Effect of Oxygen Content on Microstructure and Mechanical Properties of Cast and HIP'ed γ TiAl Alloys

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To clarify the inherent effect of oxygen content on mechanical properties of cast and HIP'ed γ TiAl alloys, two series of alloys containing an extremely low level (0.008 mass% to 0.013 mass%) and a medium level (0.051 mass% to 0.083 mass%) of oxygen were prepared. Aluminum contents of each series of alloys were varied from 44.4 to 50.0 at%. Beside these series of alloys, Ti-48 at%Al alloys containing different amounts of oxygen from 0.009 mass% to 0.230 mass% were prepared. In tensile test at room temperature, no marked ductility improvement was observed even though reducing the oxygen content below 0.01 mass%. Microstructures of the studied alloys consisted of equiaxed γ and lamellar form grains and the volume fractions of lamellar form grains and α_2 phase increased with increasing oxygen content. The 0.2% proof stresses of the alloys were analyzed by the rule of mixtures by regarding the alloys as a kind of composite material consisting of equiaxed γ and lamellar form grains. The ductility depended on the volume fraction of lamellar structure and exhibited superior ductility at around 20 vol%. Tensile properties of the alloys were strongly controlled by the microstructural factors. The oxygen content affects it through changing microstructures. In the Ti-Al phase diagram, the $\alpha(\alpha_2) + \gamma$ two phase region was expanded toward the aluminum rich side along with the increase of oxygen content, which resulted in increasing the Al content and decreasing the hardness of the γ phase.

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I. Introduction

TiAl alloys have been recognized as an attractive high-temperature structural material because of the low density, high strength and excellent oxidation resistance at high temperature. One of the most difficult problems preventing this material from extensive practical use is its poor ductility at room temperature. Since it has been found that the Ti-48 at%Al alloy with duplex microstructure consisting of equiaxed γ phase and ($\alpha_2 + \gamma$) lamellar structure exhibits relatively higher ductility than the single-phase γ alloy⁽¹⁾, extensive investigations with respect to the ductility improvement and its mechanism have been made on the titanium rich γ TiAl alloys⁽²⁾⁻⁽¹¹⁾. Some causes have been proposed concerning ductility enhancement by formation of duplex microstructure⁽⁶⁾⁻⁽¹¹⁾. One is that the α_2 phase constituting lamellar structure absorbs oxygen from the γ phase and improves ductility of the γ phase, i.e. the so-called oxygen scavenging effect⁽⁶⁾⁽⁷⁾. Recent studies performed by atom-probe field ion microscopes confirmed that the α_2 phase absorbed a large amount of interstitials contained in the γ TiAl alloys⁽¹²⁾⁽¹³⁾. Several investigations have been carried out concerning the effect of oxygen content on mechanical properties of γ TiAl alloys. Kawabata *et al.* showed that the high puri-

ty Ti-48 at%Al alloy containing 0.038 mass% oxygen exhibited superior ductility⁽¹⁴⁾. Sakamoto *et al.* reported that the ductility could be enhanced along with decreasing oxygen content up to 0.021 mass% in the as-cast material refined and melted in an electron beam remelting furnace⁽¹⁵⁾. On the other hand, it has become a common knowledge that the mechanical properties of γ TiAl alloys are significantly affected by microstructural factors⁽⁵⁾⁻⁽⁸⁾⁽¹¹⁾⁽¹⁶⁾⁻⁽¹⁸⁾. Therefore, the inherent effect of oxygen on ductility of γ TiAl alloys should be investigated and discussed separately from the microstructural factors. In this study, the cast and HIP'ed γ TiAl alloys containing extremely low oxygen below 0.01 mass% were prepared and their tensile properties were investigated. Especially, we focused on analyzing quantitatively the influence of microstructural factors on the strength and elongation, and consequently, the inherent effect of oxygen content.

II. Experimental Procedure

In this study, two levels of oxygen content in γ TiAl alloys were prepared: one was the alloys containing an extremely low level of oxygen ranging from 0.008 to 0.013 mass%, and the other is the alloys containing a medium level of oxygen from 0.051 to 0.083 mass%. Besides these series of alloys, Ti-48 at%Al alloys containing different amounts of oxygen from 0.009 to 0.230 mass% were prepared.

