Effect of Zr on Microstructure and Oxidation Behavior of α and $\alpha + \alpha_2$ Ti-Al-Nb Alloys

Sae Matsunaga^{1,2}, Ai Serizawa¹ and Yoko Yamabe-Mitarai²

¹Shibaura Institute of Technology, Tokyo 135–8548, Japan

²High Temperature Materials Design Group, National Institute for Materials Science, Tsukuba 305–0047, Japan

To develop high-temperature Ti alloys, microstructure and oxidation behavior were investigated in Ti-(10,15)Al-2Nb-(1,2)Zr (at%) alloys. For reference, ternary Ti-15Al-2Zr alloy was also investigated. A single α phase exists in Ti-10Al-2Nb-(1, 2)Zr alloys; on the other hand, an α and α_2 two-phase was observed in Ti-15Al-2Nb-(1, 2)Zr alloys. Fine α_2 precipitates of about 10 nm were observed in the Ti-15Al alloys. The oxidation behavior of Ti-Al-Nb-Zr and Ti-Al-Zr ternary alloys was investigated to understand the effect of Zr on oxidation behavior at 1023 K. It was found that Zr improves the oxidation resistance of the α phase more effectively than Nb. TiO₂ was formed in all tested alloys. The addition of Zr drastically decreased the growth rate of TiO₂. It was also found that the addition of Nb improved adhesion of the oxide layer.
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1. Introduction

Ti alloys are light materials with almost half the density of Ni-based superalloys and steel. In addition to low density, Ti alloys possess good oxidation resistance and creep properties up to 873 K; hence, they are used for the blades and disks in compressors in aircraft engines in the temperature range between 673 and 873 K¹. However, above 873 K, the oxidation and creep resistance of Ti alloys decrease drastically¹; thus, it is important to improve the strength, creep resistance, and oxidation resistance above 873 K.

Generally, near α -Ti alloys with an hcp structure are used for high-temperature applications because of the limited slip plane. Solid solution hardening by Al, Sn and Zr and precipitation hardening by α_2 -Ti₃Al and/or silicide are used to improve the high-temperature strength and creep resistance of the α phase.

Oxidation behavior of conventional α -Ti alloys such as IMI 834 and Ti1100 was investigated, and the oxide scales of both alloys were found to consist of porous mixed oxides with a coarse-grained rutile TiO₂ growing at the outer surface². The oxidation kinetics of these alloys is dominated by TiO₂ formation². It was also found that the oxidation of Ti-6Al-4Nb followed linear-parabolic kinetics between 973 and 1123 K³. The oxide scale formed on Ti-6Al-4V consisted of alternating layers of Al₂O₃ and TiO₂. Al₂O₃ always formed at the external gas/oxide interface; on the other hand, TiO₂ always formed at the oxide/substrate interface³.

Alloying is one way to improve the oxidation resistance of α -Ti alloys. For example, Nb is found to improve the oxidation resistance of α -Ti^{4,5}. Nb impedes the growth of TiO₂ in Ti-1, 2 mass% (0.5, 1 at%)⁴ and Ti-5, 10 at%⁵. There have been many reports on the effect of Nb on α_2 -Ti₃Al and γ -TiAl^{5–7}. However, there are few investigations of the effect of Nb on α -Ti-Al alloys.

In our previous study, we investigated the oxidation behavior and phase equilibrium of Ti-Al-Sn-Nb quaternary alloys⁸. We found that the mass change during isothermal oxidation tests at 1023 K was smaller in the alloy with high Nb content.

We also found that Sn accelerated oxide growth. Since then, attempts have been made to design alloys with less Sn and more Nb. The phase equilibria and oxidation behavior of Ti-Al-Nb ternary alloys were also investigated to understand the effect of Nb on the α phase⁹. It was found that the α and α_2 two-phase region was smaller than that in the calculated ternary phase diagram¹⁰. In Ti-15Al-2Nb (at%), nano-scale α_2 precipitates were formed. The oxidation rate of the Ti-15Al alloy was decreased to less than 10% of its original value by the addition of 2 at% of Nb.

