Solid Solution Hardening and Precipitation Hardening of α_2 -Ti₃Al in Ti-Al-Nb Alloys

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Microstructure and mechanical properties of Ti-Al-Nb-based alloys were investigated as they are important in the development of new generation high temperature Ti alloys due to good oxidation resistance. The alloy compositions Ti-15Al-2Nb (to obtain α_2 precipitates) and Ti-15Al-2Nb-0.5Si (at%) (to obtain solid-solution hardening by Si) were selected. Heat treatment at 1000°C after forging and rolling at 900°C transformed the β phase to α phase and α' martensite during cooling. By heat treatment at 900°C, a single α phase was obtained in both alloys. The α_2 phase was formed by aging treatment at 600 and 700°C of Ti-15Al-2Nb and at 600, 700, and 800°C of Ti-15Al-2Nb-0.5Si. Compressive strength was investigated for samples heat treated at 900°C with a single α phase and those aged at 600, 700, 800°C with α_2 precipitates. The solid solution hardening effect of Si was found at all test temperatures. Precipitation hardening effect by α_2 precipitates was also observed in both alloys and the effect improved with Si addition. Peaks of precipitation hardening were obtained at 300°C in both alloys; the precipitation hardening effect decreased with increase of test temperature above 300°C. It is suggested that a shearing mechanism occurs up to 300°C, which changes to a bypass mechanism above 450°C. [doi:10.2320/matertrans.MAW201707]

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1. Introduction

Near α -Ti alloys with mainly hcp phases are used as blades and disks in high-pressure compressors for jet engines because they are lightweight and exhibit excellent oxidation resistance and creep properties at temperatures up to 540°C¹⁾. Above 540°C, the oxidation resistance of the Ti alloy becomes lower than those of Ni-based superalloys. In long-term use at high temperature, Ti alloys form α -cases at the surface due to diffusion of oxygen. This brittle α -case leads to drastic reduction in ductility and fatigue strength¹⁾. Hence, Ni-based superalloys are still used in the hottest parts of the compressor. The densities of Ni-based superalloys are twice those of Ti alloys. If Ti alloys can replace Ni-based superalloys, the weight of jet engines will reduce, resulting in improved heat efficiency.

Therefore, improving oxidation resistance while maintaining proper creep properties is considered important. Generally, near α -Ti alloys contain Al, Zr, Sn, Mo, Nb, and Si to improve the high temperature strength and creep resistance using the solid solution strengthening of Al, Zr, Mo, and Sn, and the precipitation strengthening by α_2 -Ti₃Al and/or silicide¹⁻³⁾. Since 1954, there were many efforts to develop Ti alloys that can survive at high temperature. Several alloys such as Ti-6Al-4V, Ti-811, Ti-6242S, and IMI834 were developed, whose application temperatures are about 300, 400, 520, and 600°C, respectively¹⁾. Oxidation behaviors of conventional α -Ti alloys have been investigated⁴⁻⁷⁾. For example, in Ti-1100 and IMI 834, it was suggested that controlling the formation rate of oxide scales (mainly rutile TiO₂)⁴⁾ is important.

In our previous study, we investigated the oxidation behavior and phase equilibria of Ti-15Al-Sn-Nb (Sn + Nb =

5 at%) quaternary alloys (at%)⁸⁾ because Nb is known to improve the oxidation resistance of pure Ti^{6,7)} and Sn is known as an α stabilizer^{1,2)}. For reference, the oxidation behavior of Ti-16Al (at%), Ti-15Sn, Ti-15Al-5Nb, Ti-15Al-5Sn, and Ti-6242 were also investigated. Mass changes of the quaternary alloys during isothermal oxidation testing at 750°C were smaller than that of the conventional near α -Ti alloy, and Ti6242 and Ti-16Al binary alloys. The growth rate constant decreased with increase of Nb content and that of Ti-15Al-5Nb was lowest among the tested alloys. These results indicate that Nb addition improved oxidation resistance. On the other hand, the mass change of Ti-15Al-5Sn was larger than those of Ti-16Al and Ti-6242. Mass change of Ti-15Sn increased drastically indicating acceleration of oxidation with the addition of Sn.