Three-steps melting processes were taken to prepare

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the melting stocks for the alloys containing an extremely low level of oxygen below 0.02 mass%. In the primary melting, ingots with a mass of 300 g were prepared by using an arc melting furnace with a non-consumable electrode in an argon atmosphere. The raw materials used were sponge titanium containing about 0.05 mass% oxygen and aluminum bricks of 99.99% purity. In the secondary melting, these ingots were melted by an electron beam (EB) remelting furnace for deoxidation. Deoxidation from the molten alloys of the melting stocks took place accompanied by aluminum vaporization during EB remelting under a high vacuum of 1×10^{-4} torr⁽¹⁵⁾. Then, the plate-shaped ingots with a width of 140 mm, a length of 250 mm and a thickness of 12 mm were obtained from EB remelting. After removing their surface layers, the plates were cut into small chips. Then as the final melting process, the chips were melted in an arc melting furnace under argon atmosphere to adjust the aluminum content to the desired level. Consequently the round shape ingots with a diameter of 45 mm, a height of 13 mm and a mass of 80 g were obtained.

For the alloys containing more than 0.05 mass% oxygen, the melting stocks were melted and cast into the round shape ingots by using an arc melting furnace in argon atmosphere. The raw materials used were the same as the alloys with an extremely lower level of oxygen. The oxygen content was controlled by addition of TiO₂ powder.

An experimental casting apparatus was used to simulate precision casting of γ TiAl alloys. The apparatus consisted of an arc melting furnace with a non-consumable electrode on the top side and a casting unit on the bottom side. The round-shape melting stocks were melted again in a copper mold with the center hole in the top side. The molten alloys were dropped into the casting unit through the center hole by gravity force, the mold being made from graphite with the shape of 10 mm diameter and 60 mm length. The oxygen pick-up during remelting and casting was less than 0.003 mass%. All the cast bars were subsequently HIP'ed at 1373 K for 4 h under the pressure of 196 MPa.

The chemical compositions of γ TiAl alloys prepared by the above procedures are listed in Table 1. These were analyzed in HIP'ed bars. The oxygen contents were varied from 0.009 to 0.230 mass% for Ti-48 at% alloys. For the alloys containing an extremely low level (0.008 mass% to 0.013 mass%) and a medium level (0.051 mass% to 0.083 mass%) of oxygen, the aluminum contents were varied from 44.4 to 50.0 at%.

Tensile test specimens with the gage portion of 4 mm in diameter and 10 mm in length were machined from the HIP'ed bars. Tensile tests were performed at ambient temperature and with an initial strain rate of 5×10^{-4} s⁻¹. Tensile elongation was evaluated from the plastic strain measured by an extensometer.

Microstructural identification was carried out by optical microscopy and scanning electron microscopy equipped with the EPMA apparatus. The volume fraction of the lamellar structure was evaluated by means of

Table 1 Chemical composition of studied alloys.

	Alloy name	Al(at%)	O(mass%)
Ti-48 at%Al alloys	48Al-ELO	47.8	0.009
	48Al-B	47.9	0.034
	48Al-O1	47.8	0.125
	48Al-O2	47.6	0.230
Alloys with an extremely low level of oxygen	44.5Al-ELO	44.4	0.008
	45Al-ELO	44.9	0.013
	45.5Al-ELO	45.4	0.013
	46Al-ELO	46.3	0.013
Alloys with a medium level of oxygen	50Al-ELO	50.0	0.011
	46Al-MO	45.9	0.083
	47Al-MO	46.8	0.051
	47.5Al-MO	47.5	0.075
	48.5Al-MO	48.4	0.072
	49Al-MO	49.1	0.052

measuring the area fraction of lamellar form grains in back scattered electron images. The volume fraction of α_2 phase was calculated quantitatively from the integrated intensity of the specific Bragg peaks of α_2 and γ phases measured by an X-ray diffractometer; This is a usual procedure to measure the volume fraction of retained austenite in steel.

