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Oxidation resistance of γ-TiAl based alloy Ti–45Al–8Nb coated with intermetallic Ti–Al–Cr–Y layers and EB-PVD zirconia topcoats at 950 °C in air

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ABSTRACT

Samples of a high niobium bearing γ-TiAl based alloy were coated with intermetallic Ti–52Al–15Cr–0.4Y (in at.%) layers produced by magnetron sputtering. On some of the specimens thermal barrier coatings of 7 wt.% yttria partially stabilised zirconia were deposited using electron-beam physical vapour deposition. The oxidation behaviour of the coated Ti–45Al–8Nb (at.%) alloy with and without thermal protection was investigated at 950 °C under cyclic oxidation conditions in air. The 20 μm thick Ti–Al–Cr–Y layer exhibited excellent oxidation resistance at this exposure temperature associated with the formation of a thin continuous alumina scale. Lifetimes exceeding 1000 cycles of 1 h dwell time at 950 °C were determined for the TBC system consisting of zirconia topcoat and Ti–Al–Cr–Y bond coat.

1. Introduction

Intermetallic γ-TiAl based alloys combine low density with high specific yield strength and good creep properties up to high temperatures [1]. Therefore, these alloys have gained increasing technical importance for components in jet engines and turbines as potential replacement for nickel-based superalloys [1–4]. They also possess good oxidation resistance up to about 800 °C [5]. At higher exposure temperatures, mixed titanium and aluminium oxide scales formed, providing inadequate environmental protection. Surface modification by coatings is an appropriate approach to enhance the oxidation behaviour of components for elevated temperature applications [6–8]. Ternary Ti–Al–Cr alloys proved to be potential coating materials for the protection of titanium aluminides [6,8–11]. The addition of chromium exceeding 8–10 at.% to γ-TiAl was found to reduce the amount of aluminium necessary to establish a protective alumina scale [9]. This so-called chromium effect was postulated to be associated with the Ti(Cr,Al)$_2$ Laves phase exhibiting low oxygen permeability and forming continuous alumina scales [12]. The oxidation resistance of Ti–Al–Cr based coatings could further be improved by alloying with small amounts of quaternary elements [13–15]. In particular, yttrium and hafnium have demonstrated a beneficial effect on the oxidation resistance when added in low concentrations (0.1–0.5 at.%).

Thermal barrier coatings (TBCs) are widely used for Ni-based superalloys to increase the gas turbine efficiency [16–18]. Ceramic coatings with low thermal conductivity considerably reduce the operating temperatures of internally cooled substrates, enabling higher gas temperature or improving the endurance of the components. Recently, yttria stabilised zirconia (YSZ) topcoats were successfully deposited on γ-TiAl based alloys using electron-beam physical vapour deposition [8,19–23]. The TBCs were well adherent to intermetallic and nitride overlay coatings used as bond coats. At temperatures above 900 °C, the TBC systems failed by spallation of the oxide scales grown on the substrate after degradation of the protective coatings. For γ-TiAl specimens coated with Ti–Al–Cr layers and zirconia topcoats, failure was observed after about 300 cycles of 1 h dwell time at 950 °C [19,22]. Thus, the life-time of TBC systems on titanium aluminides significantly depends upon the oxidation protection capacity of the bond coats. The aim of the present work was to investigate the oxidation resistance of γ-TiAl based alloys with intermetallic Ti–Al–Cr–Y coatings at 950 °C in air. Furthermore, the lifetime of the TBC system consisting of zirconia topcoat and Ti–Al–Cr–Y bond coat was determined under thermal cycling conditions. Whereas Nb-rich γ-TiAl alloys of the third generation possess the potential for structural applications at temperatures up to 850 °C [24], the oxidation tests were carried out at the higher exposure temperature of 950 °C to study the long-term protection capability of the coating systems within reasonable exposure time periods.