New alloys with less Sn and more Nb have been attempted. First, the phase equilibria and oxidation behaviors of Ti-Al-Nb ternary alloys were investigated⁹⁾. We found that nano-scale α_2 precipitates formed in Ti-15Al-2Nb (at%) and oxidation resistance were saturated above 2 at%Nb. The effects of Zr on microstructure and oxidation behavior were also investigated¹⁰⁾. It was found that Zr improved oxidation resistance and Nb improved adhesion of the oxide layer, indicating the addition of both Zr and Nb is effective in improving oxidation resistance.

In this paper, mechanical properties were investigated in Ti-Al-Nb alloys with promising oxidation resistance. Ti-15Al-2Nb was selected because nano-scale α_2 homogeneously precipitated inside α phases, leading to precipitation hardening. However, it is also expected that precipitation hardening by only the α_2 phase in simple ternary alloys is not sufficient to strengthen alloys. Then, the solid solution hardening effect of Si is investigated in Ti-15Al-2Nb-0.5Si in this paper. Si is also known to improve the oxidation resistance of Ti alloys^{11,12)}, so Si should not be a harmful ele-

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ment. By comparing Ti-15Al-2Nb and Ti-15Al-2Nb-0.5Si, the effect of Si on microstructure, solid solution hardening of Si, and precipitation hardening by α_2 are clearly distinguished.

2. Experimental Procedure

Ingots (1.1 kg) of α -Ti alloys with nominal compositions Ti-15Al-2Nb and Ti-15Al-2Nb-0.5Si (at%) were produced using the cold-crucible levitation melting method. The ingots were α -forged at 900°C and groove-rolled to 18% reduction at 900°C in the α region to form square rods 14 mm in size. Small sections of the sample, with thickness of 6 mm, were cut from the square rod and subjected to two types of heat-treatments. The first was heat-treatment at different temperatures from 900 to 1050°C at 50°C intervals for three hours, followed by water quenching. The second was aging-treatment to form α_2 precipitates; samples were heat-treated at 900°C for three hours and were subsequently aged at 800, 700, and 600°C for five hours, followed by water quenching, as shown in Fig. 1.

Specimens $2.5 \times 2.5 \times 5.5 \text{ mm}^3$ in size were cut from the heat-treated bars for compression tests. The compression test was carried out at the strain rate of $3 \times 10^{-4}/\text{s}$. Samples for the compression test were held at the test temperature for 20 min before testing.

Microstructural characterizations of the heat-treated samples were performed using X-ray diffraction (XRD, RINT2500), field emission gun scanning electron microscopy (FEG-SEM, JEOL JSM 7000F or 7001F with electron backscatter diffraction EBSD), and transmission electron microscopy (TEM, JEOL JEM 2000-FX). X-ray diffractometry was carried out on a plate with dimensions $8 \times 10 \times 1 \text{ mm}^3$ at room temperature using Cu-K α radiation operated at 50 kV and 300 mA. Samples for microstructure observation were embedded in resins and polished using polishing paper and SiO₂. Disk samples 3 mm in diameter were prepared using a Twinjet electropolisher. Electrochemical polishing was executed in an electrolyte containing 5% perchloric acid, 35% n-butyl alcohol, and 60% methanol at 20 V.

3. Results

3.1 Microstructure and transformation temperature

Figures 2 and 3 show back scattered electron images of samples heat-treated at 900, 950, 1000, and 1050°C after forging and rolling. As shown in Fig. 2 (a), the Ti-15Al-2Nb alloy heat-treated at 900°C was an equiaxed single phase of

about 10 μm , determined by EBSD measurement. At 950°C, as shown in Fig. 2 (b), a phase with bright contrast began to form from grain boundaries of equiaxed grains with particle diameter of about 10 μm . At 1000°C, the amount of phase with bright contrast increased; grain boundaries and lamellar structures that penetrated into crystal grains were observed in the bright contrast phase (Fig. 2 (c)). At 1050°C (Fig. 2 (d)), martensite structure—which often forms by transformation from β to α phase in Ti alloys—was confirmed. For the Ti-15Al-2Nb-0.5Si alloy, the same structure as Ti-15Al-2Nb was observed after heat treatment, as shown in Fig. 3. The particles with dark contrast in the microstructure were introduced artificially during polishing and were not precipitates. It indicates that both alloys were found to have transformation temperatures between 1000 and 1050°C. The X-ray diffraction patterns of Ti-15Al-2Nb shown in Fig. 4 were identified as the α phase for all heat treatments between 900 and 1050°C. Similar peaks were detected for Ti-

