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Effect of temperature on oxidation behaviour of Ga-containing near-α Ti alloy

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ABSTRACT

Isothermal oxidation testing of a Ga-containing near-α Ti alloy was performed in air at 650, 700, and 750 °C for up to 500 h. Results revealed that the alloy oxidation kinetics followed a parabolic law at 650 °C and a parabolic–cubic law at 700 and 750 °C, while the abundance of Al_2O_3 in the oxide layers increased with temperature after the dissolution of Ga_2O_3 species in the Al_2O_3 phase. The activation energy of the α-case formation was close to the magnitudes obtained for conventional Ti alloys despite its temperature-dependent recrystallization near the oxide/metal interface at 700 and 750 °C.

1. Introduction

Near-α Ti alloys are attractive structural materials, which are used in high-temperature components in gas turbine engines due to their high strength-to-density ratios and excellent corrosion resistance [1]. Although increasing the service temperature of a gas turbine can improve its working efficiency and save kerosene, it also leads to the degradation of the Ti alloy components over time due to the O-containing gaseous environment [2,3]. The related degradation mechanisms involve the formation of rapidly growing non-protective oxide layers caused by the high chemical affinity of Ti to O [4,5] and embrittlement of the substrate zone due to the high solubility of O molecules (such an O-enriched substrate zone is commonly called α-case) [6–9]. The presence of α-case results in the deterioration of important mechanical properties of Ti alloys such as ductility, fracture toughness, and fatigue life.

The oxidation behaviours of Ti and Ti alloys at high temperatures have been studied by many researchers [10–21]. Kofstad et al. [10,11] systematically investigated the oxidation behaviour of pure Ti at various temperatures in different types of environments and found that its oxidation rate depended on temperature and time. In particular, the oxidation rate of Ti followed a logarithmic law at temperatures below 300 °C, a cubic law between 300 °C and 600 °C, and a parabolic law between 600 °C and 850 °C (which ultimately became a linear law after a long time). The effects of temperature and time on the oxidation behaviours of conventional Ti alloys such as Ti–6Al–4 V (Ti–64) [12–16], Ti–6Al–2Sn–4Zr–2Mo (Ti–6242) [5,6,17], IMI 834 [4,18,19], and other Ti-based alloys [18,20,21] have also been examined in detail. Frangini et al. [12] found that the oxidation rate of Ti–64 mainly followed a parabolic law between 600 °C and 700 °C but started to exhibit linear behaviour after 50 h of treatment at 700 °C (similar observations were reported by Guleryuz et al. [13]). Du et al. [14] reported the formation of a multilayered oxide-scale structure in Ti–64 between 650 °C and 850 °C and proposed its possible mechanism based on the reactivity of Ti and Al species towards O as well as the O partial pressure. Shenoy et al. [6] studied the oxidation behaviour of Ti − 6242 between 593 °C and 760 °C and found that its oxidation rate mainly followed a parabolic law up to 650 °C. Gaddam et al. [17] reported a transition of the oxidation rate of Ti–6242 from parabolic to linear behaviour at 700 °C. McReynolds et al. [5] and Gaddam et al. [17] quantitatively studied the α-case formation in Ti–6242 and found that the thickness of the α-case layer was a function of both temperature and time (in particular, its time dependence followed a parabolic relationship). The oxidation behaviours of the alloys IMI 834 [4,19], IMI 125 [4], TIME1100 [18], and Ti60 [20] were similar to that of Ti–6242.

The addition of α-stabilizing elements, such as Al, Ga, and Sn, in Ti alloys enhances their high-temperature strength via solid solution strengthening [22,23] and promotes the precipitation of the α_2 phase with the $D0_{19}$ structure, which results in dispersion strengthening and low ductility [22]. The Al equivalent (expressed in wt.%), which can be calculated using the formula $Al + 1/2 \times Ga + 1/3 \times Sn + 1/6 \times Zr + 10 \times O$ [21], has been utilized to evaluate the alloy ductility after creep exposure (thus, to avoid the embrittlement of previously studied near-α Ti alloys, their Al equivalents were less than 9). Sn, which is conventionally added to near-α Ti alloys, accelerates the growth of a TiO_2 layer and causes the spallation of oxides [21,24,25],

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Table 1
Chemical composition (wt.%), Al equivalent, and β transus temperature of TKT41 alloy.

Alloy	Ti	Al	Ga	Zr	Nb	Mo	Si	O	Al Eq.	T_β/°C
TKT41	81.8	7	3	6	1	1	0.2	0.093	10.4	995 ± 5

while the replacement of Sn with Ga leads to the dissolution of Ga species in oxide scales without their segregation at the oxide/substrate interface [21,26]. In our previous study [26], the replacement of Sn with Ga resulted in less weight gain than observed for IMI 834 and TIME1100, owing to the dissolution of Ga atoms in the Al_2O_3 layer, which might act as a barrier to O diffusion. In addition, unlike in conventional near-α Ti alloys, recrystallization was observed near the oxide/substrate interface in the Ga-containing Ti alloy during its isothermal oxidation at 750 °C after 500 h of exposure. However, the temperature dependencies of the oxidation behaviour and recrystallization of Ga-containing Ti alloys have not been elucidated in sufficient detail. In this study, the effects of temperature and time on the oxidation behaviour (especially on the oxidation reaction rate and α-case formation) of a Ga-containing near-α Ti alloy and the temperature dependence of its recrystallization process were examined.

