

The effect of an Ni–Cr protective layer on cyclic oxidation of Ti₃Al

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Summary

The effect of an 80Ni–20Cr (at.%) metallic coating on the cyclic oxidation behaviour of a Ti₃Al-based alloy with the composition Ti–25Al–11Nb (at.%) was investigated in this study. Cyclic oxidation tests were carried out in air at 600 °C and 900 °C for 120 h. For one cycle test, the specimens were held for 24 h at test temperature and then furnace-cooled to room temperature. The oxidation rate was determined by plotting the mass gain per unit surface area of the specimen vs. exposure time. The morphology and composition of the oxidation products were characterized on the cross-section of the specimens by scanning electron microscopy, energy-dispersive X-ray spectroscopy and atomic force microscopy. The oxidation scale forms during exposure at both 600 °C and 900 °C. TiO₂ is the main oxide component, whereas the Al₂O₃ layer appears only discontinuously. The remarkable improvement in oxidation resistance at 900 °C was attributed to the chemical composition and structure of the scale formed on the 80Ni–20Cr coating.

Introduction

Owing to their low densities and excellent mechanical properties at elevated temperatures, the α_2 -Ti₃Al-based intermetallic alloys are promising structural materials for high-temperature applications (Djanarthany *et al.*, 2001). These alloys, on the other hand, possess poor oxidation resistance, reducing the lifetime of components considerably. These intermetallics essentially form nonprotective mixed TiO₂ + Al₂O₃ scales in air at operating temperatures rather than a continuous Al₂O₃ scale, which offers excellent long-term oxidation protection (Dettenwanger & Schütze, 2000; Reddy, 2002). In addition, TiO₂-based scales tend to spall during cooling, resulting in the poor cyclic oxidation resistance.

Alloying with ternary and quaternary elements can improve the high-temperature oxidation resistance of these intermetallics (Taniguchi & Shibata, 1996; Mungole *et al.*, 2000). However, this is not sufficient to ensure protective oxide formation, as the oxidation process depends on a variety of factors. The deposition of coatings on the surface is the most promising approach to provide good oxidation resistance at high temperatures. Nowadays, there are several types of protective coating being applied, and improvements at various levels have been reported (Nishimoto *et al.*, 2003; Li *et al.*, 2001).

The aim of the present work was to determine the influence of cyclic oxidation conditions, such as annealing temperature and duration, as well as the presence of a protective coating, on the composition and thickness of formed multilayer surface oxide.

Materials and methods

The investigated material was Ti₃Al alloy with the chemical composition Ti–25Al–11Nb (at.%) supplied in the form of 0.5-mm-thick cold-rolled sheets. Samples, 15 × 15 mm in size, were cut from the sheets and ground with SiC paper to 1000 grit. After grinding, samples were cleaned for 30 min in an ultrasonic bath with ethanol. Prior to the annealing treatments, one group of samples was coated with a 1- μ m-thick protective 80Ni–20Cr (at.%) layer, using the sputtering technique. The cyclic oxidation tests were performed at 600 °C and 900 °C in air for 120 h, and the duration of each cycle was 24 h. After reaching the annealing temperature, samples were placed in the furnace, oxidized in air, and then furnace-cooled down to room temperature. After each cycle test, mass gain was measured with a 'Mettler' electronic balance (Mettler-Toledo Inc., Columbus, OH) with an accuracy of ± 0.0001 .

The cross-sectional analysis of cold-rolled and annealed samples was carried out with a JEOL JSM-6460LV scanning electron microscope (JEOL Ltd., Peabody, MA) equipped with an energy-dispersive X-ray spectroscopy Oxford Instruments INCA

X-sight system (Oxford Instruments Plc, Oxon, U.K.) operating at 25 kV. Scanning electron microscopy observations and energy-dispersive X-ray spectroscopy analysis were used to determine the thickness and composition of the oxide layer, and the morphology of the formed oxide scales was examined using atomic force microscopy. Atomic force microscopy investigations were performed under ambient conditions using a TM Microscopes Auto Probe CP Research device (TM Microscopes, Santa Barbara, CA) with Si and Si₃N₄ cantilevers (spring constant 0.26–0.4 N m⁻¹) in contact mode. The atomic force microscopy images were recorded at typical rates of 1.0 s per scan line.

