

Oxidation Behavior of Aluminide Coated Ti-Al-Cr-Nb-Zr-Y Alloys at High Temperatures

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Keywords: intermetallic; Ti-Al alloys; aluminide coatings; pack aluminizing; high temperature oxidation.

Abstract. Oxidation behavior of diffusion aluminide coating containing layers of $TiAl_3$ and $TiAl_2$, develop on a substrate of $\alpha_2-Ti_3Al/\gamma-Ti-40Al-2Cr-2Nb-0.4Y-0.2Zr$ intermetallic alloy using pack aluminizing method, was investigated isothermally at 800°C, 900°C, and 1000°C. The pack cementation was carried out at 850°C for 25 hours in a pack containing 20%-wt Al, 2%-wt NH_4Cl , and 78%-wt Al_2O_3 . The phases in the coatings and oxide layers were examined by optical and scanning electron microscopy as well as X-ray diffraction method, while their chemical composition were examined with EDS. The experimental results showed that the addition of Zr and Y increases the oxidation resistance of the coating by formation of complex oxides. Combination of oxidation and interdiffusion process cause transformation of $TiAl_3$ layer to $TiAl_2$ that decrease the oxidation resistance through the formation of TiO_2 rod crystals on the junction between $TiAl_2$ and Al_2O_3 in the outer layer.

Introduction

Intermetallic alloys of the Ti-Al system are developed to have combination of properties suitable for high temperature applications [1]. Nevertheless, applications of $\gamma-TiAl$ -based materials face problems as they are relatively brittle. Reducing slightly the aluminium content of the alloy to give two phase of α_2-Ti_3Al and $\gamma-TiAl$ (simplified as $\alpha_2-Ti_3Al/\gamma-TiAl$) provide better mechanical properties at room as well as high temperatures, event hough it affects in reduction of oxidation resistance [2,3]. To solve this problem two methods are available, *i.e.*, alloying with elements that increase oxidation resistance of $\alpha_2-Ti_3Al/\gamma-TiAl$, and applying aluminide based coatings. During applications at high temperatures, the coating can degrade due to the interaction between the coated system and environment of relatively high oxygen partial pressures. The $\alpha_2-Ti_3Al/\gamma-TiAl$ alloy components for high temperature applications are normally operated at a max. temperature of ~800°C. Under certain circumstances, the alloy may be subjected to overheating conditions in which temperature may reach as high as 1000°C due to abnormal engine operations. At elevated temperature, the stability of an aluminide coating is primarily affected by: (i) selective oxidation and hot-corrosion processes; and (ii) interdiffusion between the coating and the substrate. Each of these degradation processes has a profound effect on the coating structure during its service life and, hence, on its ability to protect the alloy component.

Experimental

A two phase $\alpha_2-Ti_3Al/\gamma-TiAl$ alloy with nominal chemical compositions of Ti-40Al-2Cr-2Nb-0.4Y-0.2 Zr (in at.%) was produced from high purity aluminium and titanium using a Centorr 5 SA single-arc furnace. The source materials are pure metals obtained from Sigma Aldrich. Prior to

melting, the furnace chamber was purged with argon for about 20 minutes. The argon was kept flowing during the melting. To ensure homogeneity, the alloy was melted four times. The alloy buttons were then homogenized at 1150°C for 100 hours in a tube furnace in which argon was introduced to avoid oxidation of the alloy. An aluminum-rich TiAl₃ coating was applied to the substrate coupons using a high-activity pack cementation process, with the pack composition consisted a powder mixture of 20 wt.% Al, 2 wt.% NH₄Cl and 78 wt.% Al₂O₃ at 900°C for 10 hours. The oxidation tests were performed to the bare alloy and coated samples by heating at 800°C, 900°C and 1000°C for 5, 20, 50, 100 and 200 hours in an open tube electric furnace. At the completion of a given overheating simulation, the samples were removed from the furnace and weighed to measure the weight gain.

The surface of the as-coated and oxidized samples were analysed using X-ray diffraction method. The samples were then cold mounted in an epoxy resin and polished to a 0.2 µm finish prior to etching with a mixture of 25 g CrO₃, 150 ml HCl and 50 ml H₂O. Microstructural observations were initially carried out on each etched sample using an optical microscope. Concentration analysis of phases and regions on the samples were obtained using an energy dispersive x-ray analysis (EDAX) attached on a scanning electron microscope (SEM).

