Improvement of Tensile and Fatigue Properties of β -Titanium Alloy while Maintaining Low Young's Modulus through Grain Refinement and Oxygen Addition

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To investigate methods of improving the tensile and fatigue properties of a solutionized Ti-29Nb-13Ta-4.6Zr (TNTZ) alloy without increasing its Young's modulus, two types of TNTZ alloys having oxygen contents of 0.06 and 0.14 mass% (TNTZ-0.06O and TNTZ-0.14O), respectively, were subjected to cold swaging and a subsequent heat-treatment. The effects of the grain refinement caused by the cold swaging and the subsequent heat-treatment as well as those of oxygen addition on the microstructures, Young's moduli and tensile and fatigue properties of the two alloys were investigated.

The grain diameters of the TNTZ-0.06O and TNTZ-0.14O decrease from 27 μm (as-received) to 1.7 μm and from 33 μm (as-received) to 1.0 μm , respectively, after subjected to cold swaging and the subsequent heat-treatment. These results suggest that cold swaging, followed by heat treatment, is effective in refining the grains of TNTZ alloys. However, a β (110) texture develops in the alloys as a result of the cold swaging.

Young's moduli of as-cold swaged and heat-treated TNTZ-0.06O and TNTZ-0.14O are within the range of 61–68 GPa and as low as those of solutionized TNTZ-0.06O and TNTZ-0.14O.

The tensile strengths and elongations of the as-cold swaged, heat-treated and solutionized TNTZ-0.14O are approximately 30% higher and 20% lower, respectively, than those of the corresponding TNTZ-0.06O. Moreover, the 0.2% proof stresses of the heat-treated TNTZ-0.14O are approximately 110% higher than that of the corresponding TNTZ-0.06O. On the other hand, the values of the Hall-Petch constant (k) for the TNTZ-0.06O ($k_{\text{TNTZ-0.06O}} = 0.02$) and TNTZ-0.14O ($k_{\text{TNTZ-0.14O}} = 0.005$) are much smaller than those for pure Ti and another β -type Ti alloy (Ti-15.2Mo). These results indicate that the addition of oxygen can improve the tensile properties of TNTZ alloys. However, the grain refinement caused by cold swaging and a subsequent heat-treatment does not have a significant effect on the tensile properties of TNTZ.

The fatigue limit of the heat-treated TNTZ-0.14O (540 MPa) is much higher than those of the heat-treated and solutionized TNTZ-0.06O (290 and 230 MPa) and solutionized TNTZ-0.14O (330 MPa). These results indicated that it is possible to improve the fatigue properties of solutionized TNTZ using grain refinement, which can be induced by cold swaging and a subsequent heat-treatment and by the addition of oxygen. [[doi:10.2320/matertrans.M2013151](https://doi.org/10.2320/matertrans.M2013151)]

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1. Introduction

Young's modulus is one of the most important parameters for evaluating the suitability of metallic biomaterials for implant devices. This is because a large mismatch between Young's modulus of the implant material and that of cortical bone can cause stress shielding, resulting in inhomogeneous stress transfer between the bone and the implant device.¹⁾ This can lead to bone atrophy, resulting in the loosening of the implant device and refracturing of the bone. A number of β -type titanium alloys, including the alloys Ti-29Nb-13Ta-4.6Zr (mass%, TNTZ)²⁾ and Ti-24Nb-4Zr-7.9Sn (mass%),³⁾ have been developed as low Young's modulus alloys in order to overcome these problems. Young's modulus of solutionized TNTZ is approximately 60 GPa,⁴⁾ which is much closer to that of cortical bone (10–30 GPa)⁵⁾ than are those of pure Ti (CP-Ti: 105 GPa)⁶⁾ and (α + β)-type Ti alloys (Ti-6Al-4V ELI (Ti64 ELI): 110 GPa).⁷⁾ Therefore, β -type Ti alloys are expected to be suitable materials for implant devices.