Results and Discussion

Scanning electron microscopy observations showed that the outer oxidation scale formed on any of the samples exposed at both 600 °C and 900 °C. However, the thickness and phase constitution of the scale differed greatly, depending on oxidizing conditions. As can be seen from the mass gain results shown in Fig. 1(a), the oxidation behaviour of Ti–25Al–11Nb alloy was temperature-dependent. At 600 °C, the alloy showed good oxidation resistance, due to the beneficial effect of Nb addition. The results of X-ray diffraction analysis (not presented in this article) revealed that after 120 h of exposure, a compact 4.8–5.9- μm -thick oxide scale (Fig. 1b) consisted of nitride, TiO₂ and Al₂O₃, with a certain amount of Nb, reducing the oxidation rate. On the basis of these results, an 80Ni–20Cr layer deposited on the sample surface further enhanced the resistance to oxidation at 600 °C. This improvement was linked to the formation of a continuous Cr₂O₃ scale, reducing the outward diffusion of Al from the matrix to the scale. As a result, a thin Al₂O₃ layer, ranging from 1.4 to 1.6 μm , was formed after 120 h of exposure (Fig. 1c).

On the other hand, the oxidation resistance was reduced drastically when the exposure temperature was higher. Variation of mass gain with time indicated a change in the composition and properties of scales with the progress of oxidation. Cross-sectional analysis of scales using scanning electron microscopy with a compositional determination facility indicated that the oxide scale was multilayered with an internal oxidation-affected zone. As shown in Figs 2 and 3, such a structure formed *in situ* with alternate layers of phases was more pronounced in the case of uncoated samples. The individual layer thickness was smaller, and more layers were formed (Fig. 2a). Elemental X-ray maps revealed that the overall 54.4–63.3- μm -thick oxide scale formed after 120 h of exposure was composed of TiO₂ and mixed TiO₂ and Al₂O₃ layers in which the Nb was dissolved (Fig. 2b). Al₂O₃ was enriched near the interface between the two layers, so that they consisted of many thin Al₂O₃ and TiO₂ films. Owing to the numerous interfaces, the detachment of the oxide layers took place during cooling of the sample.

The diffusion-affected zone of the matrix subsurface was about 25 μm thick and divided into two layers (Fig. 2a). The first

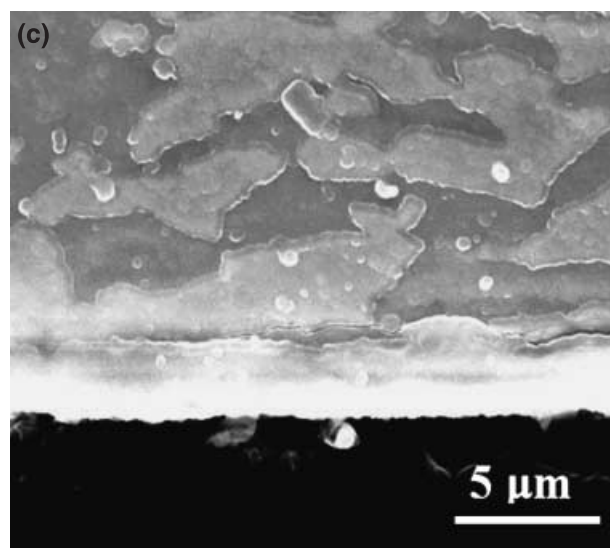
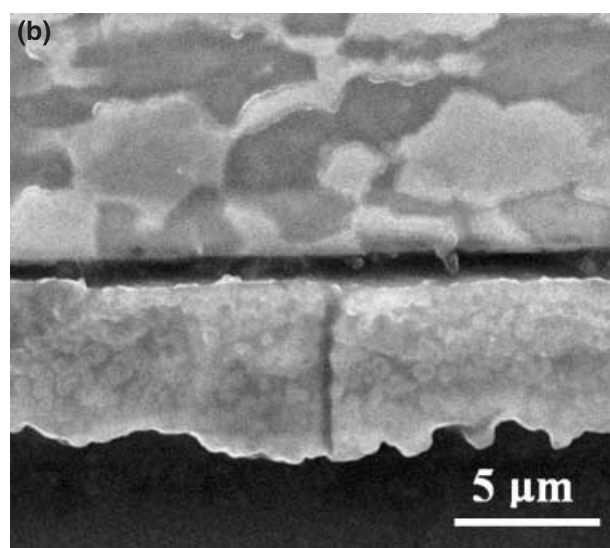
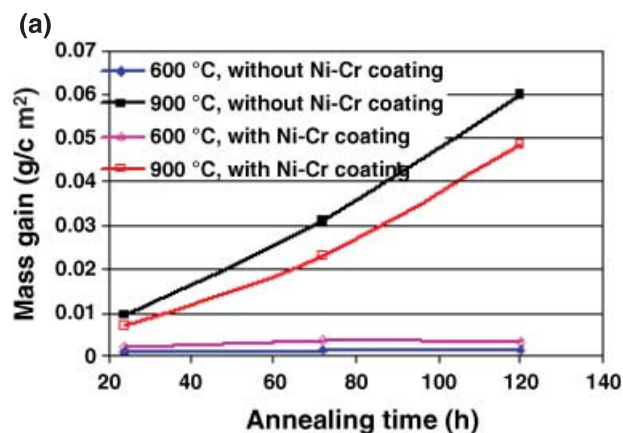


