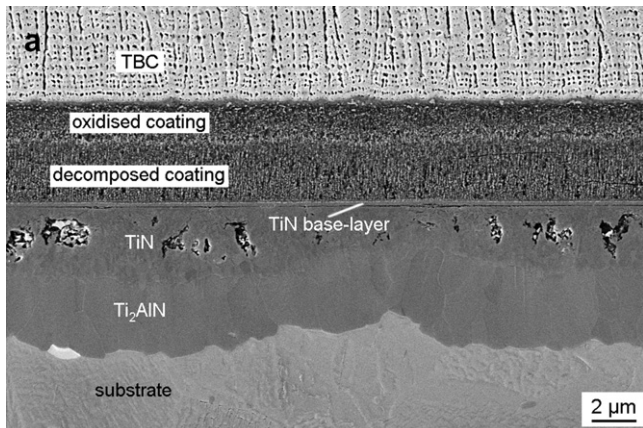
Fig. 9. Scanning electron micrographs of a  $\gamma$ -TiAl sample coated with CrAlN + 2% YN and TBC which was exposed to air at 900 °C for 1000 cycles, showing (a) the reaction zone between nitride coating and substrate and (b) the TBC/coating interface.

The titanium nitride layers formed below the decomposed coating were completely oxidised. The severe degradation might be associated with cracks or other defects in the nitride coating. Due to an increased oxygen partial pressure titanium nitride was oxidised to  $\text{TiO}_2$ , and oxidation of the  $\gamma$ -TiAl substrate proceeded. Below the TBC, large oxide nodules formed exhibiting a columnar structure. These protrusions consisted of fine alumina particles in a string of beads-like array embedded in titania [42]. The TBC exhibited excellent adhesion to this outer oxide scale (Fig. 11b).

#### 4. Discussion

Thin films of CrAlN + 2 mol.% YN provided effective oxidation protection to  $\gamma$ -TiAl alloys exposed to air at 850 and 900 °C due to the formation of an adherent dense mixed  $(\text{Al,Cr})_2\text{O}_3$  oxide scale. Degradation of the CrAlYN layers deposited on  $\gamma$ -TiAl was associated with oxidation and decomposition during prolonged thermal exposure. The decomposition was promoted by a reaction between nitrogen withdrawn from the nitride film and titanium of the  $\gamma$ -TiAl based substrate at the coating/substrate interface.

As reported in the literature, high temperature exposure of CrAlN thin films in air caused formation of mixed  $\text{Cr}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  scales [18,20,43]. Depending on the aluminium content of the coating, a chromium or aluminium-rich outer oxide layer formed. The oxidation mechanism was mainly controlled by inward diffusion of oxygen and outward diffusion of chromium and aluminium [19,20,43]. Rapid outward diffusion of chromium can result in the formation of  $\text{Cr}_2\text{O}_3$  grains dispersed in the outer oxide layer [43].



**Fig. 10.** Scanning electron micrographs of a  $\gamma$ -TiAl sample coated with CrAlN + 2% YN + TiN base-layer and TBC which was exposed to air at 900 °C for 1000 cycles, showing (a) the reaction zone between nitride coating and substrate and (b) the transition region between coating and titanium nitride layer.

**Fig. 11.** Scanning electron micrographs of a  $\gamma$ -TiAl sample coated with CrAlN + 2% YN + TiN base-layer and TBC which was exposed to air at 900 °C for 1000 cycles, showing (a) protrusion of an outer oxide scale and (b) good adhesion of the TBC to the outer oxide scale with columnar structure.

The mixed chromia/alumina scale was found to be an effective diffusion barrier, retarding or preventing further oxidation of the coating [18,20]. This was confirmed by the present study. Although the CrAlN coating was entirely degraded, oxidation of titanium nitride formed below the coating did not occur. During high temperature exposure of bare  $\gamma$ -TiAl alloys in air, the thin TiN zone grown in the transition region between oxide scale and substrate oxidised to  $\text{TiO}_2$  due to an increasing oxygen partial pressure through the porous titania layer [29,39].