However, the tensile strength and fatigue limit of solutionized TNTZ are lower than those of Ti64 ELI, which is the most widely used alloy for biomedical applications, including for implant devices. The tensile strengths of solutionized TNTZ and aged Ti64 ELI are approximately 600 MPa⁴⁾ and 1050 MPa,⁷⁾ respectively. The fatigue limit of

solutionized TNTZ is 320 MPa⁴⁾ and that of aged Ti64 ELI ranges from 610 MPa (in the case of the acicular α phase) to 800 MPa (in the case of the equiaxed α phase).⁸⁾ Several studies have reported that the tensile strength of solutionized TNTZ can be increased by subjecting it to a cold rolling process. The reported tensile strength of cold rolled TNTZ is 800 MPa.⁹⁾ However, the fatigue properties of solutionized TNTZ are not improved by the cold rolling process.⁴⁾ On the other hand, aged TNTZ shows excellent tensile strength and fatigue properties because of precipitation strengthening by the ω and/or α precipitated phase.^{4,9)} However, Young's modulus of aged TNTZ is higher than 85 GPa because of the formation of the ω and/or α precipitated phase.^{4,9)} Therefore, new methods for improving the tensile and fatigue properties of solutionized TNTZ without increasing its Young's modulus are required.

Grain refinement strengthening is an effective method for improving the tensile properties of Ti alloys.^{10,11)} Moreover, by controlling the grain refinement processes, it is possible to keep the phase constitutions of the alloys unchanged. Therefore, one can assume that the grain refinement strengthening of solutionized TNTZ should have no effect its Young's modulus. In addition, it is known that the solid solution strengthening of Ti alloys with oxygen can improve their tensile strengths significantly.^{12,13)} Young's modulus of a metallic material is not only dependent on its phase constitution but also on the interatomic distance in the crystal

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Table 1 Chemical compositions of hot forged TNTZ-0.06O and TNTZ-0.14O.

Material	Ti	Nb	Ta	Zr	C	N	O
TNTZ-0.06O	Bal.	29.4	13.0	4.6	0.013	0.008	0.06
TNTZ-0.14O	Bal.	28.7	12.7	4.4	0.006	0.007	0.14

lattice of the material. Therefore, the addition of oxygen may decrease the interatomic distance, resulting in an increase in its Young's modulus. However, Geng *et al.* have reported that if the oxygen content is less than 0.33 mass%, the effect of oxygen addition on Young's modulus of TNTZ is insignificant.¹⁴⁾ Therefore, grain refinement and the addition of oxygen are expected to improve the tensile and fatigue properties of solutionized TNTZ without increasing its Young's modulus.

In this study, two types of TNTZ having different oxygen contents were subjected to a cold swaging process and a subsequent heat-treatment for grain refinement. The microstructures, Young's moduli and tensile and fatigue properties of these TNTZ were investigated.

2. Experimental Procedures

2.1 Material preparation

The chemical compositions of the two types of hot forged TNTZ (as received) having different oxygen contents used in this study are listed in Table 1. The TNTZ containing 0.06 mass% oxygen is denoted as TNTZ-0.06O and that containing 0.14 mass% oxygen as TNTZ-0.14O. The diameters of the bars used of TNTZ-0.06O and TNTZ-0.14O were 20 and 25 mm, respectively. The oxide layer formed on the bars was removed mechanically before the bars were subjected to cold swaging, followed by heat-treatment.

2.2 Cold swaging and heat-treatment processes

Figure 1 shows a schematic drawing of the cold swaging and heat-treatment processes employed in this study. The diameters of the TNTZ-0.06O and TNTZ-0.14O bars were reduced from 20 to 5.5 mm and from 25 to 6.5 mm, respectively, (with the reduction ratio being 92%) through the cold swaging process, which was performed at room temperature in air. The cold swaged TNTZ-0.06O and TNTZ-0.14O bars were then subjected to heat-treatment at 923 or 973 K for 3.6 or 10.8 ks in vacuum and were then quenched into water. Moreover, for comparison, cold swaged bars of TNTZ-0.06O and TNTZ-0.14O were subjected to a solution treatment at 1063 K for 3.6 ks in vacuum, followed by quenching in water.