2. Experimental procedure

A 1 kg ingot of the Ga-containing near-α Ti alloy TKT41 was produced via cold crucible levitation melting (its nominal chemical composition is listed in Table 1). The Al equivalent calculated using the formula Al + 1/2 × Ga + 1/3 × Sn + 1/6 × Zr + 10 × O [21] was set to 9.5 [26], and the obtained ingot was melted twice to enhance its compositional homogeneity. The cast ingot was β-forged at 1130 °C and then groove-rolled to a 90% reduction in the α + β region at 980 °C to form square rods with side lengths of 14 mm. The β transus temperature of TKT41 determined through the microstructural observations conducted after heat treatment at different temperatures was 995 ± 5 °C. After heat treatment at 970 °C for 1 h with air cooling followed by ageing at 700 °C for 2 h and subsequent air cooling, a bimodal microstructure containing silicide precipitates was obtained (see Fig. 1). The volume fraction of the equiaxed α phase estimated using ImageJ software was 62.9% [26].

Cylindrical samples for oxidation testing with diameters of 8 mm and heights of 4 mm were cut from the centres of the as-aged samples via wire electrical discharge machining. The surfaces of the specimens were finally polished using #800 SiC paper followed by ultrasonic cleaning in acetone. Isothermal oxidation testing was performed in air at 650, 700, and 750 °C. One sample was used for each temperature in the test. To perform the oxidation test for 500 h, (1) the sample-containing alumina crucible was removed from the furnace with air cooling, (2) the mass change of the sample was measured, and (3) the sample-containing crucible was put back into the furnace at 20, 45, 70, 90, 110, 140, 240, 340, and 500 h during the test. To measure the change of the α-case thickness, the aforementioned test was terminated at 20, 45, 90, 140, and 500 h at each temperature. The mass change of each sample was measured with an accuracy of ± 0.0001 g using a microbalance.

Microstructural characterization of the aged samples was performed using a focused ion beam scanning electron microscope (FIB-SEM, ZEISS AURIGA Laser, Carl Zeiss, Germany) at accelerating voltages of 5 kV and 15 kV. The samples for SEM observation were embedded in resin and polished with polishing paper and colloidal silica.

After oxidation testing, the constituent oxide phases were identified via X-ray diffraction (XRD) using an X-ray diffractometer (RINT2500, Rigaku, Japan) with Cu Kα radiation operated at a voltage of 50 kV and current of 300 mA. Before microstructural characterization, the oxidized samples were cold mounted, cut, and metallographically polished with polishing paper and colloidal silica. Hardness measurements were performed using a MMT–7 Matsuzawa Vickers microhardness tester at a load of 10 g and duration of 15 s. The cross-sectional microstructures of the oxidized samples were analysed via SEM and electron backscatter diffraction (EBSD) observations (performed with the EBSD module attached to the SEM equipment) at an accelerating voltage of 15 kV using an AMETEK EDAX Digiview 5 detector (USA).

3. Results and discussion

Fig. 2 shows the weight gains per unit surface area (ΔW/A) measured for the alloy samples oxidized at 650, 700, and 750 °C in air for up to 500 h, which are 0.72, 1.39, and 1.91 mg/cm^2, respectively. The obtained results indicate that the overall weight gain increased with both time and temperature. To compare the oxidation behaviour of the studied Ga-containing alloy with those of conventional alloys, it was assumed that the oxidation behaviour followed a parabolic law, which corresponded to Eq. (1) and was used to fit the data presented in Fig. 2:

$$\left(\frac{\Delta W}{A}\right) = \sqrt{k_p t}, \tag{1}$$

where k_p is the parabolic rate constant expressed in $g^2\,cm^{-4}\,s^{-1}$. The k_p values for the studied alloy are listed in Table 2 and are compared with the results obtained for other alloys in Fig. 3 [16,17,27]. The magnitudes of k_p calculated for the Ga-containing alloy are smaller than those obtained for other conventional Ti alloys, indicating that the former exhibited a lower oxidation rate. It is well known that the oxidation behaviours of Ti and Ti alloys depend on the oxidation temperature; hence, the obtained weight gain data were fitted using the following power law [12,14,17]:

$$\left(\frac{\Delta W}{A}\right)^n = k_n t, \tag{2}$$

where n is the reaction index, k_n is the reaction rate constant, and t is the time. Therefore, n could be obtained by performing regression

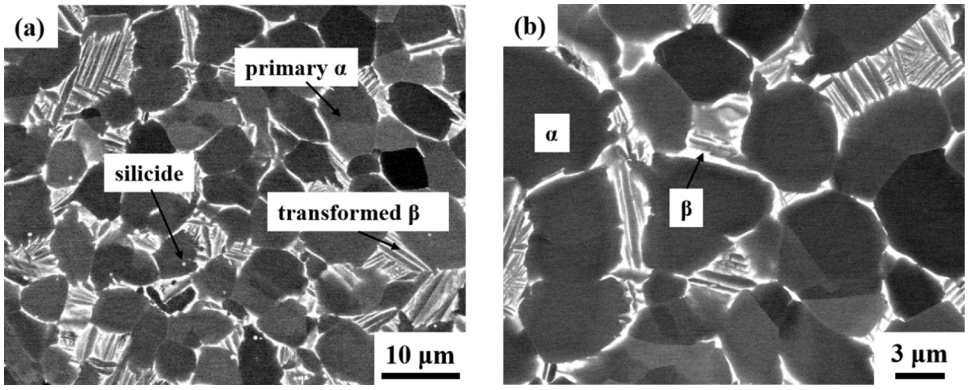

Fig. 1. Backscattered electron images of the microstructure of the heat-treated TKT41 alloy.