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Intermetallic Ti-Al-Cr based layers and zirconia topcoats deposited on gamma titanium aluminides for environmental protection

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Abstract. Intermetallic Ti-Al-Cr layers with small additions of Si, Zr, W, and Y were deposited on γ-TiAl specimens using magnetron sputtering. The oxidation behaviour of the coated γ-TiAl alloy was studied in the temperature range between 950 and 1000°C under cyclic oxidation conditions in air. Compared to the bare substrate material, the coatings exhibited higher oxidation resistance. During prolonged exposure the intermetallic layers degraded losing their capability to form a protective alumina scale. On coated γ-TiAl samples zirconia topcoats were deposited by electron beam physical vapour deposition. These thermal barrier coating systems exhibited lifetimes exceeding the maximum exposure length of 1000 1 h cycles at 950°C, but failed at 1000°C. Failure was caused by degradation of the bond coats resulting in spallation of the thermally grown oxides.

Introduction

Intermetallic alloys based on γ-TiAl are considered as potential light-weight materials for high temperature applications in automobiles and aero engines [1,2]. However, their oxidation resistance is poor at temperatures above 800°C [3]. The use of protective coatings is a suitable method to improve the oxidation resistance of γ-TiAl components. Intermetallic Ti-Al-Cr coatings were found to form a continuous alumina scale associated with the presence of the Laves phase [4,5]. Their oxidation resistance could be further enhanced by adding small amounts of further alloying elements such as yttrium, hafnium and silicon [6,7].

Thermal barrier coatings (TBCs) are widely used in turbine engines to increase the gas inlet temperature. In combination with internal cooling, the components can operate at substantially higher environment temperatures. Zirconia topcoats were successfully deposited on γ-TiAl alloys and promising lifetimes of the TBC systems were obtained [5,8-10]. Failure observed was related to deterioration in the oxidation resistance of the protective coatings. The aim of the present work was to study the oxidation resistance of γ-TiAl coated with Ti-Al-Cr based intermetallic layers and to determine lifetimes of TBC systems using these intermetallic layers as bond coat.

Experimental

The materials used were annealed extruded rods of gamma titanium aluminide provided by g·t alloys, Nürnberg, Germany. The nominal chemical composition was Ti-45Al-8Nb-0.2C (in at.%). From these extrusions disc-shaped specimens with 15 mm diameter and 1 mm thickness were machined using spark erosion. The samples were coated with 20 µm thick intermetallic Ti-Al-Cr based layers using unbalanced magnetron sputtering. These oxidation protective layers had the following chemical compositions (in at.%): 34.7Ti-50.2Al-14.5Cr-0.6Si, 31.4Ti-49.5Al-18.7Cr-0.4Zr, 32.5Ti-49.2Al-17.9Cr-0.4W, and 35.6Ti-45.1Al-18.9Cr-0.4Y. On some of the coated specimens thermal barrier coatings of 7 wt.% yttria partially stabilized zirconia were deposited using electron-beam physical vapour deposition (EB-PVD). Before TBC deposition, the coated samples were pre-oxidised in air at 750°C for 100 h to form a thin oxide scale of predominantly alumina. The thickness of the zirconia topcoats varied between 150 and 170 µm.

The oxidation behaviour of the coated γ-TiAl samples was studied in laboratory air at 950 and 1000°C under cyclic oxidation conditions. 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. Post-oxidation analysis of the coating systems was carried out using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS).

Results and discussion

Figure 1a shows the mass gain data of γ-TiAl specimens coated with Ti-Al-Cr layers containing minor additions of Si, Zr and W which were thermally cycled at 950°C in air. The coated samples exhibited a higher oxidation resistance in comparison to the bare substrate material which failed by severe oxide scale spallation after 140 cycles. A slow oxidation rate was observed for the Ti-Al-Cr-Si coating up to about 500 cycles of exposure; thereafter the mass gain increased indicating degradation of the intermetallic layer. The zirconium containing coating also exhibited low mass gain during the initial stages of thermal cycling. After 150 cycles, spallation of small oxide particles around the suspension hole and at the circumferential side of the disc-shaped samples caused a slight continuous drop in mass gain. Being coated with intermetallic layers by magnetron sputtering, the specimens were suspended from wire hooks. The wire suspension disturbed the deposition process near the hole, leading to an uncoated or less coated region around the hole. Similarly, variation of process parameters (bias voltage) to adjust the chemical composition of the Ti-Al-Cr-W coating caused a reduced layer thickness and a change in composition at the edge regions (near the rim of the samples, the Al concentration significantly decreased, whereas the amount of Cr and Ti increased). During thermal cycling, the coating degraded rapidly at these less protected areas, leading to enhanced oxidation and oxide spallation for prolonged exposure time periods.