To design new high-temperature Ti alloys, we also focus on Zr because Zr is expected to strengthen α -Ti alloys. Furthermore, Zr is known to be a neutral element, which means that the β transus is almost flat after the addition of Zr, and hence the α phase is stabilized by the addition of Zr. Stabilizing of the α phase is very important when using Ti alloys at high temperatures. The goal of the present study was to determine whether Zr improves the oxidation resistance of α Ti alloys. Although it has been found that the oxidation resistance of TiAl is improved by the addition of Zr¹¹, the effect of Zr on the oxidation behavior of α -Ti alloys has not yet been ascertained. Therefore, in the present study, we focused on α -Ti-10Al-2Nb alloys (at%) and $\alpha + \alpha_2$ two-phase Ti-15Al-2Nb alloys to investigate the effect of adding Zr on the microstructure and the oxidation resistance of Ti-Al-Nb alloys. The oxidation behavior of Ti-Al-Nb-Zr alloys was compared with that of Ti-Al-Zr and binary Ti-Al alloys^{8,9} and ternary Ti-Al-Nb alloys^{8,9}.

2. Experimental Procedure

Twenty-gram alloy ingots of Ti-(10,15)Al-2Nb-(1,2)Zr and Ti-15Al-2Zr alloys (at%) were melted by arc melting. The nominal composition and analyzed composition using an energy dispersive x-ray spectroscopy (EDS) of the ingots are listed in Table 1. Each ingot was melted five times to ensure compositional homogeneity. The ingots were solution treated at 1273 K for 2 h and air cooled to room temperature, followed by ageing at 973 K for 24 h and air cooling to room

Table 1 Compositions of prepared alloys.

Composition (at%)	Ti (at%)	Al (at%)	Nb (at%)	Zr (at%)
Ti-10Al-2Nb-1Zr (Ti-6Al-4Nb-2Zr, mass%)	88.7	8.50	1.83	0.93
Ti-10Al-2Nb-2Zr (Ti-6Al-4Nb-4Zr, mass%)	87.9	8.07	1.95	2.05
Ti-15Al-2Nb-1Zr (Ti-9Al-4Nb-2Zr, mass%)	84.4	12.8	2.02	0.87
Ti-15Al-2Nb-2Zr (Ti-9Al-4Nb-4Zr, mass%)	83.9	12.8	1.56	1.77
Ti-15Al-2Zr (Ti-9Al-4Zr, mass%)	84.8	12.9	-	2.19

temperature.

Microstructural characterizations of the aged samples were carried out using X-ray diffraction (XRD), field emission gun scanning electron microscopy (FEG-SEM, JEOL JSM 7000F or 7001F) and transmission electron microscopy (TEM, JEOL JEM 2000FX). The XRD measurement was carried out for a plate with dimensions of $8 \times 10 \times 1$ mm at room temperature on a RINT2500 X-ray diffractometer using Cu $K\alpha$ radiation, operated at 50 kV and 300 mA. Samples for SEM observation were embedded in resin and polished using polishing papers and SiO_2 . The specimens for TEM observation were prepared by electrolytic polishing of thin, 3-mm-diameter discs, punched from thin sections with a thickness of $\sim 50 \mu\text{m}$. Electrochemical polishing was carried out in an electrolyte containing 5% perchloric acid, 35% n-butyl alcohol and 60% methanol at 20 V, using a twin jet polisher. The temperature of the electrolyte was maintained at 253–263 K, using liquid nitrogen, throughout the process of electrochemical thinning.

Isothermal oxidation tests were performed for a $4 \times 4 \times 1$ mm sample at 1023 K in laboratory air. Each sample was put in an alumina crucible, and the weight change was measured together with the weight of the crucible. The samples in alumina crucibles were removed from the furnace after 24, 48, 72, 144, 168, 192, and 208 h of exposure. The mass change of each sample was measured using a microbalance with an accuracy of ± 0.0001 g. After oxidation testing, the structure of the oxide was investigated using XRD. The cross-sectional microstructures of the oxidized samples were also observed by SEM, and line analysis was performed to measure the range of composition using EDS attached to the FEG-SEM to identify oxides.

3. Results

3.1 Constituent phase

To identify the phase, X-ray diffraction analysis was performed at room temperature; the X-ray diffraction patterns are shown in Fig. 1. The diffraction patterns were based on the α phase in all tested alloys. α_2 - Ti_3Al is the ordered structure of the α phase, and can be distinguished from the α phase by the existence of peaks at 26° and 30° , however, neither peak was observed. Moreover, there are no obvious diffraction peaks from the β phase, which often forms near α Ti alloys.

Since microstructures with clear contrast were not found

Fig. 1 X-ray diffraction patterns of (a) Ti-10Al-2Nb-1Zr, (b) Ti-10Al-2Nb-1Zr, (c) Ti-1Nb-1Zr-5Al-1Zr, (d) Ti-1Nb-1Zr-5Al-2Zr, and (e) Ti-15Al-2Zr after heat treatment at 1273 K for 3 h following by air cooling.

