High Temperature Oxidation of Ti–(45, 47)%Al–2%Mn–2%Nb–0.8 vol%TiB$_2$ Alloys

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The oxidation behavior of XD45 (Ti45Al2Mn2Nb–0.8 vol%TiB$_2$) and XD47 (Ti47Al2Mn2Nb–0.8 vol%TiB$_2$) alloys that were thermomechanically treated to have ($\gamma + \alpha$) duplex microstructures was studied between 1073 and 1273 K in air. XD47 displayed a little slower oxidation rate and better scale adherence than XD45. The oxide scales consisted primarily of an outer TiO$_2$ layer, an intermediate Al$_2$O$_3$-rich layer, and an inner (TiO$_2$ + Al$_2$O$_3$) mixed layer. Mn and Nb tended to segregate at the outer TiO$_2$ layer and the inner (TiO$_2$ + Al$_2$O$_3$) mixed layer, respectively. The outer layer grew primarily by the outward diffusion of Ti and Mn, and the inner mixed layer by the inward transport of oxygen. Dispersoids of TiB$_2$ oxidized to semiprotective TiO$_2$ and highly volatile B$_2$O$_3$ which evaporated. A small amount of TiN and Ti$_2$AlN formed during oxidation.

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1. Introduction

Near gamma titanium aluminides are being considered as potential replacements for superalloys and steel components in aerospace, automotive applications because of their high specific strength and melting points. The small addition of Nb and Mn, together with fine TiB$_2$ dispersoids, in two phase TiAl + (Ti$_3$Al) alloys was found to provide superior mechanical properties. Discontinuous reinforcement of TiB$_2$, which is an extremely hard and inert in titanium aluminides, led to grain refinement and increased the mean strength and fracture toughness without compromising other desirable mechanical properties.

On the other hand, Haanappel et al. recently studied the oxidation of the TiB$_2$-free Ti48Al2Mn2Nb alloy. The oxidation rate changed sensitively with the exposure temperature, and the scale was susceptible to spallation when compared to Ti48Al2Cr2Nb. The oxidation of as-cast XD45 (Ti45Al2Mn2Nb–0.8 vol%TiB$_2$) and XD47 (Ti47Al2Mn2Nb–0.8 vol%TiB$_2$) was investigated by Yoshihara et al. Niobium was detected in the inner oxide layer, while Mn was found in the outermost oxide layer. An enrichment of Nb at the scale-matrix interface was also observed, like TiB$_2$-free Ti48Al2Mn2Nb. However, the oxidation mechanism and the role of TiB$_2$-dispersoids in XD alloys were not properly studied. This study aims to describe the oxidation behavior of thermomechanically treated XD45 and 47 between 1073 and 1273 K in air. The results of the Pt-marker test and the TEM study on oxide scales were newly presented.

2. Experimental Procedure

As-cast XD45 and 47 alloys that were supplied by Howmet Corp. were hot-isostatically-pressurized at 1533 K for 14.4 ks under 172 MPa in order to eliminate casting porosity, and heat treated in the $\gamma + \alpha$ phase field at 1283 K for 36 ks followed by cooling in a static argon atmosphere to obtain very fine duplex microstructures that consisted of equiaxed and lamellar grains. After cutting into sizes of 10 × 5 × 5 mm$^3$, the thermomechanically treated alloys were ground on 1000 grit emery paper, ultrasonically cleaned in acetone and methanol, and oxidized isothermally and cyclically at 1073, 1173 and 1273 K in atmospheric air.

The mass changes during isothermal oxidation were continuously monitored as a function of time using a thermogravimetric analyzer (TGA). Cyclic oxidation was performed using a horizontal tube furnace. The test cycles involved exposing the specimens for 3.6 ks, cooling quickly to room temperature, measuring mass changes excluding spalled oxides, and returning them to the furnace for a total exposure of 216 ks (60 cycles). Marker experiments using fine platinum powders (1–7 μm) were also conducted to elucidate the oxide growth mechanism.

Following oxidation, the specimens were investigated by scanning electron microscope (SEM), electron probe microanalyzer (EPMA), X-ray diffractometer (XRD), and high-resolution transmission electron microscope equipped with an energy-dispersive-spectrometer (HR-TEM/EDS). The TEM specimens were glued onto a thin Si dummy plate using epoxy to preserve the oxide scale, mechanically polished, and ion milled to perforation.