SEM examination of a sample coated with Ti-Al-Cr-Si, which was exposed to air at 950°C for 1000 cycles, revealed a thin continuous alumina scale on top of the coating (Fig. 2a). Below the alumina scale, the B2-phase containing ~13 at.% oxygen and the Z-phase ($Ti_5Al_3O_2$) formed, as confirmed by EDS analysis. In the initial stages of exposure, the Ti-Al-Cr based coatings exhibited a two-phase microstructure consisting of the γ-TiAl, $Ti(Cr,Al)_2$ Laves or τ phases [4-7]. Due to rapid Cr diffusion into the substrate and growth of the alumina scale, the coatings depleted in chromium and aluminium with continuing thermal cycling. This resulted in the formation of the Al and Cr leaner B2 and Z-phases. Both phases established a stable protective alumina layer. Silicon was enriched in the B2-phase, probably retarding its dissolution. Many large pores were observed in the coating after thermal exposure. In some areas, the Ti-Al-Cr-Si layer was entirely degraded and a thick mixed oxide scale formed.

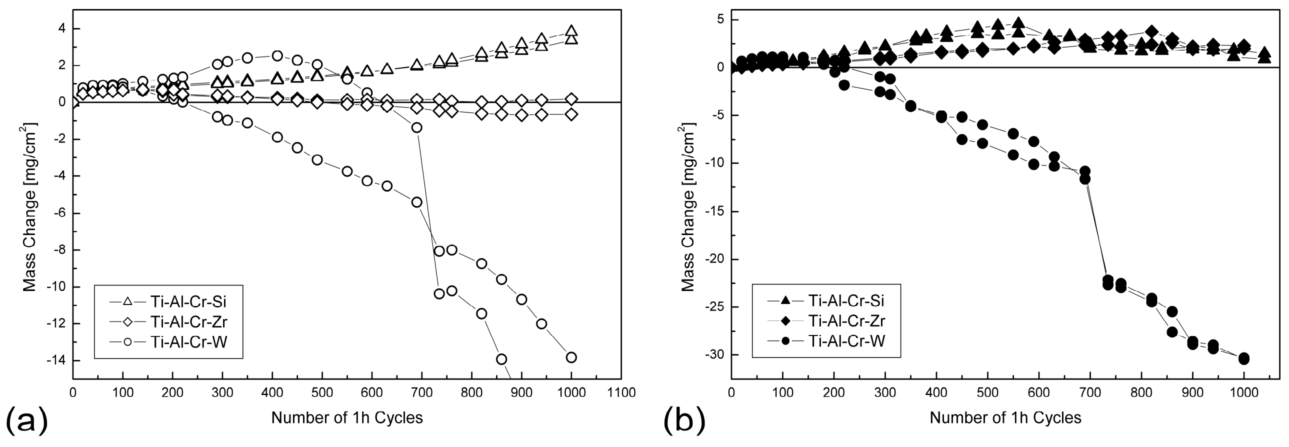

Figure 1: Mass change vs. number of cycles of γ-TiAl specimens coated with intermetallic Ti-Al-Cr-(Si, Zr, W) layers and (a) without and (b) with TBC which were thermally cycled at 950°C in air