When annealed in an inert atmosphere, CrAlN films were found to be stable up to 900 °C [17,44]. With increasing temperature, grain boundary precipitation of hexagonal AlN occurred, resulting in chromium enrichment of the matrix grains [44,45]. Chromium nitrides decomposed at elevated temperatures. Freestanding CrN thin films annealed in helium transformed to  $\text{Cr}_2\text{N}$  with concomitant release of nitrogen in the temperature range between 1000 and 1250 °C [46]. Finally,  $\text{Cr}_2\text{N}$  dissociated into chromium and  $\text{N}_2$  at further rise of temperature. CrAlN films deposited on  $\gamma$ -TiAl exhibited a reduced thermal stability. The nitride layers decomposed at the coating/substrate interface due to a strong reaction between nitrogen and titanium to form titanium nitride. After 2000 cycles of exposure at 850 °C, metallic chromium was found at the coating/TiN interface, indicating completion of the CrAlN decomposition process (Fig. 2).

The CrAlN coating exposed to air at 850 °C was entirely oxidised after 2000 1-h cycles, as revealed by SEM examinations. The oxide scale consisted of a mixture of two  $(\text{Al,Cr})_2\text{O}_3$  phases with different compositions and a thin chromia-rich top layer. The  $\text{Cr}_2\text{O}_3$ - $\text{Al}_2\text{O}_3$

system exhibits a complete mutual solubility at temperatures above 1300 °C. Below this temperature, an asymmetric miscibility gap exists on the alumina-rich side of the phase diagram [47,48]. At 1050 °C, the solubility of alumina in chromia was determined to exceed 30 mol.%, whereas that of chromia in alumina was less than 10 mol.%. The composition difference between the two phases increased when annealing was carried out at lower temperatures in the miscibility gap. The two-phase microstructure of the oxidised nitride coating consisting of chromia-lean alumina and alumina-rich chromia might result from decomposition of the CrAlN film into regions enriched with Al and Cr, e.g. AlN-rich grain boundaries and Cr-rich grain interiors, which subsequently oxidised to predominantly alumina and a mixture of chromia and alumina. The low concentration of oxygen detected in the latter phase ( $\sim 48$  at.%) might indicate that this oxide mixture also contained metallic chromium, as corroborated by metallic Cr precipitation found at the coating/TiN interface.

The incorporation of yttrium into the coating has a beneficial effect on both the oxidation and the decomposition resistance of the nitride thin film. Compared to the yttrium free coating, CrAlN + 2% YN thin films were not entirely oxidised during exposure at 850 and 900 °C for 2000 and 1000 h, respectively, but were composed of an outer mixed oxide scale and an inner oxy-nitride layer with a columnar structure. The improvement of the oxidation behaviour might be associated with the so-called reactive element effect [24,25]. Segregation of the large yttrium ions to scale grain boundaries and to the scale/coating interface reduced the oxide growth rate and improved scale adhesion. After the formation of

a dense  $(Al,Cr)_2O_3$  scale on the surface of the coating, further oxidation proceeded by lattice diffusion through the scale due to the blocked fast diffusion paths.

Based on the data presented the oxidation rates of the CrAlN + 2% YN film obeyed a parabolic law at both exposure temperatures for prolonged exposure time periods, as shown in Fig. 12. Plots of the square of mass gain data versus number of cycles exhibited linear dependence after approximately 500 and 200 cycles at 850 °C and 900 °C, respectively. At the latter temperature, oxidation at the unprotected spots and circumferential side became significant, leading to deviation from the parabolic law. The following parabolic constants ( $k_p$ ) were obtained from the linear fits of the square of mass change versus number of cycles (corresponding to the exposure time in hours at high temperature):  $8.4 \times 10^{-14}$  and  $2.5 \times 10^{-13} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$  for exposure at 850 and 900 °C, respectively. For samples coated with Y-free CrAlN films, no parabolic oxidation kinetics were observed.

After the initial stages of oxidation, the further mass gain of the samples coated with CrAlN + 2% YN was controlled by diffusion, primarily by oxygen diffusion through the outer oxide scale, and associated with proceeding oxidation of the remaining oxy-nitride layer. The dense  $(Al,Cr)_2O_3$  oxide mixture grown on the coating probably acted as diffusion barrier to nitrogen released by the oxidation reactions. Thus, enclosed within the coating and consumed

for the formation of titanium nitrides, the released nitrogen did not contribute the mass change measured. In contrast,  $N_2$  elapse to the environment, as concluded for CrAlN thin films freestanding and deposited on Ni-based superalloys during annealing in helium atmosphere and oxidation in air, respectively [43,49], should result in deviation from parabolic oxidation kinetics.