2.3 Material characterization

The microstructures of cross sections of the as-received, as-cold swaged, heat-treated and solutionized TNTZ-0.06O and TNTZ-0.14O bars were evaluated using an optical microscopy (OM). The specimens, which were cut from each bar into round slices, for the OM observations were wet-polished using waterproof emery papers of up to #4000 grit and buff polished using a colloidal SiO₂ suspension. They were then etched using a 5% HF etching solution. The grain

Fig. 1 Schematic drawing of cold swaging and heat-treatment processes employed in this study.

diameters of the as-received, heat-treated and solutionized TNTZ-0.06O and TNTZ-0.14O were quantified from the OM images using the average grain intercept (AGI) method.

The phase constitutions of cross sections of the as-received, as-cold swaged, heat-treated and solutionized TNTZ-0.06O and TNTZ-0.14O bars were investigated by X-ray diffraction (XRD) analyses. The specimens, which were cut from each bar into round slices, for the XRD analyses were wet-polished using waterproof emery papers of up to #4000 grit. In addition, the phase constitutions of the fractured sections of the heat-treated and solutionized TNTZ-0.06O and TNTZ-0.14O after subjected to a fatigue test were also investigated directly, i.e., without being polished, by XRD analyses. The XRD analyses were performed using a Cu target, with an operation voltage of 40 kV and a tube current of 40 mA.

The microstructures of the fractured sections of the heat-treated and solutionized TNTZ-0.06O and TNTZ-0.14O after subjected to a tensile test were evaluated by transmission electron microscopy (TEM). The specimens used for the TEM observations were cut from the fractured sections of the samples subjected to the tensile test. These specimens were wet-polished using waterproof emery papers of up to #4000 grit and then dimpled with a phosphor bronze ring to form dimples up to 30 μ m in size. Finally, these specimens were ion milled to form thin foils. The TEM observations were performed at an accelerating voltage of 200 keV.

2.4 Mechanical properties

Young's moduli of the as-cold swaged, heat-treated and solutionized TNTZ-0.06O and TNTZ-0.14O were measured using a free resonance method. Young's modulus measurements were made at room temperature in air. For the measurements, bars of TNTZ-0.06O and TNTZ-0.14O with a length of 50 mm and diameters of 5 and 6 mm, respectively, were used. These specimens were wet-polished using waterproof emery papers of up to #1500 grit.

The tensile properties of the as-cold swaged, heat-treated and solutionized TNTZ-0.06O and TNTZ-0.14O were evaluated at room temperature in air using an Instron-type testing machine that had a cross-head speed of 8.33×10^{-6} m·s⁻¹. For the tensile test, dog bone-shaped specimens with a gage length of 11 mm and a gage diameter of 3 mm were used. These specimens were wet-polished using waterproof emery papers of up to #1500 grit.

The fatigue properties of the heat-treated and solutionized TNTZ-0.06O and heat-treated TNTZ-0.14O were evaluated using an electro-servo-hydraulic testing machine. The fatigue tests were performed at a frequency of 10 Hz, with a stress

ratio, R , of 0.1, under the tension-tension mode at room temperature in air. The maximum cyclic stress, i.e., the stress at which the specimen being tested did not undergo failure after 1×10^7 cycles, was defined as the fatigue limit (run out). For the fatigue test, dog bone-shaped tensile specimens with a gage length of 11 mm and a gage diameter of 3 mm were used. These specimens were wet-polished using waterproof emery papers of up to #4000 grit and buff polished using a colloidal SiO_2 suspension.