Fig. 2 Two bright-field images and diffraction patterns of (a) Ti-10Al-2Nb-1Zr and (b) Ti-10Al-2Nb-2Zr.

by SEM observation, TEM observation was performed to investigate whether the α_2 phase forms within the α phase. In Fig. 2(a) and (b), the bright-field images of Ti-10Al-2Nb-1Zr and Ti-10Al-2Nb-2Zr represent a single phase, and contrast resulting from any precipitates was not observed. The α grain size of Ti-10Al-2Nb-1Zr was several tens of μm and elongated grains with a width of several μm and length of several tens of μm were observed in Ti-10Al-2Nb-2Zr. The microstructure of Ti-10Al-2Nb-2Zr is similar to the typical lamellar structure with thin β phase obtained in α Ti alloys. Although the existence of the β phase was not clear in this study, it is possible that a thin β phase surrounded the α phase. Diffraction patterns of these alloys showed a single α phase; superlattice spots from an α_2 phase were not observed. In the binary phase diagram as shown in Fig. 3¹²⁾, the composition of Ti-10Al at 1273 K is in the α phase. The present result indicates that the α phase is stable even with the addition of 2 at% Nb and 2 at% Zr. On the other hand, the diffraction patterns of Ti-15Al-2Nb-2Zr and Ti-15Al-2Zr clearly revealed the superlattice spots from the α_2 phase as shown in Fig. 4(a) and (b). Dark-field images of these alloys taken using the superlattice spots indicated by the white circles clearly showed fine α_2 particles smaller than 10 nm. It is known that an α and α_2 two-phase region exists in Ti-15Al-2Zr¹³⁾, and the present re-

dependencies, as shown in Fig. 5(b). Comparing Ti-15Al and Ti-15Al-2Nb, the addition of Nb decreased the mass gain by less than 50% of its original value. Moreover, the addition of Zr into Ti-15Al-2Nb decreased the mass gain compared with simple Nb addition. However, the weight gain of Ti-15Al-2Nb-(1,2)Zr was almost the same as that of Ti-15Al-2Zr. This indicates that the oxidation behavior was governed by Zr rather than Nb in quaternary alloys. Comparing Ti-15Al, Ti-15Al-2Nb, and Ti-15Al-2Zr, the weight gain was 6.5, 2, and 1 mg/cm², respectively. The addition of Zr decreased the weight gain by about 85%, which was greater than the 70% reduction caused by Nb. In the case of Ti-15Al alloys, the weight gain of alloys by the addition of Nb and/or Zr was less than that of Ti-6242, indicating an improvement of oxidation resistance for the alloys with an α and α_2 two-phase structure.

Comparing Ti-10Al and Ti-15Al, the weight gain of Ti-15Al was smaller than that of Ti-10Al, indicating the effect of Al. However, this difference became small when the amounts of Nb and Zr increased. The weight gains of Ti-10Al-2Nb-2Zr and Ti-15Al-2Nb-2Zr were almost the same although the weight gain after 200 h of oxidation decreased slightly in Ti-15Al-2Nb-2Zr. Further investigation is necessary to determine whether this decrease of weight gain indicates a change in the mechanism of oxidation or simply an experimental error.

It is suggested that Nb and Zr have the following effects on Ti-Al alloy:

1. The addition of Nb alone improves the oxidation resistance of Ti-Al.
2. The addition of Zr alone improves the oxidation resistance of Ti-Al much more than the addition of Nb alone.
3. Furthermore, the addition of Nb to Ti-Al-Zr alloys did

not change their oxidation resistance.

To identify the oxide formed on the surface, X-ray diffraction analysis was carried out on the surfaces of the oxidized alloys. The X-ray diffraction patterns are shown in Fig. 6. The major peaks were assigned to rutile-TiO₂ in all tested alloys. The peaks of α -Ti phase were also detected from the substrate. The peaks of other oxides such as Al₂O₃, Nb₂O₅, or ZrO₂ were not detected in the X-ray diffraction patterns.

The cross section of alloys oxidized at 1023 K for 208 h are shown together with a line analysis from the sample surface to the interior of the samples in Fig. 7 and Fig. 8. The thickness of the observed oxide layer of Ti-10Al-2Nb-1Zr, Ti-10Al-2Nb-2Zr, Ti-15Al-2Nb-1Zr and Ti-15Al-2Nb-2Zr was around 2–4 μ m, showing no large difference. This is reasonable because the weight gains of these alloys were almost

Fig. 6 X-ray diffraction patterns of (a) Ti-10Al-2Nb-1Zr, (b) Ti-10Al-2Nb-2Zr, (c) Ti-15Al-2Nb-1Zr, (d) Ti-15Al-2Nb-2Zr, and (e) Ti-15Al-2Zr after isothermal oxidation testing at 1023 K.