Fig. 1. (a) Mass gain data for cyclic oxidation of Ti–25Al–11Nb alloy and scanning electron micrographs of cross-sectional analysis of the external layer after exposure in air at 600 °C for 120 h of the sample (b) without and (c) with an Ni–Cr coating.

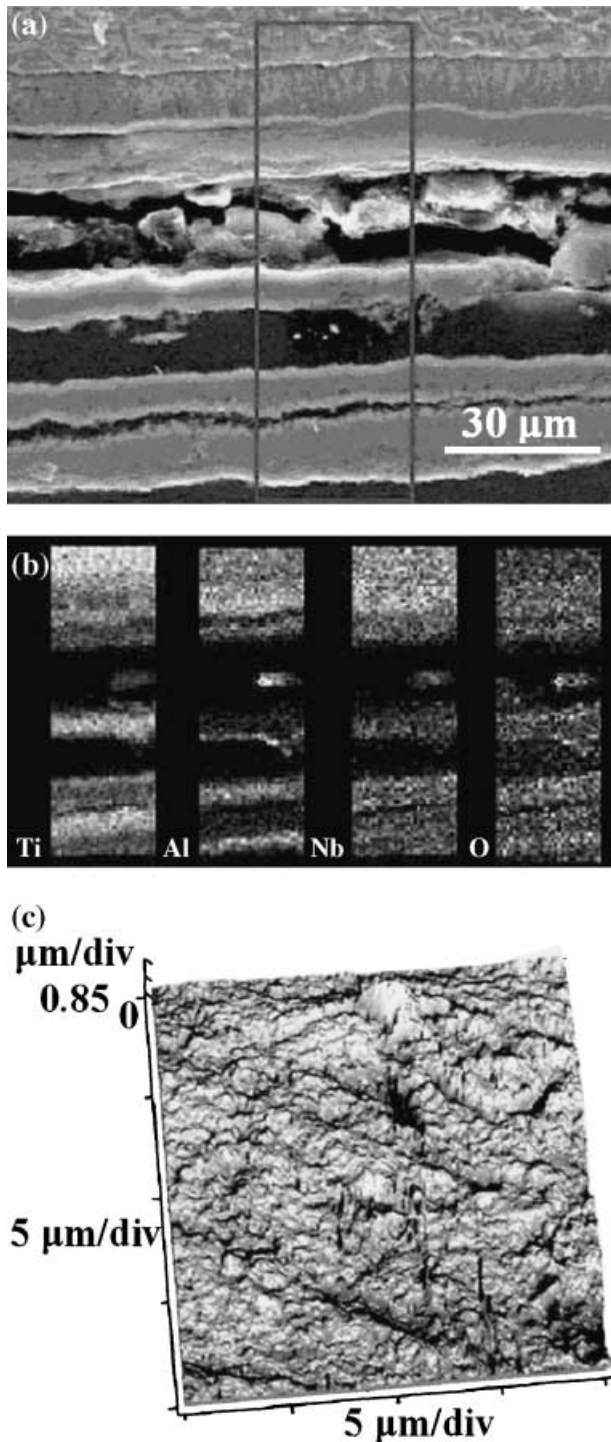


Fig. 2. Cross-sectional analysis of the external layer formed on an uncoated Ti-25Al-11Nb sample after cyclic oxidation at 900 °C in air for 120 h: (a) scanning electron micrograph; (b) energy-dispersive X-ray spectroscopy mapping (the same magnification as the scanning electron micrograph); (c) atomic force microscopy image.