III. Results

Figure 1 shows the effect of oxygen content on the 0.2% proof stress and elongation of Ti-48 at%Al alloys. The strength increases rapidly with an increase in oxygen content up to 0.125 mass% and levels off with a further increase in oxygen content. On the other hand, the elongation increases initially as the oxygen content rises. After it exhibits a maximum value at 0.034 mass%, however, it decreases again with a further increase of oxygen. It should be noted that no marked ductility improvement is observed even though reducing the oxygen content below 0.01 mass%. The microstructures at the center portion of HIP'ed bars are shown by the back scattered electron images in Fig. 2. In this figure, the α_2 (Ti₃Al) and γ (TiAl) phases are represented by the bright plates and the gray or black region, respectively. All Ti-48 at%Al alloys exhibit a duplex microstructure consisting of equiaxed γ grains and lamellar structure. It is clearly observed that the volume fraction of lamellar form grains increases with increasing oxygen content. The lamellar structure with substantially coarse spacing is partially observed in the alloys with lower oxygen content. It appears that the coarse lamellar structure was formed during HIP'ing at 1373 K. Figure 3 shows the volume fractions of lamellar form grains and the α_2 phase as a function of oxygen content. Initially both factors increase rapidly with increasing oxygen content and then tend to increase gradually in a high range of oxygen contents.

Effects of aluminum content on the tensile properties in two series of the alloys containing the extremely low and medium levels of oxygen are shown in Fig. 4. In both

Fig. 1 Tensile properties of Ti-48 at%Al alloys as a function of oxygen content. (a) shows elongation and (b) shows 0.2% proof stress.

alloys, the strength increases with decreasing aluminum content. At the same aluminum content, the alloys with a medium level of oxygen are higher in strength than the alloys with an extremely low level of oxygen (Fig. 4(a)). In contrast to the ductility of the alloys with a medium level of oxygen which shows a monotonous increase with increasing aluminum content, the alloys with an extremely low level of oxygen has a peak value of elongation at 44.9 at% aluminum (Fig. 4(b)). However, no marked ductility improvement is again brought by reducing the oxygen content below 0.01 mass%. Figure 5 shows that the microstructural differences between the alloys containing the extremely low and medium levels of oxygen.

Fig. 3 Volume fraction of lamellar form grains and α_2 phase in Ti-48 at%Al alloys as a function of oxygen content.

Figure 6 shows the volume fraction of lamellar form grains and the α_2 phase as a function of aluminum content. It is observed that the alloys with a lower level of oxygen have small amounts of the volume fractions of both the lamellar form grains and the α_2 phase in a given aluminum content.

IV. Discussion

Although reduction in oxygen content below 0.01 mass% resulted in no marked ductility improvement, the tensile strength significantly depended on oxygen content. It has been well recognized that the tensile properties of γ TiAl alloys were affected markedly not only by chemical composition but also by microstructural factors. As shown in Figs. 3 and 6, the microstructure was strongly affected by the oxygen content. Therefore the effect of microstructural factors on the tensile properties should be analyzed in order to clarify the inherent effects of oxygen content on the mechanical properties of γ TiAl alloys.

Figure 7 shows the relationships between the 0.2% proof stress and the volume fraction of lamellar form

Fig. 2 Back scattering electron images of cast and HIP'ed Ti-48 at%Al alloys. Oxygen content; (a) 0.009 mass%, (b) 0.034 mass%, (c) 0.125 mass%.

Fig. 4 Effect of aluminum content on tensile properties of the alloys containing an extremely low and a medium level of oxygen. (a) shows 0.2% proof stress and (b) shows elongation.

Fig. 5 Back scattered electron images of cast and HIP'ed γ TiAl alloys. The upper and lower row represents the alloys with an extremely low and a medium level of oxygen, respectively. Aluminum content; (a) 45.4 at%, (b) 47.8 at%, (c) 50.0 at%, (d) 45.9 at%Al, (e) 47.5 at%, (f) 49.1 at%.