Fig. 2 Back scattered electron images of Ti-15Al-2Nb after heat treatment at (a) 900°C, (b) 950°C, (c) 1000°C, and (d) 1050°C for 3 hours followed by water quench.

Fig. 3 Back scattered electron images of Ti-15Al-2Nb-0.5Si after heat treatment at (a) 900°C, (b) 950°C, (c) 1000°C, and (d) 1050°C for 3 hours followed by water quench.

Fig. 1 Schematic diagram of heat treatments.

15Al-2Nb-0.5Si indicating formation of the α phase. The structures shown in Fig. 2 (c) and Fig. 3 (c) are obviously two phases with different compositions. However, the peaks of other phases, e.g., β or α'' phases were not detected. The peak observed at 45° was not identified as either a β or α'' phase, because the angle does not match the peak angle of β (38° , 56° , 69° , 82°) or α'' (37° , 42° , 54° , 62°). The crystal structure was investigated using EBSD and the bright contrast phase was found to have hcp structure. Since the martensitic structure was observed in the region of bright contrast, it is considered the phase was the martensitic α' phase which is the hcp structure obtained by quenching β phase¹³. The ratio of α' phase obtained from Figs. 2 and 3 by image analysis is shown in Table 1. The volume fractions of the α' phase of two alloys were almost the same. Further, Si is considered to have neutral behavior for α and β at the heat treatment temperatures.

3.2 Microstructure after aging

Back scattered electron images of Ti-15Al-2Nb and Ti-

15Al-2Nb-0.5Si subjected to aging treatment are shown in Fig. 5. The grain size of each sample was about $10\ \mu\text{m}$, and large differences were not observed between the different aging treatments in the two alloys. α_2 precipitation was not observed in the SEM images. The particles with dark contrast in the microstructure were introduced artificially during polishing and were not precipitates. X-ray diffractometry was performed to verify the existence of α_2 precipitates. However, peaks of the α_2 phase were not detected in samples besides Ti-15Al-2Nb heat-treated at 700°C , as shown in

Table 1 Volume fraction (%) of α' in Ti-15Al-2Nb and Ti-15Al-2Nb-0.5Si after heat treatment at 900, 950, 1000, and 1050°C for 3 hours followed by water quench (%).

Temperature($^\circ\text{C}$)	Ti-15Al-2Nb	Ti-15Al-2Nb-0.5Si
900	0	0
950	1.5	0.9
1000	13	10
1050	100	100

Fig. 4 X-ray diffraction patterns of (a) Ti-15Al-2Nb and (b) Ti-15Al-2Nb-0.5Si after heat treatment for 3 hours followed by water quench.

Fig. 5 Back scattered electron images of (a)–(c) Ti-15Al-2Nb and (d)–(f) Ti-15Al-2Nb-0.5Si aged at (a), (d) 600°C , (b), (f) 700°C , (c), (f) 800°C for 5 hours after solution treatment at 900°C for 3 hours followed by water quench.

Fig. 6. Therefore, microstructure observation was performed using TEM. Figures 7 and 8 show the dark field images and diffraction patterns of Ti-15Al-2Nb and Ti-15Al-2Nb-0.5Si. Superlattice reflection from the α_2 phase was clearly observed in the electron diffraction patterns of both alloys, except for the Ti-15Al-2Nb alloy subjected to aging treatment at 800°C. This indicates that the α_2 phase did not form and only a single α phase formed with aging treatment at 800°C. In the dark field image using α_2 phase superlattice reflection

Fig. 6 X-ray diffraction patterns of Ti-15Al-2Nb and Ti-15Al-2Nb-0.5Si after aging at 600°C, 700°C, and 800°C for 5 hours followed by water quench.