Furthermore, yttrium seems to retard the decomposition of CrAlYN coatings, as indicated by the partially retained columnar structure of the YN containing film compared to the Y-free CrAlN layer (Figs. 2 and 3). Studies on the thermal stability of magnetron sputtered CrAlYN coatings revealed that diffusion processes were effectively retarded by yttrium incorporation, thus shifting the onset of decomposition to higher temperatures [49]. On the sample coated with Y-free CrAlN, a thick TiN layer was found between coating and substrate after 2000 cycles of exposure at 850 °C (Fig. 2a), whereas the titanium nitride layer formed below the CrAlN + 2% YN thin film consisted of TiN and  $Ti_2AlN$  (Fig. 3a). The growth of a noticeable  $Ti_2AlN$  zone with reduced nitrogen content compared to TiN might be associated with a lower amount of nitrogen released from the yttrium-containing coating by oxidation and decomposition.

The reaction between titanium and nitrogen to form TiN was initiated at the initial stages of high temperature exposure, as found by SEM examinations of a sample coated with CrAlN + 2% YN and TBC, which was thermally cycled at 900 °C in air for 20 cycles (Fig. 13). Adjacent to the TiN layer, the CrAlYN film exhibited a pronounced columnar structure similar to that observed for the decomposed coating (as shown in Fig. 3), whereas the structure was more homogeneous in the outer region. A thin oxide scale formed on the coating. The chemical composition of the nitride film in the centre was 24.6Cr-30.6Al-0.9Y-0.4Ti-43.4N (at.%), whereas that measured at the bottom was 28.3Cr-29.3Al-1.0Y-0.6Ti-40.7N. In contrast, the composition of the as deposited CrAlYN thin film was approximately 22.5Cr-27.5Al-0.8Y-0.3Ti-48.9N, as measured for coatings after TBC deposition (during TBC deposition, the coated samples were exposed to a low pressure oxygen atmosphere at  $\sim 900$  °C for 30 min). Thus, during high temperature exposure to air, the coating was depleted in nitrogen, indicating its decomposition via precipitation of AlN and, subsequently, formation of  $Cr_2N$  and Cr with concomitant release of nitrogen diffusing inwards to form titanium nitride. Decomposition of nitride coatings deposited on titanium aluminides and formation of titanium nitride layers were observed in several studies [11–14,36].

CrAlN + 2 mol.% YN thin films proved to be a suitable bond coat for thermal barrier coatings on gamma titanium aluminides. The

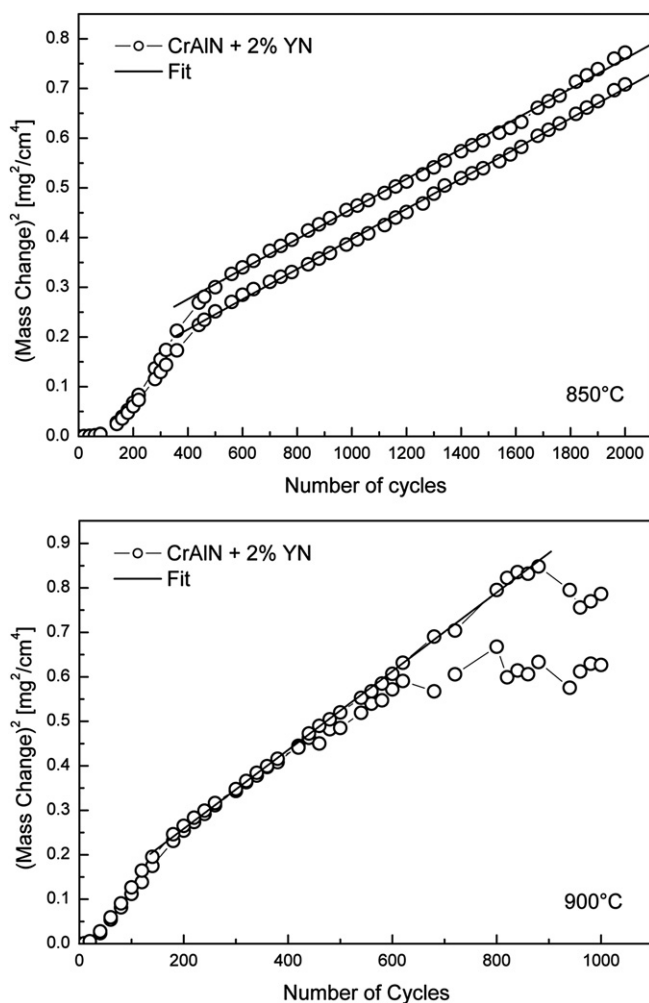


Fig. 12. Linear fitting of square of mass change vs. number of cycles of Ti-45Al-8Nb specimens coated with CrAlN + 2% YN thin films which were thermally cycled at (a) 850 °C and (b) 900 °C in air. Two samples were tested for each condition.