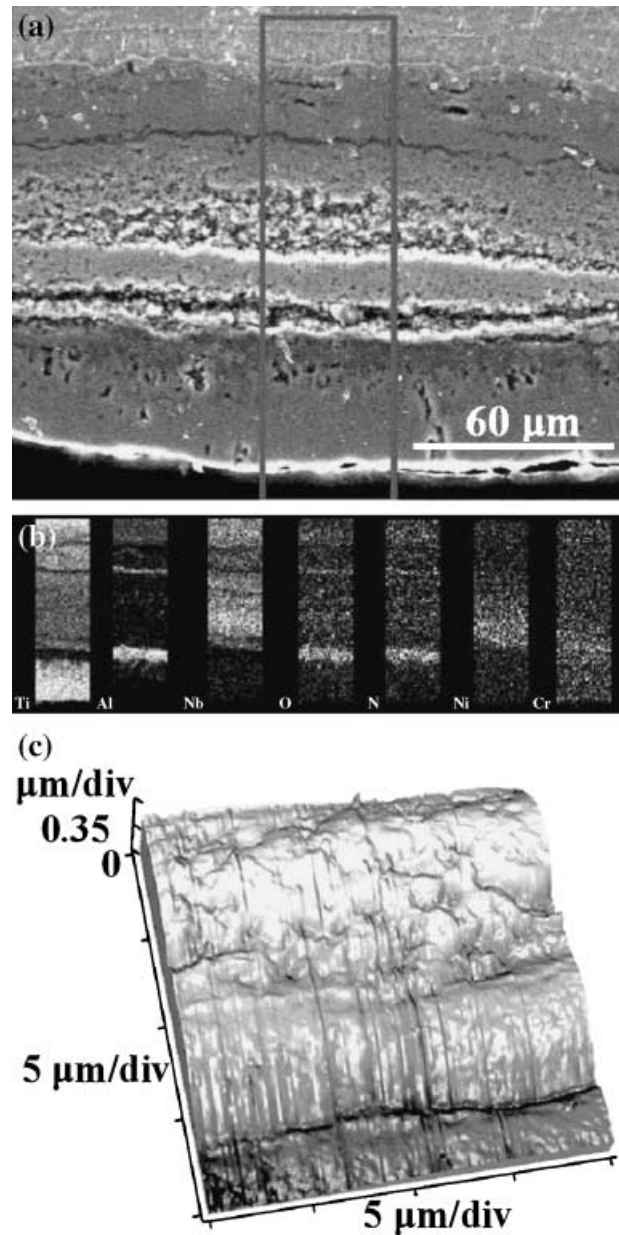


Fig. 3. Cross-sectional analysis of the external layer formed on a Ti-25Al-11Nb sample with an 80Ni-20Cr coating after cyclic oxidation at 900 °C in air for 120 h: (a) scanning electron micrograph; (b) energy-dispersive X-ray spectroscopy mapping (the same magnification as the scanning electron micrograph); (c) atomic force microscopy image.

layer, which was a mixture of TiO_2 and Al_2O_3 , had a thickness of 13–15 μm , and several small cracks near the interface could be seen. Beneath this layer, a 10–12- μm -thick layer with a lamellar structure could be distinguished. The thin Al_2O_3 platelets were present in this layer, running perpendicular to the matrix surface.

The coating improved the oxidation resistance of this alloy at 900 °C. Although the oxidation was still faster than that at 600 °C (Fig. 1a), an obvious reduction in mass gain could be

observed in the sample with the protective coating. Scanning electron microscopy and energy-dispersive X-ray spectroscopy analysis revealed that the formation of a continuous protective layer consisting of Cr and Ni oxides was effective in decreasing the external oxidation rate. The surface morphology of the oxide scale showed a particular dependence on the matrix microstructure (Taniguchi & Shibata, 1996). Namely, there was a flat area covered with a 20- μm -thick Al₂O₃ scale and the oxide mound illustrated in Fig. 3(a), which had a two-layer structure. The inner layer was Al-rich, whereas the porous and thicker outer layer was TiO₂ (Fig. 3b). The N enrichment in the Al₂O₃ layer indicated probable AlN formation in the scale. The nitride, acting as a barrier to some extent, was also observed in a diffusion zone beneath the coating. The suppression of external oxidation resulted in extensive internal oxidation. A very thick (~52 μm) oxidation-affected zone was layered with Ti- and Al-enriched regions. The Nb distribution in this zone was similar to that in the external scale. It also contained many pores and small cracks, so that these layers were not dense. An atomic force microscopy image of the TiO₂ region beneath the coating is shown in Fig. 3(c). It can be seen that the TiO₂ grains were coarser than those observed in the layers of oxidation scale formed on the uncoated sample (Fig. 2c).

Conclusions

In layers formed during exposure at both 600 °C and 900 °C, a discontinuous Al₂O₃ layer was detected, whereas TiO₂ was

the major oxide component. The remarkable improvement in oxidation resistance of the Ti₃Al alloy, even at 900 °C, was obtained using an 80Ni–20Cr protective coating, which promotes formation of Cr and Ni protective oxides.

Acknowledgements

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