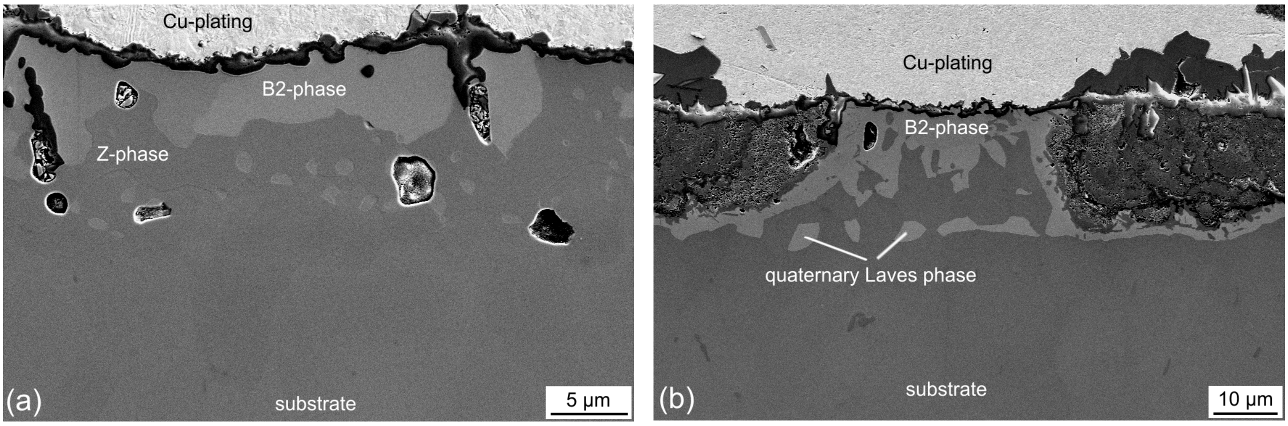

Figure 2: Scanning electron micrographs of γ-TiAl specimens coated with (a) Ti-Al-Cr-Si and (b) Ti-Al-Cr-Zr layers which were exposed to air at 950°C for 1000 cycles

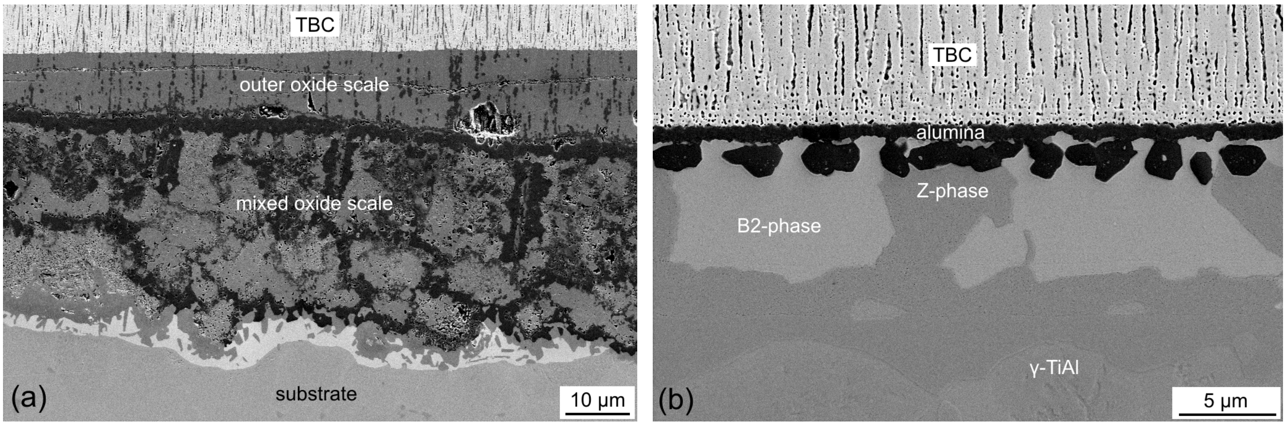

Figure 3: Scanning electron micrographs of γ-TiAl specimens coated with (a) Ti-Al-Cr-Zr and (b) Ti-Al-Cr-W layers and TBC which were exposed to air at 950°C for 1000 cycles

After 1000 cycles of exposure at 950°C, the Ti-Al-Cr-Zr coating was strongly oxidised, as revealed by scanning electron microscopy. In some areas, a protective alumina scale was still present on a nearly continuous zone of the B2-phase with dissolved oxygen (Fig. 2b). The quaternary alloying element Zr was found in the B2-phase. At the coating/substrate interface the niobium containing $Ti(Cr,Al)_2$ Laves phase precipitated. Its chemical composition determined by EDS analysis was 27.5Ti-34.9Al-29.5Cr-8.1Nb (in at.%). Cross-sectional analysis of a sample coated with Ti-Al-Cr-W, which was thermally cycled at 950°C for 1000 cycles, revealed an almost completely oxidised coating and a thick thermally grown oxide scale on the substrate. In a few areas in the centre of the face sides, the coating was not degraded. Instead, a continuous zone of the B2-phase was observed followed by the α_2-Ti_3Al phase. A thin protective alumina scale formed on the B2-phase. Again, pronounced macro-porosity was observed in the coating.