Results and Discussion

Figure 1(a) shows the microstructure of an as-coated α_2 -Ti₃Al/ γ -TiAl sample. It is clearly seen from the microstructure that the coating consists of two distinct layers (i) an outer layer of high-Al TiAl₃ and (ii) an intermediate layer of TiAl₂. The total thickness of the coating was about 50 µm. From the EDS results it was confirmed that the aluminium content in the outer and inner layers is in the range of 72-60 at.%, with the highest content being at the coating surface. No Nb and Cr in the coating were identified, probably these element only dissolved slightly in the coating. By contrast, the concentration of nickel in the inner and intermediate layers increased from 39 at.% at the coating surface to 46 at.% at the inner layer/intermediate layer boundary.

Figs. 1(b) up to 1(e) show the cross section microstructures of the coated samples oxidized at 1000°C for 5, 20, 50, 100 and 200 hours respectively. Due to the limited space available, only microstructures of samples oxidized at 1000°C were shown in this paper. The EDS analysis results confirm that two layers of TiAl₂ and TiAl₃ in the coating were still identified in the samples oxidized up to 200 hours. However, only TiAl₂ layer was left after oxidation for 200 hours. Two types of Al₂O₃, i.e., θ and α were identified from the XRD analysis on the surface of coated sample oxidized at 1000°C for 200 hrs. The SEM micrographs shows that θ -Al₂O₃ has porous needle like structure, as shown in Figure 2 (a), while relatively compact solid oxide was identified for α -Al₂O₃, as shown in Figs. 2 (b) and (c). TiO₂ crystals, however, were found on the surface of TiAl₂ layer, especially at the spall zone, as shown in Fig. 2 (d). No layer of TiAl₂ underneath outside Al₂O₃ oxide layer was identified indicated that inward diffusion of O²⁻ inwardly through Al₂O₃ layers is confirmed and this is believed controls the oxidation rate.

The experimental results show that protective scale of Al₂O₃ attributed to the oxidation resistance of the coated α_2 -Ti₃Al/ γ -Ti-40Al-2Cr-2Nb-0.4Y-0.2Zr intermetallic alloy, as all the coated samples oxidized at 800, 900 and 1000°C up to 200 hours provides outer scales of Al₂O₃. Nevertheless, exception was found at the junction between TiAl₂ grain boundaries and outer scale, where TiO₂ crystals were formed. It is interesting to note that the phases that left in the coating of the sample oxidized at 1000°C was only a single TiAl₂, as the TiAl₃ layers has diminished due to combination process of oxidation and interdiffusion. Effect of Y and Zr elements addition and aluminide coating on the oxidation resistance of α_2 -Ti₃Al/ γ -TiAl intermetallic alloy is represented by the relation between square root of mass change per unit area (mg/cm²) and oxidation time at 1000°C as shown in Figure 4. The results of previous study [3] were also presented on this figure to compare them with the existing results. This figure demonstrates the effect of aluminide coated on Y and Zr doped α_2 -Ti₃Al/ γ -TiAlCrNb intermetallic alloy in decreasing the oxidation rate represented by reducing the weight gain of the samples. It is clearly seen that even though the addition of Y and Zr were done into the alloy, the coated alloy can obtain the benefit from the effect

of the addition of these elements in increasing the resistance of the oxide scale from the spallation in isothermal oxidation.

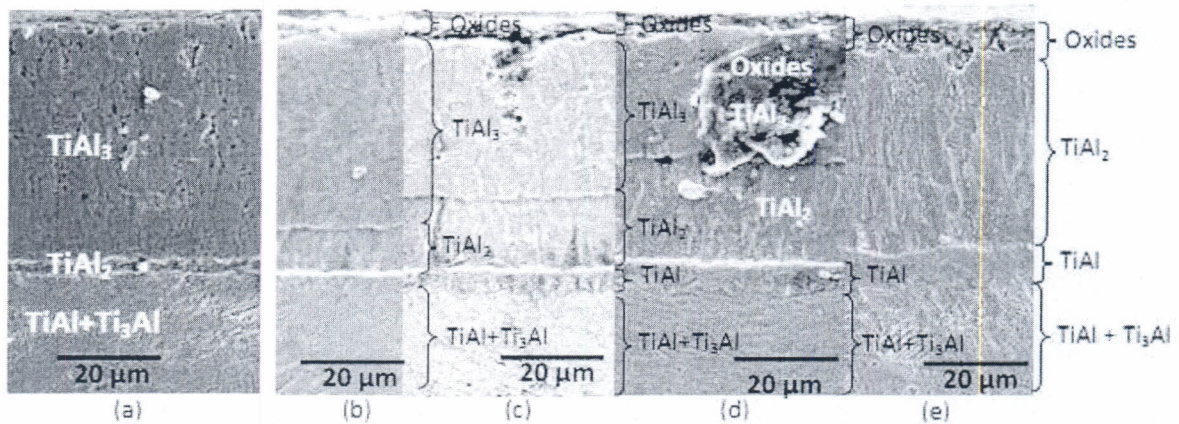


Fig. 1. Cross section microstructures of (a) as coated alloy sample, and coated samples oxidized at 1000 °C for (b) 20, (c) 50, (d) 100 and (e) 200 hours.