2. Experimental

The material used was an extruded and annealed rod of a γ-TiAl based alloy with the nominal composition Ti–45Al–8Nb–0.2C (in at.%) provided by GfE Gesellschaft für Elektrometallurgie, Nürnberg, Germany. The alloy exhibited a two-phase microstructure consisting of the niobium containing γ-TiAl and α_2-Ti$_3$Al phases [22]. From this rod

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disc-shaped specimens with 15 mm diameter and 1 mm thickness were machined using spark erosion. The surfaces of the samples were ground (using SiC emery paper up to P4000 grit), polished (using subsequently 3 μm diamond and a colloidal 0.1 μm silica suspensions) and ultrasonically cleaned in isopropanol.

The specimens were coated with intermetallic Ti–Al–Cr–Y layers deposited by magnetron sputtering in a laboratory coater equipped with two sources [25]. Prior to coating deposition, the substrates were sputter-etched in argon plasma using a hollow cathode powered by a radio frequency generator (13.56 MHz) at a power level of 150 W. The samples were exposed to the ion bombardment for 30 min at a pressure of about 1 Pa. The oxidation protective layers were produced by sputtering from two opposing cathodes with 90 mm diameter powered by direct current and radio frequency. The chemical composition of the coatings was adjusted using composite targets consisting of pure titanium and chromium discs with cylindrical inserts of aluminium and plugs of the quaternary alloying element yttrium, respectively. The Ti–Al and Cr–Y targets were used on the direct current and radio frequency sources, respectively, operated at 260 W and 70 W. Argon pressure during sputtering was 0.4 Pa. No external heating was applied, resulting in a substrate temperature of about 120 °C, as measured using a thermocouple placed close to the samples. During deposition, the specimens were rotated in the middle of both sources at 13 rpm, allowing to coat all sides of the sample. The substrate holder was kept at floating potential, being between −20 and −25 V. The deposition rate was ~2 μm/h. The coating thickness was approximately 20 μm, and the chemical composition of the as-sputtered layer was 32.1Ti–52.4Al–15.1Cr–0.4Y (in at.%), determined by standardless energy dispersive X-ray analysis using a scanning electron microscope (see below). Microstructural examinations of the coatings after deposition were not performed. The Ti–Al–Cr–Y layers were probably amorphous, as found with as-sputtered Ti–Al–Cr films [25,26]. Such coatings deposited at low temperatures compared to the melting temperature of the coating have been reported to exhibit columnar growth structure with voided open boundaries [27].

On some of the samples with oxidation protective layers, thermal barrier coatings of 7 wt.% yttria partially stabilised zirconia were deposited using electron-beam physical vapour deposition (EB-PVD). TBC systems for gas-turbine engine applications comprise bond coats typically forming alumina [16]. Therefore, before TBC deposition, the coated specimens were pre-oxidised in air at 750 °C for 100 h to form a thin oxide scale of predominantly alumina. As found in oxidation tests of γ-TiAl samples with Ti–Al–Cr coatings at 750 °C in air, a significantly reduced mass gain was observed after about 100 h in comparison to the initial stage of exposure, indicating protective oxide scale formation [28]. During this heat treatment, Ti–Al–Cr coatings transformed from the amorphous as-coated to a crystalline microstructure exhibiting the γ-TiAl and $Ti(Cr,Al)_2$ Laves phases [29]. A 150 kW dual-source coater with chambers for loading, pre-heating and deposition was used to produce the ceramic coatings [30]. A high energy electron beam melted and evaporated a ceramic source ingot in the deposition chamber into which a controlled amount of oxygen was bled to achieve defined stoichiometry of zirconia. During evaporation the ingots were bottom fed into the crucibles to ensure continuous growth of the TBC coating. Pre-heated substrates were positioned into the vapour cloud. Typical deposition rates of the EB-PVD process were between 5 and 10 $\mu m\ min^{-1}$ on specimens rotated at 12 rpm. The substrate temperature was about 900 °C. The thickness of the YSZ topcoats was approximately 170 μm.