Fig. 6 Effect of aluminum content on volume fractions of lamellar form grains and α_2 phase for the alloys containing an extremely low and a medium level of oxygen. (a) shows the volume fraction of α_2 phase and (b) shows the volume fraction of lamellar form grains.

Fig. 7 0.2% proof stress as a function of volume fraction of lamellar form grains.

Table 2 Vickers hardness of equiaxed γ and lamellar form grains.

	Alloy name	Hardness of γ grain	Hardness of lamellar grain
Ti-48at%Al alloys	48Al-ELO	292	416
	48Al-B	281	441
	48Al-O1	249	446
	48Al-O2	210	447
Alloys with an extremely low level of oxygen	44.5Al-ELO	290	450
	45Al-ELO	290	463
	45.5Al-ELO	282	441
	46Al-ELO	295	422
	50Al-ELO	278	410
Alloys with a medium level of oxygen	46Al-MO	259	435
	47Al-MO	286	441
	47.5Al-MO	265	445
	48.5Al-MO	262	442
	49Al-MO	278	443

grains for all the alloys investigated here. For two series of the alloys containing an extremely low and a medium level of oxygen, the strength is proportional to the volume fraction of lamellar form grains. This result indicates that the strength is mostly controlled by the volume fraction of lamellar form grains. For Ti-48 at%Al alloys, however, this relationship begins to deviate above the 0.125 mass% oxygen level; this corresponds to the results of Figs. 1 and 3 that the strength increment comes to level off in spite of the monotonous increase of the volume fraction of lamellar form grains.

Table 2 summarizes the Vickers hardnesses of equiaxed γ and lamellar form grains in all the alloys measured under a load of 0.098 N. In the alloys containing the extremely low and medium levels of oxygen, there are no large differences in hardness of the lamellar form grains except for a somewhat lower value in the alloys with lower oxygen and higher aluminum contents (46Al-ELO, 48Al-ELO, 50Al-ELO).

In our previous study⁽¹⁹⁾, the microstructural effects on the tensile properties of the cast and HIP'ed Ti-48 at% Al-2 at%X (X=Cr, Mn, V, Nb, Ta and Hf) alloys with

duplex microstructures having about from 20 to 60 vol% lamellar form grains were investigated. We found that the aluminum content and the addition of substitutional alloying elements varied markedly the microstructural factors such as the volume fraction of lamellar form grains and lamellar spacing, and the strength of the alloys was strongly controlled by these microstructural factors. The hardness of lamellar form grains was proportional to the reciprocal root of lamellar spacing which was measured by transmission electron microscope. In this study, it appears that the low hardness in the three alloys, 46Al-ELO, 48Al-ELO and 50Al-ELO, is brought about by coarse lamellar spacing as shown in Figs. 2 and 5. On the other hand, the hardnesses of equiaxed γ grains for the two series of the alloys were in a much lower range of around 260 to 290 than the hardness of lamellar form grains and exhibited no distinct dependence on the oxygen and aluminum contents. Then in the two series of the alloys containing the extremely low and medium levels of oxygen, it is concluded that overall strength is mainly controlled by the microstructural factors, volume fraction of lamellar form grains and lamellar spacing, and oxygen affects the strength through variations of these factors. It should be noted that the hardness of equiaxed γ grains in Ti-48 at%Al alloys decreases with increasing oxygen content especially in the range of above 0.125 mass%. The saturation of overall strength in Fig. 1 seemed to result from the balance of this softening of equiaxed γ grains and the increment of volume fraction of lamellar form grains. The softening of equiaxed γ grains will be discussed later.