Mass gain data of γ-TiAl specimens coated with intermetallic Ti-Al-Cr-(Si, W, Zr) layers and TBCs which were thermally cycled at 950°C are presented in Figure 1b. Drops observed in the mass change curves were associated with edge chipping of the TBC near the suspension hole and at the circumferential surface. Furthermore, severe oxidation and spallation occurred at the unprotected area where the sample holder pin was removed. During the EB-PVD process, the samples were clamped to holders via their pin. After TBC deposition the pin was cut off, leaving a weak spot where enhanced oxidation occurred. The TBC systems did not spall off at the face sides during the maximum exposure time period of 1000 cycles.

The intermetallic Ti-Al-Cr based layers used as bond coats were severely degraded and largely oxidised after 1000 1 h cycles of exposure at 950°C, as found by SEM analysis. A thick mixed oxide scale grew on the substrate with protrusions of an outer scale exhibiting a columnar structure (Fig. 3a). These protrusions consisting of fine alumina particles in a string of beads-like array embedded in titania formed by outward diffusion of Ti and Al cations [8,9,11]. The inter-columnar gaps and pores of the TBC above the columnar scale were filled with titanium and aluminium oxides. The EB-PVD zirconia topcoat exhibited excellent adhesion to these thermally grown oxide scales. However, in some areas of the cross-sections, the intermetallic layers were degraded less, particularly the Ti-Al-Cr-W coating at the centre of the face sides (Fig. 3b). Below the thin alumina scale, the B2 and Z-phases were observed, often followed by the α_2-Ti_3Al phase. The thermal barrier coating was well adherent to the protective alumina scale.

Figure 4a shows the mass change versus number of cycles of γ-TiAl specimens coated with Ti-Al-Cr-Y, Ti-Al-Cr-Zr and Ti-Al-Cr-W layers which were thermally cycled at 1000°C. The intermetallic Ti-Al-Cr based coatings failed during 300 cycles of exposure by oxide spallation, particularly at the circumferential side and near the edge of the disc-shaped samples.

SEM micrographs of a sample coated with Ti-Al-Cr-Y which was exposed to air at 1000°C for 1000 cycles are presented in Figure 5. At one side of the sample, the intermetallic layer was almost entirely oxidised, whereas the coating was still present at the other side. There, the two-phase microstructure of the intermetallic layer transformed into single Z-phase with a continuous alumina layer on top. Below the Z-phase, the α_2-Ti_3Al phase was found. Small precipitates of the niobium containing quaternary Laves phase were occasionally observed at the coating/substrate interface. Microstructural examinations of samples with Ti-Al-Cr-Zr and Ti-Al-Cr-W layers revealed that the coatings were entirely oxidised after 1000 and 400 cycles of exposure, respectively, and thick thermally grown mixed oxide scales were observed at areas where no scale spallation occurred.

Mass change data of TBC systems thermally cycled at 1000°C are plotted in Figure 4b. The decrease in weight change for the different curves was associated with spallation of the TBC systems predominantly at the circumferential side of the samples and at the unprotected area where the sample holder pin was removed. With prolonged high temperature exposure, edge chipping of the TBC was observed around the rim of the specimens. Furthermore, flakes of the TBC spalled off near the suspension hole. The zirconia topcoat did not spall off at the centre of the face sides of the samples.

As revealed by SEM cross-sectional analysis, the intermetallic Ti-Al-Cr-Y layer was entirely oxidised after 500 1 h cycles of exposure at 1000°C (Fig. 6a). A thick mixed oxide scale grew on the substrate, and protrusions of an outer oxide scale with columnar structure formed beneath the TBC. The TBC was well adherent to the outer oxide scale. Microstructrual examinations of a sample coated with Ti-Al-Cr-Zr and TBC which was exposed to air at 1000°C for 500 cycles revealed a continuous alumina scale formed on the intermetallic coating (Fig. 6b). The thermal barrier coating was again well adherent to the alumina scale. After 1000 cycles of exposure, the Ti-Al-Cr-Zr coating was entirely oxidised at one side of the sample, whereas at the other side the protective alumina scale was mainly still present with the B2 and Z-phases below. Similar results were observed for a sample coated with Ti-Al-Cr-W and TBC which was exposed at 1000°C for 400 cycles. At the centre of the face sides, a thin protective alumina scale was observed on top of a nearly continuous layer of the B2-phase with dissolved oxygen. Towards the edges of the samples the intermetallic layer and the substrate were oxidised. In these outer regions, the TBC system failed by spallation of the thermally grown oxide scale. Failure occurred in the mixed oxide scale.