(Fig. 8), the α_2 phase glowed with bright contrast and precipitation of the α_2 phase was confirmed homogeneously. The size of the α_2 phase was about 15 nm after aging treatment at 600°C. In addition, it was found that large precipi-

	Ti-15Al-2Nb		Ti-15Al-2Nb-0.5Si	
900°C 3h		α		α
900°C 3h 600°C 5h		$\alpha+\alpha_2$		$\alpha+\alpha_2$
900°C 3h 700°C 5h		$\alpha+\alpha_2$		$\alpha+\alpha_2$
900°C 3h 800°C 5h		α		$\alpha+\alpha_2$

Fig. 7 Diffraction patterns of Ti-15Al-2Nb and Ti-15Al-2Nb-0.5Si.

Fig. 8 Dark field images of (a), (b) Ti-15Al-2Nb and (c)–(e) Ti-15Al-2Nb-0.5Si aged at (a), (c) 600°C, (b), (d) 700°C and (e) 800°C for 5 hours after solution treatment at 900°C for 3 hours followed by water quench.

tates formed as the aging treatment temperature increased; α_2 phase having a size of about 35 nm was generated during 800°C aging treatment. On the other hand, precipitation of silicide was not found even with TEM observation.

3.3 Mechanical properties

Figure 9 shows the compression test results of Ti-15Al-2Nb and Ti-15Al-2Nb-0.5Si. In Ti-15Al-2Nb-0.5Si (Fig. 9(b)), the strengths of single α phase samples prepared by heat-treatment at 900°C were the lowest among all tested temperatures. In other words, strengths of samples with an α_2 phase were higher than those of samples with only an α phase, indicating a precipitation hardening effect. Among the samples with an α_2 phase, the strength of samples aged at 700°C was the highest and the strength of samples aged at 600°C was the lowest. In Ti-15Al-2Nb, a similar behavior was observed, as shown in Fig. 9 (a). Samples aged at 800°C had a single α phase and the strength was similar to that of samples heat-treated at 900°C, which was the lowest among the tested alloys. Higher strength was observed in samples with α_2 phases aged at 600 and 700°C than at other test temperatures, indicating a precipitation hardening effect. In Ti-15Al-2Nb-0.5Si and Ti-15Al-2Nb, strengths of samples aged at 700°C were higher than those of samples aged at 600°C. However, this trend was not clear at room temperature and at test temperatures above 600°C.

To clarify the solid solution hardening effect by Si, the difference between the strength of samples without the α_2 phase was compared. That is, the difference between the strengths of Ti-15Al-2Nb aged at 800°C after solution treatment at 900°C ($\sigma_{\text{no-si}}$) and Ti-15Al-2Nb-0.5Si heat-treated at 900°C (σ_{si}) ($\Delta\sigma = \sigma_{\text{si}} - \sigma_{\text{no-si}}$) was plotted as a function of test temperature in Fig. 10 (a). The solid solution hardening effect by Si was clear at test temperatures between room temperature and 450°C, but the effect was small at room temperature and above 600°C. To clarify the α_2 precipitation hardening effect, the difference between the strength of aged samples with α_2 phases (σ_{α_2}) and the strength of samples with a single α phase and without α_2 phase (σ_{α}) ($\Delta\sigma = \sigma_{\alpha_2} - \sigma_{\alpha}$) was plotted as a function of test temperature in Fig. 10(b). A large precipitation hardening effect was obtained at temperatures between 300 and 450°C and the effect became small at room temperature and above 600°C. This indicates another strengthening mechanism is necessary above 600°C to further strengthen the alloys. Precipitation hardening of α_2 was larger in alloys with Si than the alloys without Si.

4. Discussion

4.1 Phase equilibrium

Table 2 indicates the volume fraction of α_2 phase calcu-

Fig. 9 0.2% proof stress by compression test of (a) Ti-15Al-2Nb and (b) Ti-15Al-2Nb-0.5Si.