Further evidence obtained in the previous study⁽¹⁹⁾ was that the strength of cast and HIP'ed Ti-48 at%Al-2 at%X (X=Cr, Mn, V, Nb, Ta and Hf) alloys could be analyzed based on the rule of mixtures by regarding the alloys as a kind of composite material consisting of equiaxed γ and lamellar form grains in the following way. The relationship between the 0.2% proof stress (YS) and Vickers hardness measured under a load of 49 N of the alloys was expressed by the following equation:

$$YS(\text{MPa}) = 3.17H_v - 367.3 \quad (1)$$

The macrohardness was expressed by a rule of mixture as follows:

$$H_v = (H_{v\gamma}f_{v\gamma} + H_{v_l}f_{v_l}) - 110 \quad (2)$$

where $H_{v\gamma}$ and H_{v_l} is the Vickers hardness measured under a load of 0.098 N, of equiaxed γ grains and lamellar form grains, respectively. $f_{v\gamma}$ and f_{v_l} are the volume fractions of equiaxed γ grains and lamellar form grains, respectively. Substituting eq. (2) for eq. (1), 0.2% proof stress is calculated based on a rule of mixtures by the following equation:

$$YS(\text{MPa}) = 3.17\{(H_{v\gamma}f_{v\gamma} + H_{v_l}f_{v_l}) - 110\} - 367.3 \quad (3)$$

In the previous study, the calculated strength derived from the way described above showed good agreement with the measured strength.

The present study using the alloys with the extremely

low and medium levels of oxygen confirmed again that the strength was strongly controlled by microstructural factors. The strength calculated using data in Fig. 3, Fig. 6 and Table 2 show an excellent agreement with the measured strength as shown in Fig. 8.

The elongation of Ti-48 at%Al, as shown in Fig. 1, showed a maximum value at 0.034 mass% oxygen. On comparing the results of the alloys containing two levels of oxygen as shown in Fig. 4(b), the aluminum content exhibiting a maximum elongation was shifted toward the titanium-rich side by reducing level of oxygen. It is possible that the ductility is controlled dominantly by microstructure in a way similarly to the strength. Figure 9 shows elongations of all the alloys as a function of volume fraction of lamellar form grains. In the previous study⁽¹⁹⁾, it was shown that the ductility decreased monotonously with increasing volume fraction of lamellar form grains in the range of 20 to 60 vol% lamellar form grains. In this study although the ductility of the alloys with more than 20 vol% lamellar form grains exhibits the same tendency as the results of the previous study⁽¹⁹⁾, in that the alloys with lamellar volume fraction below 20 vol% decreased along with the reduction in the volume fraction of lamellar form grains. This poor ductility ob-

served in the low lamellar volume fraction region seems to be caused by the coarser grain size enhancing grain boundary fracture.

In Ti-48 at%Al alloys, the Vickers hardness of equiaxed γ grains decreases in a high oxygen region as shown in Table 2. It is reported that the hardness of equiaxed γ phase is softened with increasing aluminum content in titanium-rich γ TiAl alloys and exhibits a minimum hardness at stoichiometry⁽²⁰⁾. The softening observed in this study may be also caused through the effect of aluminum content. Figure 10 shows the aluminum content in equiaxed γ grain measured by EPMA. It is obvious that the aluminum content in the equiaxed γ phase increases with increasing total oxygen content. In other words, this result indicates that γ solvus in the Ti-Al phase diagram shifts toward the aluminum-rich side with increasing oxygen content as shown in Fig. 11.

V. Conclusion

Cast and HIP'ed γ TiAl alloys containing an extremely low oxygen below 0.01 mass% were prepared and their tensile properties were investigated. The following results were obtained with respect to the effect of oxygen content

Fig. 8 Comparison of measured and calculated strength by the rule of mixtures.

Fig. 9 Relationship between volume fraction of lamellar form grains and elongation.

Fig. 10 Aluminum content in equiaxed γ grains of Ti-48 at%Al alloys measured by EPMA.

Fig. 11 Schematic illustration for the effect of oxygen content on the Ti-Al phase diagram.

on the tensile property and microstructural factors.

(1) No marked ductility improvement is observed in spite of reducing the oxygen content to less than 0.01 mass%.

(2) Mechanical properties of alloys containing various levels of oxygen are mainly controlled by the microstructural factors and the oxygen content affect the mechanical properties through changing the microstructure.

(3) It is indicated that, in the Ti–Al phase diagram, the $\alpha(\alpha_2) + \gamma$ two phase region is expanded toward the aluminum-rich side along with increasing oxygen content, which results in increasing the Al content and decreasing the hardness of the γ phase.

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