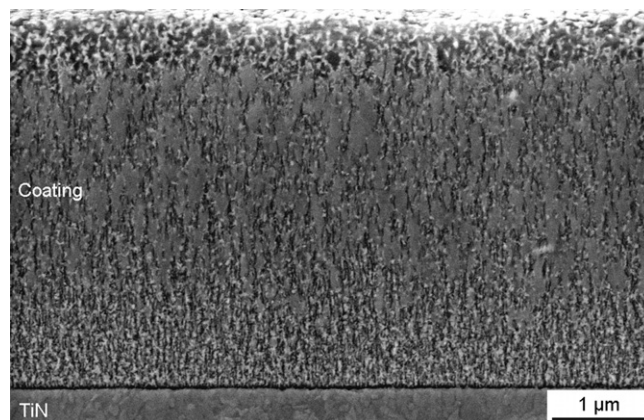


Fig. 13. Scanning electron micrograph of a  $\gamma$ -TiAl sample coated with CrAlN + 2% YN and TBC which was exposed to air at 900 °C for 20 cycles.

EB-PVD zirconia topcoats exhibited excellent adherence to the mixed alumina/chromia scale grown on the coating during thermal exposure. Spallation of the TBC system was not observed up to 1000 1-h cycles at 900 °C. Recent investigations on the performance of TBCs on  $\gamma$ -TiAl alloys revealed good adherence of the EB-PVD zirconia topcoats to the alumina scales formed on Ti–Al–Cr and aluminide coatings as well as to mixed alumina and titania scales grown on bare substrate materials or degraded oxidation protective layers [9,29–34]. Failure observed with TBC systems on  $\gamma$ -TiAl alloys was associated with spallation of the thermally grown oxide scale, predominantly in the porous titania layer. For some regions, beneath the YSZ topcoat, protrusions of an outer oxide scale exhibiting a columnar structure formed around cracks in the oxidation resistant bond coats (Fig. 11). These outer oxide scales consisting mainly of titania and alumina grew by outward diffusion of Ti and Al cations [31,32].

However, thermal barrier coatings exhibited excellent adherence to this outer oxide scale. The adhesion might be strengthened by mechanical bonding due to growth of titania into the inter-columnar gaps of the TBC above the protrusions. Thus, the TBC offers certain tolerance against localised degradation of the protective coating, resulting in enhanced oxidation, but failure of the TBC system may occur by spallation of the thermally grown oxides when oxidation of the substrate material proceeds. Long lifetimes of the TBC system observed in the present study were associated with good adherence of the YSZ topcoat to the mixture of chromia and alumina and an effective diffusion barrier presented by this mixed scale, thus retarding oxidation of the substrate material.

## 5. Conclusions

1. CrAlN + 2 mol.% YN thin films exhibited a slow oxidation rate at 850 °C in air, providing effective oxidation protection to  $\gamma$ -TiAl for exposure time periods exceeding 2000 cycles of 1-h dwell time at high temperature.
2. Compared to the bare  $\gamma$ -TiAl alloy, samples coated with CrAlN + 2 mol.% YN revealed significantly lower mass gain during 1000 1-h cycles of exposure at 900 °C. The coating oxidised to a mixed alumina and chromia scale being an effective barrier to oxygen inward diffusion.
3. Beneath the coating titanium nitride layers formed due to a reaction of nitrogen released from the degrading coating with titanium of the  $\gamma$ -TiAl alloy.
4. An intermediate TiN base-layer did not prevent the formation of TiN and Ti<sub>2</sub>AlN layers in the transition region between coating and substrate.
5. Thermal barrier coatings deposited on  $\gamma$ -TiAl specimens with nitride bond coat exhibited lifetimes exceeding 1000 1-h cycles at 900 °C. The EB-PVD YSZ topcoat was well adherent to the mixed oxide scale of chromia and alumina formed on the degraded CrAlN + 2 mol.% YN thin films.

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