Fig. 7 Cross-section microstructure and line analysis of the oxide layer for (a) Ti-10Al-2Nb-1Zr and (b) Ti-10Al-2Nb-2Zr.

Fig. 8 Cross-section microstructure and line analysis of the oxide layer for (a) Ti-15Al-2Nb-1Zr, (b) Ti-15Al-2Nb-2Zr and (c) Ti-15Al-2Zr.

the same after oxidation for 208 h. However, in Ti-15Al-2Zr, the oxide layer was not observed clearly, indicating spalling of the oxide layer as shown in Fig. 8(c). The thickness of the oxide layer of Ti-10Al, Ti-10Al-2Nb, Ti-15Al, and Ti-15Al-2Nb was 40, 10, 40, and 5 μm in our previous study⁹). Compared with binary and ternary alloys, it is clear that growth of the oxide layer was drastically suppressed in quaternary alloys. On the other hand, the addition of Zr by itself causes the oxide layer to spall as shown in Ti-15Al-2Zr. The addition of both Nb and Zr together improved the adhesion of the oxide layer; this indicates that Nb not only reduces oxidation but also improves oxide adhesion.

In Ti-10Al-2Nb-1Zr, a thin outer gray layer, a thin dark layer and a thick inner gray layer were observed as shown in Fig. 7(a). Line analysis of the thick inner gray layer gave a Ti:O ratio of about 1:2, indicating the formation of TiO_2 . In TiO_2 , large cracks were observed. The bottom diagram indicates enlarged scale line analysis. In TiO_2 , the concentrations of Al, Nb and Zr were less than 1 at%. The outer dark layer included a higher concentration of Al. It is assumed that titanium oxide and aluminum oxide formed together in the outer layer. The concentration of Ti increased again in the thin outer gray layer suggesting formation of TiO_2 . Small particles with similar contrast in the outer layer were observed in the TiO_2 layer, suggesting the formation of particles of Al_2O_3 . Therefore, oxide layers were divided into three parts: 1) gray outer layer (mainly TiO_2), 2) dark outer layer (mainly Al_2O_3) and 3) gray inner layers ($\text{TiO}_2 + \text{Al}_2\text{O}_3$ particles). The Nb and Zr content was very small, less than 1 at% in both Al_2O_3 and TiO_2 layers as shown in the bottom diagram. The oxide layers with the same structure were observed in Ti-15Al-2Nb-2Zr as shown in Fig. 8(b). In Ti-10Al-2Nb-2Zr, an outer layer of Al_2O_3 was not observed, but the structure of oxide was again same as oxide in Ti-10Al-2Nb-1Zr as shown in Fig. 7(b). In Ti-15Al-2Nb-1Zr and Ti-15Al-2Zr, the oxide layer was not clearly observed because of spallation of the oxide layer; this indicates low adhesion of oxide after Zr addition as shown in Fig 8(a) and (c). These observations indicated that the forma-

tion of oxide is the same for all tested quaternary alloys; that is, TiO_2 and Al_2O_3 formed layer by layer, although in some alloys the outer thin TiO_2 was missing because of spallation.

4. Discussion

4.1 Formation process of oxide

Oxide formation in Ti alloys is well known from previous studies^{3,7}). Oxygen diffuses into pure Ti, forming a wide oxygen diffusion zone; and TiO_2 forms in the outer layer. As the Al content increases, the thickness of the oxygen diffusion zone decreases and a multilayer oxide consisting of TiO_2 and Al_2O_3 is formed. The number of the TiO_2 and Al_2O_3 layers increases with increasing exposure time and temperature³).

In this study, the phase constituents and microstructures are different in Ti-10Al-2Nb-(1, 2)Zr and Ti-15Al-2Nb-(1, 2)Zr alloys; that is, the α single phase exists in Ti-10Al alloys and the α_2 phase forms as fine precipitates in the α phase in Ti-15Al alloys. Even with this difference in phase constituents and microstructures, the formation of oxide is similar in both alloys. The TiO_2 was the main oxide with small particles of Al_2O_3 and a thin layer of Al_2O_3 or TiO_2 of about 100 nm formed on this mixed layer in some cases. A composition of Nb and Zr less than 1 at% represents that solid solution of Nb and Zr to TiO_2 is very small or fine Nb and Zr oxides distribute in TiO_2 although Nb oxide or Zr oxide was not detected in the oxide layer in either composition analysis or in X-ray diffraction analysis. A zone that had been depleted of Ti, Al, Nb, and Zr was observed under the oxide layer as shown in Figs. 7 and 8. This indicates that outward diffusion of ions of Ti, Al, Nb, and Zr occurred.