The bare sample oxidized at 1000°C indicates the formation of TiO₂ at the surface and the mixture of TiO₂ and Al₂O₃ underneath, as shown in Fig. 3. The microstructure of cross section and corresponding surface oxides of bare alloy samples after oxidation at 1000 °C for 200 hours are shown in Fig. 3. The early stage of oxidation, represented by the coated samples oxidized for 5 and 20 hours, gave relatively porous θ-Al₂O₃ which is believe caused higher oxidation rate. This rate decreased significantly with longer time of oxidation period due to the formation of more dense α-Al₂O₃.

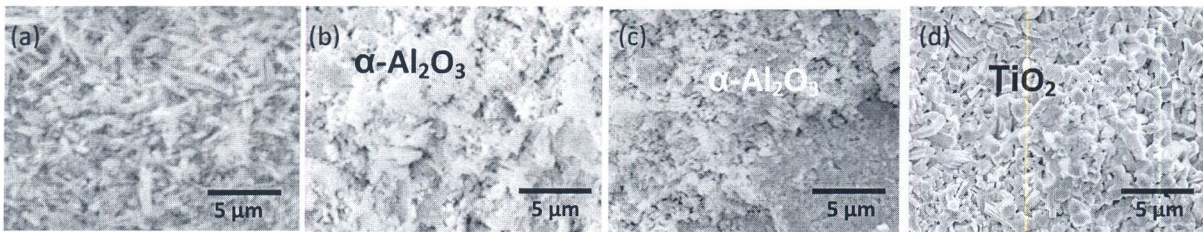


Fig. 2. Microstructures of surface oxides found on the coated samples oxidized at 1000°C, for (a) 20 hrs, (b) 50 hrs, (c) 100 hrs, and (d) 200 hrs at a certain position.

Relatively thick of mixed Al₂O₃ + TiO₂ oxide layer was found. The outer surface oxide mainly contains columnar crystals of TiO₂. This fact shows that aluminide coatings of TiAl₃ base intermetallic is essential in increasing the oxidation resistance of the α₂-Ti₃Al/γ- Ti-40Al-2Cr-2Nb-0.4Y-0.2Zr alloy.

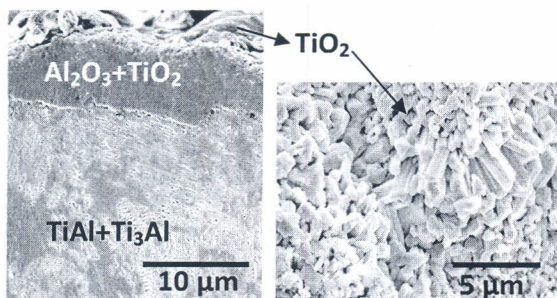


Fig. 3. Microstructure of cross section of bare alloy sample oxidized at 1000 °C for 200 hours.

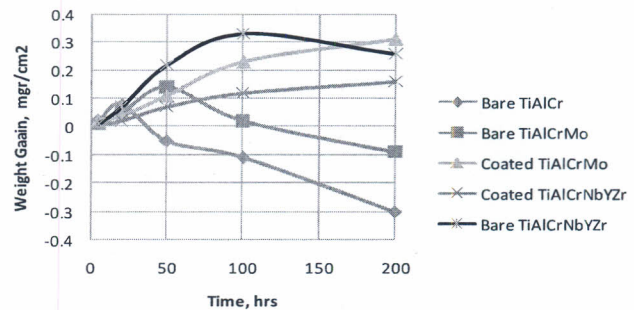


Fig. 4. Oxidation resistance of bare and coated α₂-Ti₃Al/γ-TiAl intermetallic alloys.

Summary

Isothermal oxidation at 800, 900 and 1000°C gave Al₂O₃-scale on the coated samples up to 200 hours. However, TiO₂ formed at region between Al₂O₃ in coated sample oxidized at 1000°C for 200 hours in the junction between Al₂O₃ and TiAl₂ grain boundaries. This TiO₂ formation increased the oxidation rate of the coating. The depletion of aluminium in the coating that cause the transformation of TiAl₃ to TiAl₂ was due to the combination of oxidation and diffusion processes. Even though the addition of Y and Zr were done into the alloy, the coated alloy can obtain the benefit from the effect of the addition of these elements in increasing the resistance of the oxide scale from the spallation in isothermal oxidation.

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