Cyclic oxidation tests were carried out at 950 °C in laboratory air using automatic rigs. One cycle consisted of 1 h exposure at high temperature and 10 min at ambient temperature during which the specimens cooled down to about 70 °C. The specimens were periodically inspected and weighed. Duplicate specimens were tested to estimate reproducibility. The maximum exposure time period was 1000 cycles. The TBC system was considered failed when substantial spallation of the zirconia topcoat occurred (at about 20% of the total surface of the sample). Cross-sectional analyses of oxidised samples were performed using scanning electron microscopy (SEM) with field emission source and energy-dispersive X-ray spectroscopy (EDS). Imaging of the cross-sections was carried out at 5 kV with secondary electrons. The SEM was operated at 12 kV for standardless EDS analysis. Due to limitations to determine reliable concentrations of different elements exhibiting similar emission lines, the EDS results were verified by wavelength-dispersive X-ray spectroscopy (WDS). WDS analysis was carried out using an electron microprobe operated at 15 kV. X-ray diffraction measurements were conducted using a Siemens D5000 diffractometer in Bragg–Brentano geometry with secondary graphite monochromator employing CuKα radiation. The thermally exposed coating was also investigated by analytical transmission electron microscopy (TEM) at an operating voltage of 300 kV. The thin TEM specimens were prepared by dimple grinding and ion beam thinning.

3. Results and discussion

Fig. 1 shows thermo-gravimetric results obtained from thermal cycling tests at 950 °C in air. Mass change data vs. number of cycles are plotted for γ-TiAl specimens coated with Ti–Al–Cr–Y layers and with the TBC system consisting of Ti–Al–Cr–Y bond coat and zirconia topcoat. Data for bare Ti–45Al–8Nb alloy with and without TBC are included for comparison. The Ti–Al–Cr–Y coating was found to improve the oxidation resistance of Nb-containing γ-TiAl alloys. After 1000 cycles of exposure, samples with this intermetallic layer exhibited mass gains below 2 $mg \cdot cm^{-2}$, whereas bare γ-TiAl failed by severe scale spallation after 100 cycles. Similarly, the TBC on the bare substrate material spalled off after 140 cycles, whereas no spallation of the TBC system was observed for specimens with a Ti–Al–Cr–Y bond coat during exposure time periods up to 1000 cycles. The negligible mass loss of the samples with TBC after 20 cycles of exposure was associated with evaporation of water vapour adsorbed on the EB-PVD zirconia topcoat from natural air humidity during the storage prior to testing. Furthermore, the specimens with thermal protection were pre-oxidised before TBC deposition. Therefore, during the initial stages of cyclic oxidation testing, their mass gain was less in comparison to that of as-coated samples without the thin oxide scale grown on the former specimens during the heat pre-treatment.

Microstructural examinations of the cross-section of an uncoated sample which was exposed to air at 950 °C for 130 cycles revealed an about 20 μm thick thermally grown oxide scale in areas where the oxides did not spall off (Fig. 2a). The scale exhibited a layered structure with an outermost dense and pore-free layer of TiO_2, an alumina-rich layer and an inner porous titania layer with interspersed alumina particles. In the transition region between scale and substrate, a nitride layer

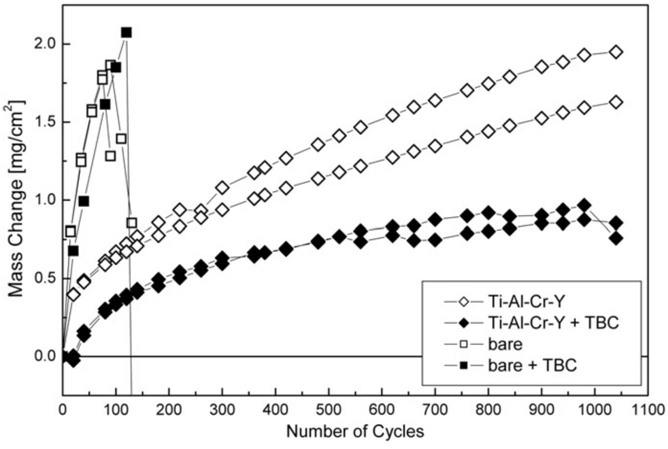

Fig. 1. Mass change vs. number of cycles of Ti–45Al–8Nb specimens with and without TBC systems which were thermally cycled at 950 °C in air. YSZ topcoats were deposited on γ-TiAl samples, with and without an intermetallic Ti–Al–Cr–Y layer.