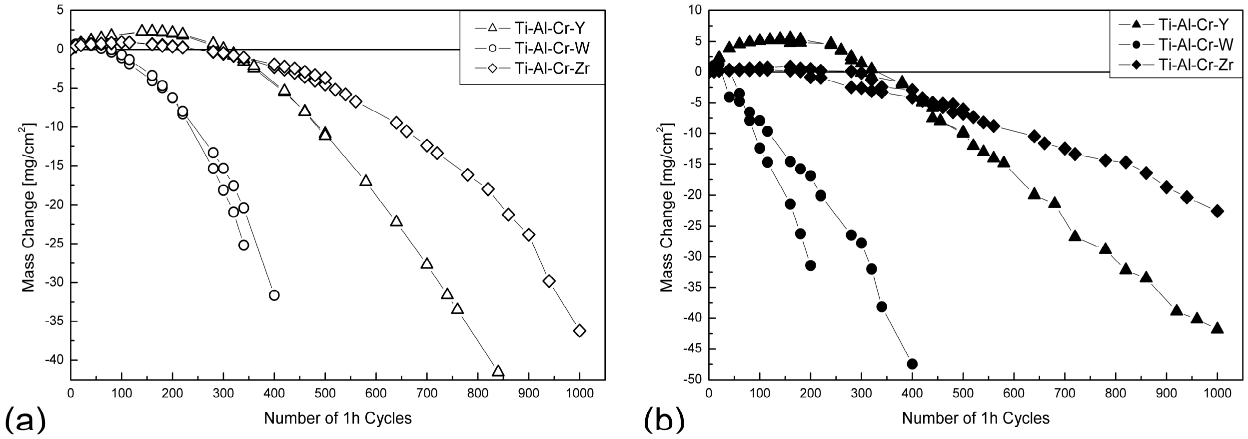

Figure 4: Mass change vs. number of cycles of γ-TiAl specimens coated with intermetallic Ti-Al-Cr-(Y, W, Zr) layers and (a) without and (b) with TBC which were thermally cycled at 1000°C in air

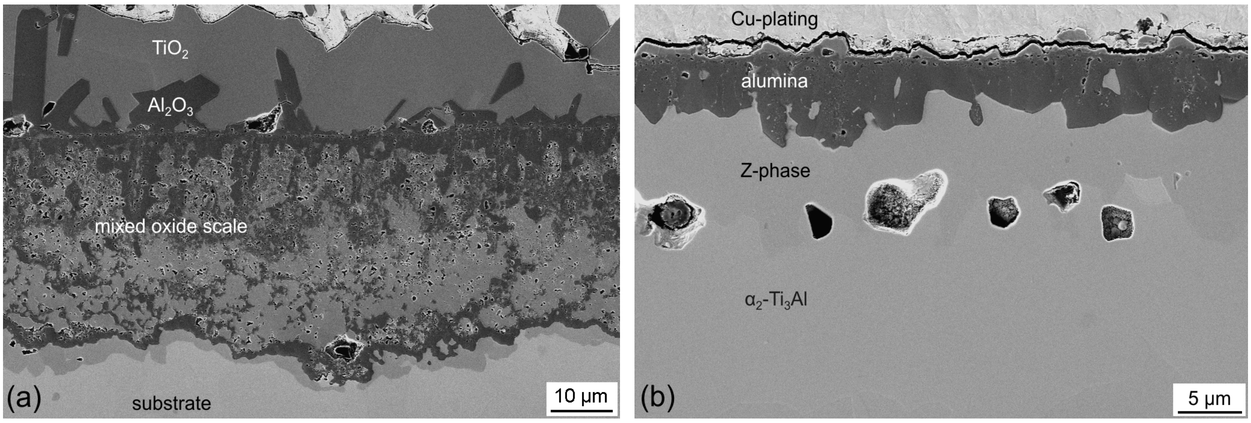

Figure 5: Scanning electron micrographs of a γ-TiAl sample coated with Ti-Al-Cr-Y which was exposed to air at 1000°C for 1000 cycles, showing (a) the thermally grown mixed oxide scale on the degraded coating and (b) the transformed coating with a protective alumina scale on top