Fig. 10 (a) Solid solution hardening effect by Si and (b) precipitation hardening effect.

lated using Thermo-Calc (Data base: TI-DATA-v3). It shows the α_2 phase of 2% precipitated by heat treatment at 800°C in Ti-15Al-2Nb and the α_2 phase of 12% precipitated in Ti-15Al-2Nb-0.5Si indicating Si stabilizes α_2 formation. In our study, α_2 was not observed with TEM in Ti-15Al-2Nb aged at 800°C. This is considered due to small volume fraction of α_2 . On the other hand, α_2 was clearly observed in Ti-15Al-2Nb-0.5Si. Our results also support that α_2 formation is stabilized by the addition of Si.

4.2 Precipitation hardening

As shown in Fig. 10, precipitation hardening by α_2 precipitate was large between 300 and 450°C and it was fairly small at the test temperatures of room temperature and 600°C (or higher). Similar behaviors were reported in Ti-Al and Ti-Al-Si¹⁴⁾. The peaks of the yield stress and 0.1% proof stress were obtained around 300°C. TEM observation indicated the cutting mechanism of α_2 precipitates by paired dislocations up to 300°C. During the cutting of α_2 precipitates, the leading dislocation destroys the order of the α_2 precipitate resulting in the formation of an antiphase domain boundary (APB). Then, the trailing dislocation restores order by removing the APB. However, when deformation progresses at 300°C, the trailing dislocation encounters a restored particle due to diffusion and has to be cut by the formation of APBs. This causes increase of resistance to dislocation movement at 300°C. Increase of stress due to cutting of α_2 precipitates was estimated at 80 MPa by Gysler *et al.*¹⁴⁾, using the Gleiter and Hornbogen model¹⁵⁾. In our case, the peak of the precipitation hardening effect was found at 300°C and precipitation hardening at 300°C was twice (or more) that at room temperature. Hence, it is considered that the same deformation mechanism occurs in Ti-15Al-2Nb-0.5Si and Ti-15Al-2Nb alloys.

After precipitation hardening peaked, it decreased with increasing test temperature, as shown in Fig. 10 (b). This is considered due to a change in deformation mechanism, i.e., shearing mechanism to bypass mechanism. TEM observations of deformed Ti-Al at 500 and 600°C by Gysler and Weissmann¹⁴⁾ indicated a bypass mechanism of the particles. The transition from the particle cutting mechanism to the bypass mechanism occurs by reducing the critical resolved shear stress (CRSS) for the secondary slip system with increase in deformation temperature. When the magnitudes of the CRSS in the primary and secondary slip systems become comparable above 500°C, dislocations can move from the primary slip plane to the secondary plane easily.

Precipitate size also affects the deformation mechanism¹⁵⁾. The increase in stress by the bypass mechanism is shown as $Gbf^{1/2}r^{-1}$, where G is the shear modulus, b is

Burgers vector, f is the volume fraction, and r is the diameter of particle. On the other hand, increase in stress by the shearing mechanism is shown as $Gb^{-1/2}|\varepsilon|^{3/2}f^{1/2}r^{1/2}$, where ε is the lattice misfit between the matrix and precipitates. Then, the critical precipitate size (r_c) to transit from shearing to the bypass mechanism is shown as $r_c = b/|\varepsilon|$. Using $b = 3 \times 10^{-10}$ m and $\varepsilon = 2.5 \times 10^{-2}$ (estimated from the lattice parameters of α and α_2 ¹⁶⁾), r_c is roughly estimated to be about 12 nm. The observed α_2 size in our study is smaller than 12 nm at 600 and 700°C or comparable size at 800°C; hence, they are small enough to undergo the shearing mechanism. However, at elevated temperature, these small precipitates are easily bypassed when primary and secondary slip systems work together. This is the reason the stress reduced with increase in test temperature.