The process of formation of oxide in α Ti alloys with/without α_2 precipitates is believed to be as follows (Fig. 9): Initially, TiO_2 forms preferentially on the surface of Ti alloy because of the higher activity of Ti compared to Al (stage 1)³). Then, outward diffusion of Ti^{4+} and Al^{3+} cations occurs through the TiO_2 , and TiO_2 grows together with a small amount of Al_2O_3 (stage 2). At this stage, Nb^{5+} and Zr^{4+} cat-

Fig. 9 Formation process of oxide in α Ti alloys.

ions also diffuse outward, but the amount of outward diffusion of Nb and Zr is small. Then, Nb^{5+} and Zr^{4+} dissolve into TiO_2 or form fine Nb or Zr oxides in TiO_2 . After the growth of TiO_2 , a thin layer of Al_2O_3 starts to form—perhaps because the supply of Ti was delayed or the activity of Al became high at the air/ TiO_2 interface as shown in Ref. 3) (stage 3). However, the Al content in Ti alloys is low, and the formation of stable, thick Al_2O_3 is difficult. Then, TiO_2 again forms on the Al_2O_3 (stage 4). In Ti-6Al-4V, similar oxidation behavior was observed; that is, an Al_2O_3 layer formed outside of the TiO_2 , and a TiO_2 layer and Al_2O_3 layer formed alternately³⁾.

4.2 Effect of Zr and Nb

In our study, the weight gain of ternary Ti-Al-Nb and Ti-Al-Zr alloys during the oxidation test was smaller than that of conventional Ti-6242 alloys as shown in Fig. 5. The addition of Zr to the Ti-Al-Nb alloys decreased the weight gain even more (Fig. 5(b)). Our results indicate that the addition of Zr to Ti-Al and Ti-Al-Nb alloys is a very effective way to improve oxidation resistance. Although there are not many studies on the effects of Zr on oxidation behavior of α -Ti alloys, several investigations on the effect of Zr on the oxidation behavior of pure Ti or TiAl have been reported^{11,14)}. The mass gain of Ti-Zr and Ti-Nb binary alloys was investigated and found to decrease with increasing Zr content. The suppression of oxide growth of Nb to pure Ti was more effective than Zr. It is well known that TiO_2 is a non-stoichiometric compound and mainly grows by inward diffusion of oxygen through oxygen vacancies¹⁵⁾. It is believed that the Nb^{5+} cation decreases the number of oxygen vacancies to maintain the electro-neutrality in TiO_2 because of the higher valance of Nb compared to Ti. As a result, suppression of oxide growth occurs¹⁵⁾. On the other hand, since the valance of Zr (Zr^{4+}) is the same as that of Ti (Ti^{4+}), the decrease of oxygen vacancies is considered to be smaller than in the case of Nb, resulting in less suppression of oxide growth. However, in our study, Zr addition to Ti-Al alloys was effective to suppress oxide growth. If Al^{3+} , with a smaller valance than Ti^{4+} , is substituted in TiO_2 , oxygen vacancies will be increased to maintain the electro-neutrality.

However, it is well known that Al addition suppresses the formation of TiO_2 . It is said that if Al^{3+} occupies interstitial positions, oxygen vacancies will decrease¹⁶⁾. The existence of Al in TiO_2 is believed to change the electrical field in the TiO_2 ; as a result, the behavior of Zr^{4+} and Nb^{5+} is also changed and Zr^{4+} will decrease oxygen vacancy in TiO_2 . Although further investigation is necessary to understand the role of Zr clearly, at least it can be said that the effect of Zr addition is different in Ti-(10–15)Al alloys and in pure Ti. Zr in TiO_2 suppresses the growth rate of TiO_2 in Ti-(10–15)Al alloys. On the other hand, the effect of Zr on TiAl is enhancement of formation of Al_2O_3 and suppression of growth of TiO_2 , which is different mechanism for improvement of oxidation resistance in Ti-10–15Al alloys¹⁴⁾.

5. Conclusions

(1) A single α phase was formed in Ti-10Al-2Nb-(1, 2)Zr while α and α_2 phases were formed in Ti-15Al-2Nb-(1, 2)Zr; however, the formation of oxide was similar regardless of differences in the constituents and microstructures.

(2) The addition of Zr by itself greatly improved the oxidation resistance of Ti-(10–15)Al alloys. Also, the addition of Nb together with Zr improved the adhesion of the oxide layer.

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