3. Results and Discussion

The isothermal oxidation kinetics of XD45 and 47 alloys at 1073, 1173, and 1273 K are displayed in Fig. 1. Superimposed are the oxidation curves of Ti48Al2Cr2Nb, Ti48Al2Mn2Nb, and Ti48Al2Cr2Nb which were hot-extruded at 1493 K to have $\alpha_2/\gamma$ lamellas and $\gamma$-grains. Generally, the oxidation kinetics of the alloys approximately followed the familiar parabolic rate law, displaying an increase in mass gains with increasing the temperature. There were some discrepancies between the oxidation curves of Ti48Al2Cr2Nb in this study and those of the same compositional alloy at 1073 and 1173 K, which may be aroused...
partly from the scatter in the obtained small mass gains. Nevertheless, the oxidation resistance of XD47 was slightly better than that of XD45 owing to higher Al content. Interestingly, XD alloys displayed better oxidation behavior than Ti48Al2Cr2Nb or Ti48Al2Mn2Nb, despite the presence of TiB2 which oxidized to TiO2 and B2O3. It is noted that TiO2 is semi-protective due to relatively high growth rate, and B2O3 has little protectiveness due to high vapor pressure at high temperature. However, our study on TiAl-(3–10 mass%)TiB2 alloys indicated that the evaporation of B2O3, which could provide microscopic channels within the oxide scale, was not harmful to isothermal oxidation resistance. The TiB2 dispersoids beneficially promoted rapid formation of protective oxide scales by acting as oxide nucleation sites through the commonly known beneficial roles of dispersoids.

At 1073 K, XD45 and 47 had excellent scale adherence, with little scale spallation due to thin scale formation. However, they spalled recognizably above 1173 K, as depicted in Fig. 2. It is seen that the scale adherence deteriorates in the order of Ti48Al2Cr2Nb, XD47, and XD45, which was also confirmed from visual inspection on the oxide scales.

Fig. 1 Isothermal oxidation curves of the prepared alloys at 1073, 1173, and 1273 K in air. Ti48Al2Cr2Nb and Ti48Al2Mn2Nb were included for comparison.

Though the isothermal oxidation resistance was better, the cyclic oxidation resistance of XD alloys was poorer than that of Ti48Al2Cr2Nb. The harmful effects of volatilization and volume expansion owing to B2O3 formation may be partly responsible. The poor adherence of oxide scales that formed on Ti48Al2Mn2Nb at 1173 K and as-cast XD45 and 47 at 1143 K was reported previously. As did during isothermal oxidation, XD47 displayed better cyclic oxidation behavior than XD45 due primarily to the thinner scale formation.

The XRD analyses revealed that the oxide scales always consisted of TiO2 as the major phase, and Al2O3 as the minor one for both isothermally and cyclically oxidized XD alloys. A few typical diffraction patterns are shown in Fig. 3. Besides TiO2, Al2O3 and γ(TiAl) + α2(Ti3Al) matrix peaks, weak TiN and/or Ti2AlN peaks were additionally seen in Figs. 3(b) and (c). The strong matrix peaks shown in Fig. 3(c) were due to excessive scale spallation at 1273 K. Oxides of Nb, Mn, and B were never detected. The brittle layers of TiN and Ti2AlN, which normally exist at the scale-matrix interface, can initiate cracks. Previous studies showed that the ox-
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Fig. 4 EPMA cross-sectional image and corresponding line profiles of the scale formed after isothermal oxidation: (a) XD 45 at 1073 K for 1800 ks; (b) XD 45 at 1173 K for 360 ks; (c) XD 47 at 1173 K for 900 ks. Etched. A = TiO₂ layer, B = Al₂O₃-rich layer, and C = (TiO₂ + Al₂O₃) mixed layer.