3. Results and Discussion

3.1 Microstructures and phase constitutions

Figure 2 shows typical OM images of cross sections of the as-received, as-cold swaged, heat-treated and solutionized (a) TNTZ-0.06O and (b) TNTZ-0.14O bars. As can be seen from Fig. 2, it is difficult to observe the grain boundaries of the as-cold swaged TNTZ-0.06O and TNTZ-0.14O. This result suggests that plastic flow is caused in them by the cold swaging process. After the heat-treatment at 923 K for 3.6 ks, clear grain boundaries appear in the TNTZ-0.06O and TNTZ-0.14O specimens. The grain diameters of the as-received, heat-treated and solutionized TNTZ-0.06O and TNTZ-0.14O quantified from the OM images, are shown in Fig. 3 as functions of the heat-treatment time. The grain diameters of the TNTZ-0.06O and TNTZ-0.14O heat-treated at 923 K for 3.6 ks decrease from 27 μm (as-received) to 1.7 μm and from 33 μm (as-received) to 1.0 μm , respectively. However, the grain diameters of the TNTZ-0.06O and TNTZ-0.14O increase from 1.7 to 4.0 μm and from 1.0 to 1.5 μm , respectively, with an increase in the heat-treatment time from 3.6 to 10.8 ks for a heat-treatment temperature of 923 K. Moreover, the diameters increase from 6.4 to 8.5 μm and from 2.6 to 8.3 μm , respectively, with an increase in the heat-treatment time from 3.6 to 10.8 ks for a heat-treatment temperature of 973 K. Even though the grain diameters of the heat-treated TNTZ-0.06O and TNTZ-0.14O increase with an increase in the heat-treatment time and heat-treatment

Fig. 2 Typical OM images of cross sections of as-received, as-cold swaged, heat-treated and solutionized (a) TNTZ-0.06O and (b) TNTZ-0.14O bars.

Fig. 3 Grain diameters of as-received, heat-treated and solutionized (a) TNTZ-0.06O and (b) TNTZ-0.14O quantified using OM images, as functions of the heat-treatment time.

Fig. 4 Typical XRD profiles of cross sections of as-received, as-cold swaged, heat-treated and solutionized (a) TNTZ-0.06O and (b) TNTZ-0.14O bars.

Fig. 5 Young's moduli of as-cold swaged, heat-treated and solutionized (a) TNTZ-0.06O and (b) TNTZ-0.14O.

temperature, they are still smaller than those of the as-received and solutionized TNTZ-0.06O and TNTZ-0.14O. These results suggest that cold swaging, followed by heat-treatment at 923 or 973 K for 3.6 or 10.8 ks, is effective method for achieving grain refinement in TNTZ.

Figure 4 shows typical XRD profiles of cross sections of the as-received, as-cold swaged, heat-treated and solutionized (a) TNTZ-0.06O and (b) TNTZ-0.14O bars. Here it is noted that these profiles were normalized using an intensity of each β (110) peak. As shown in Fig. 4, only diffraction peaks attributable to β (110), β (200) and β (211) are detected in the profiles of the TNTZ-0.06O and TNTZ-0.14O. These results indicate that the as-received, as-cold swaged, heat-treated and solutionized TNTZ-0.06O and TNTZ-0.14O consist of single β phase. Moreover, the intensities of the β (200) and β (211) peaks decrease significantly after the cold swaging process. This result suggests that the β (110) texture develops as a result of the cold swaging process.