The effect of aging temperature on precipitation hardening was clearly observed. Samples aged at 700°C showed the highest effect; those aged at 800°C showed the second highest effect; those aged at 600°C exhibited the smallest effect (Fig. 10(b)). The stress increase by the shearing mechanism is represented as $Gb^{-1/2}|\varepsilon|^{3/2}f^{1/2}r^{1/2}$. In Ti-Al-Nb, the volume fraction of α_2 decreases with an increase in aging temperature. On the other hand, the α_2 precipitate size increases with an increase in aging temperature. Figure 11 represents the concentration change of the α and α_2 phase in Ti-Al-Nb alloys calculated by Thermo-Calc. The concentration of Al and Nb in the α phase increased with an increase in aging temperature. However, they are almost same in the α_2 phase between 600 and 800°C. In the Ti-Al-Nb-Si alloy, the concentration of Al and Nb was close to that of Ti-Al-Nb alloy. Si tended to distribute higher in the α_2 phase and the concentration increased with increase in temperature. However, the amount of distribution is very small; thus, the Si effect is neglected in this discussion. With an increase in Al and Nb in the α phase along with an increase in aging temperature and almost constant Al and Nb concentrations in the α_2 phase, it is expected that the lattice parameters of α and α_2 become close each other and the lattice misfit ε will become small with an increase in aging temperature. The highest precipitation hardening effect should appear by balancing these three effects at 700°C.

Another reason is considered for the concentration change in the α phase by formation of the α_2 phase. The precipitation hardening effect was obtained by subtracting the

Table 2 Volume fractions (%) of phases in Ti-15Al-2Nb and Ti-15Al-2Nb-0.5Si at arbitrary temperatures calculated using Thermo-Calc.

Temperature(°C)	Ti-15Al-2Nb		Ti-15Al-2Nb-0.5Si	
	α	α_2	α	α_2
600	0.679	0.320	0.636	0.354
700	0.792	0.208	0.726	0.265
800	0.980	0.020	0.876	0.117

Fig. 11 Concentration change in α and α_2 phase for aging temperature.

strength of the alloy without the α_2 phase in this study. The Al content of the α phase without an α_2 phase is about 15 at%. However, that of the α phase with an α_2 phase is less than 15 at%, as shown in Fig 11. This indicates higher strength in the α phase without an α_2 phase than that of the α phase with α_2 phase. This may cause an underestimation of precipitation hardening, especially at 600°C because the difference of Al content becomes large at 600°C rather than 700 and 800°C. One reason for the lower precipitation hardening of the sample aged at 600°C may be a result of the changing Al content in the α phase.

Precipitation hardening of Ti-15Al-2Nb-0.5Si was larger than that of Ti-15Al-2Nb at most test temperatures, even with similar precipitate sizes and volume fractions of α_2 . It is suggested that Si addition increases the strength of the α_2 phase.

4.3 Solid solution hardening

As shown in Fig. 10 (a), solid solution hardening by Si was observed at all temperatures tested. However, the dependence of test temperature on solid solution hardening was not systematic. Solid solution hardening decreased from room temperature to 300°C, but increased to 600°C and decreased again to 650°C. In a previous report¹⁷⁾, it was suggested that solid solution hardening by Si is greater at higher temperature. Our results may support their findings.

In Fig. 9(a), the strength of Ti-15Al-2Nb aged at 900°C was higher than the strengths of samples with α_2 precipitates. In the previous study, although no superlattice spot was found, very weak superlattice maxima could be observed in the Kikuchi lines¹⁸⁾. This is shown as the evidence of fine α_2 precipitates, although they could not obtain dark-field images of the α_2 precipitate. Considering the high strength of Ti-15Al-2Nb aged at 900°C, a fine α_2 phase that is difficult to observe via TEM may be formed during cooling from 900°C, although superlattice spots from the α_2 phase were not observed.

5. Conclusions

(1) The microstructure and mechanical properties of Ti-15Al-2Nb and Ti-15Al-2Nb-0.5Si (at%) were investigated.

(2) α_2 precipitates were obtained by aging Ti-15Al-2Nb at 600 and 700°C and Ti-15Al-2Nb-0.5Si at 600, 700, and 800°C. However, silicide formation was not found in Ti-15Al-2Nb-0.5Si.

(3) The solid solution hardening effect by Si was found at all test temperatures.

(4) Precipitation hardening effect by the α_2 phase was observed at all test temperatures. Precipitation hardening greatly affected the samples at 300 and 450°C, but was ineffective at room temperature and above 600°C.

(5) The shearing mechanism was observed up to 300°C and it changed to the bypass mechanism above 450°C.

(6) Precipitation hardening effect was increased by adding Si.

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