Figure 4 shows typical EPMA results of cross-sectional scales formed on XD 45 and 47. The oxide scales formed on both alloys consisted primarily of an outer TiO₂ layer, an intermediate Al₂O₃-rich layer, and an inner, porous (TiO₂ + Al₂O₃) mixed layer. Micrometer-size, needle-like TiB₂ particles were distributed randomly in the matrix. The Al₂O₃ formation at the middle of the scale caused an aluminum deficiency underneath. Apparently, the Al₂O₃ layer was neither continuous nor dense enough to be protective so that rather thick scales were formed under the given oxidizing conditions. The scale-matrix interface was mechanically weak due partly to different volume expansion ratio and void formation during scaling. Mn tended to segregate at the outer oxide layer, while Nb preferred to reside at the inner mixed oxide layer.⁸,⁹ Enrichments of less active elements of Nb⁸,⁹ and Mn were frequently observed at the scale-matrix interface owing to the selective oxidation of more active elements of Ti and Al within the oxide scale. Boron was difficult to identify because of background noise. Our study on TiAl–(3–10 mass%)TiB₂ alloys however indicated that B₂O₃ escaped from the oxide scale during oxidation.¹⁰ The Pt marker placed prior to oxidation was located just above the intermediate Al₂O₃ layer (Fig. 4(b)). This demonstrated that the outer TiO₂ layer grew predominantly by outward diffusion of Ti interstitial ions, and the inner (TiO₂ + Al₂O₃) mixed layer by inward transport of oxygen ions. Like Ti, Mn tended to diffuse outwardly to a certain extent, while Nb did not, as was observed in Ti48Al2Mn2Nb.⁹ Therefore, it is suggested that the primary mode of ionic transport for the scale growth in XD alloys was not changed by the TiB₂ addition.

Figure 5 shows SEM morphological features of oxides formed on XD alloys. To trace TiB₂ oxidation, the specimens were oxidized after etching (Figs. 5(a)–(c)). As the oxidation progressed, the etched surface became smeared, and quite fine round oxide crystallites developed. It appeared that the dispersoid oxidized to fine TiO₂ crystallites, accompanied by B₂O₃ evaporation (arrow in Fig. 5(c)). In Fig. 5(d), the fast outward diffusion of cations to form the outer, coarse, rod-like TiO₂ crystals caused some void formation.¹³ The grains of the intermediate Al₂O₃-rich layer was coarser than those of the inner (TiO₂ + Al₂O₃) mixed layer.

Figure 6 shows the TEM images and the corresponding EDS spectra of the oxide scale formed on XD47. The EDS spot analyses employing a focal size of 3 nm enabled to analyze the composition of specific oxide grains. Figure 6(a) shows the outer, entangled arrays of TiO₂ grains that have dissolved Nb ions (Fig. 6(b)). As the oxidation progressed, all the oxide grains grew. Figure 6(c) shows the inner, (100–200) nm-size (TiO₂ + Al₂O₃) mixed oxide grains. These grains had dissolved Mn (Fig. 6(d)) and/or Nb ions, which would affect the oxide growth rate via doping effect. The Nb dissolution would suppress TiO₂ growth, and promote the formation of Al₂O₃⁸,⁹ whereas Mn²⁺ or Mn³⁺ having lower valencies than Ti⁴⁺ would increase the growth rate of TiO₂ to maintain electroneutrality.¹⁴,¹⁵ Beneath the oxide layer, a (Ti-enriched, Al-depleted) layer formed, because of preferential consump-
Fig. 5 SEM micrographs of the scales formed after isothermal oxidation: (a) XD 45 at 1073 K for 120 s; (b) XD 47 at 1173 K for 120 s; (c) XD 45 at 1173 K for 300 s; (d) XD 47 at 1173 K for 216 ks. (a)–(c) are top view, and (d) is the fracture surface.

tion of Al above (Fig. 6(e)). Clearly, the outward diffusion of Al was faster than Ti in the matrix. The matrix shown in Fig. 6(c) was dark owing to different ion-milling rates during TEM sample preparation.

4. Conclusion

The isothermal and cyclic oxidation resistance of XD47 was better than that of XD45 owing to higher Al content. These XD alloys displayed better isothermal oxidation but poorer cyclic oxidation behavior than Ti48Al2Cr2Nb. The oxide scales that formed on XD alloys consisted primarily of an outer TiO2 layer, an intermediate Al2O3-rich layer, and an inner (TiO2 + Al2O3) mixed layer. Alloying elements of Mn and Nb tended to segregate as dissolved ions at the outer TiO2 layer and the inner (TiO2 + Al2O3) mixed layer, respectively. Dispersoids of TiB2 oxidized to TiO2 and B2O3 which evaporated.

Acknowledgments

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REFERENCES