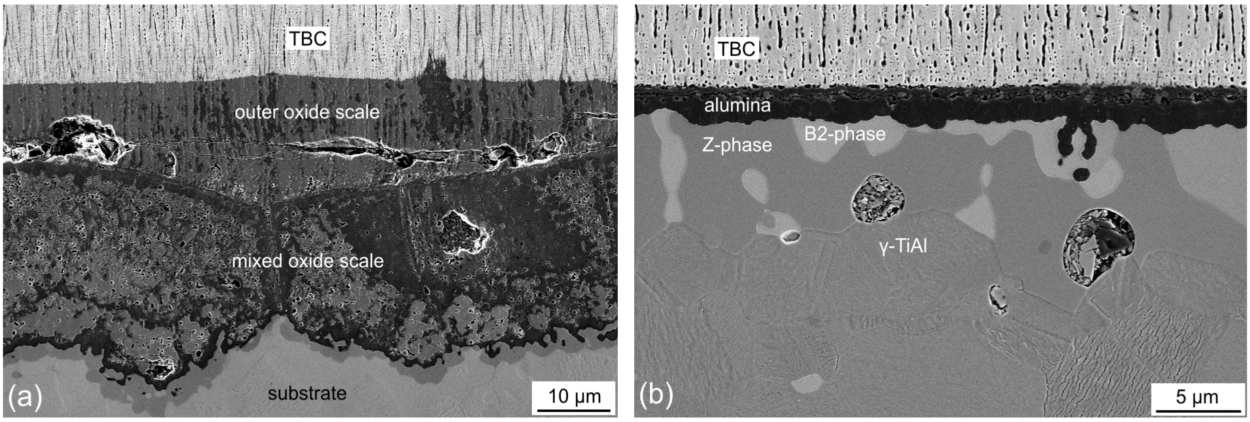

Figure 6: Scanning electron micrographs of γ-TiAl specimens coated with (a) Ti-Al-Cr-Y and (b) Ti-Al-Cr-Zr layers and TBC which were exposed to air at 1000°C for 500 cycles

The Ti-Al-Cr based intermetallic layers proved to be promising protective coatings on γ-TiAl alloys. During long-term exposure the coatings depleted in chromium, and the B2-phase establishing the formation of a protective alumina scale dissolved. The quaternary alloying elements were primarily enriched in the latter phase, probably retarding its dissolution. In addition, the degradation of the coatings was associated with not optimized parameters of the magnetron sputtering process, resulting in variations of the chemical composition at the rim of the disc-shaped samples. Furthermore, the as deposited intermetallic layers exhibited structural defects like inter-columnar porosity, voids and crevices between the columns. These growth defects caused premature localised degradation and oxidation of the substrate. When manufactured applying process parameters adjusted to obtain a dense coating structure free of defects, however, intermetallic Ti-Al-Cr layers alloyed with small amounts of Y, Zr, W, and Si have the potential to withstand prolonged exposure to air up to 1000°C.

Conclusions

Intermetallic Ti-Al-Cr based layers with minor additions of the quaternary elements Si, Zr, W, and Y significantly improved the oxidation resistance of coated γ-TiAl alloys at 950 and 1000°C. Although the coatings considerably degraded after 1000 cycles of exposure at 950°C, a protective alumina scale stabilised by the B2 and Z-phases was quite often observed. The intermetallic layers failed by breakaway oxidation during 300 cycles of exposure at 1000°C. The coatings were entirely oxidised except the Ti-Al-Cr-Y layer which still established a protective alumina scale at one side of the sample after 1000 cycles.

TBC systems consisting of Ti-Al-Cr based bond coats and zirconia topcoats exhibited lifetimes exceeding 1000 1 h cycles when exposed to air at 950°C. Protrusions of an outer oxide scale with columnar structure formed on the degraded intermetallic layers. When thermally cycled at 1000°C, the TBC systems failed after exposure time periods less than 300 cycles by spallation of the thermally grown mixed oxides at the circumferential side and near the edges of the disc-shaped samples. The EB-PVD zirconia topcoat was well adherent to the alumina scale formed on the intermetallic layers. The TBC also exhibited excellent adhesion to the outer columnar-structured oxide scale.

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