3.2 Mechanical properties

3.2.1 Young's moduli

Figure 5 shows the values of Young's moduli of the as-cold swaged, heat-treated and solutionized (a) TNTZ-0.06O and (b) TNTZ-0.14O. As shown in Fig. 5, Young's moduli of the as-swaged TNTZ-0.06O and TNTZ-0.14O are 68 and 66 GPa, respectively. In addition, Young's moduli of the heat-treated and solutionized TNTZ-0.06O and TNTZ-0.14O are 62–66 and 61–63 GPa, respectively. The differences of the Young's moduli between low and high oxygen contents and before and after the heat-treatment are very small. This is because, as above mentioned, these TNTZ alloys consist of single β phase. Young's modulus of a metallic material mainly depends on its phase constitution. Therefore, the as-cold swaged and heat-treated TNTZ-0.06O and TNTZ-0.14O exhibited Young's moduli similar to, and as low as, that of the solutionized TNTZ-0.06O and TNTZ-0.14O, which have single β phase.

Fig. 6 Tensile strengths, 0.2% proof stresses and elongations of as-cold swaged, heat-treated and solutionized (a) TNTZ-0.06O and (b) TNTZ-0.14O.

3.2.2 Tensile properties

Figure 6 shows the values of the tensile strength (σ_B), 0.2% proof stress ($\sigma_{0.2}$) and elongation of the as-cold swaged, heat-treated and solutionized (a) TNTZ-0.06O and (b) TNTZ-0.14O. As shown in Fig. 6, the tensile strengths of the as-swaged TNTZ-0.06O and TNTZ-0.14O are 841 and 1001 MPa, respectively. After the heat and solution treatments, the tensile strengths of the TNTZ-0.06O and TNTZ-0.14O decrease from 841 to 513–526 MPa and from 1001 to 665–679 MPa, respectively. Moreover, the elongations of the as-swaged TNTZ-0.06O and TNTZ-0.14O are both 16%. After the heat and solution treatments, the elongations of the TNTZ-0.06O and TNTZ-0.14O increase from 16% to 26–30% and to 20–26%, respectively. The decrease in the tensile strengths and increase in the elongations of the TNTZ-0.06O and TNTZ-0.14O after the heat and solution treatments are caused by the disappearance of dislocations, which are accumulated in the alloys during the cold swaging process, as a result of the heat and solution treatments.

The tensile strengths of the as-swaged, heat-treated and solutionized TNTZ-0.14O are approximately 30% higher than those of TNTZ-0.06O. Moreover, the 0.2% proof stresses of the as-swaged, heat-treated and solutionized TNTZ-0.14O are approximately 20, 110 and 70% higher, respectively, than those of TNTZ-0.06O. However, the elongations of the heat-treated and solutionized TNTZ-0.14O are approximately 20% lower than those of TNTZ-0.06O. These results indicate that solid solution strengthening using oxygen has a significant effect on the tensile properties of TNTZ.

On the other hand, the dependence of the tensile properties of the TNTZ-0.06O and TNTZ-0.14O on their grain diameters is not significant. Figure 7 shows the tensile strengths of the heat-treated and solutionized TNTZ-0.06O and TNTZ-0.14O as functions of the inverse square root of their grain diameters ($d^{-1/2}$) (Hall-Petch plots). As can be seen from the Fig. 7, these Hall-Petch plots have positive slopes. However, the values of the Hall-Petch constant (k) for the TNTZ-0.06O ($k_{\text{TNTZ-0.06O}} = 0.02$) and TNTZ-0.14O ($k_{\text{TNTZ-0.14O}} = 0.005$) are much smaller than those of pure Ti ($k_{\text{CP-Ti}} = 0.2$) and another β -type Ti alloy (Ti-15.2Mo,

Fig. 7 Tensile strengths of heat-treated and solutionized (a) TNTZ-0.06O and (b) TNTZ-0.14O as functions of the inverse square root of their grain diameters ($d^{-1/2}$) (Hall-Petch plots).

$k_{\text{Ti-15.2Mo}} = 0.4$).¹⁵⁾ These results indicate that the grain refinement caused by the cold swaging process and the subsequent heat treatment does not have a significant effect on the tensile properties of TNTZ. As above mentioned, the XRD profiles of the heat-treated TNTZ-0.06O and TNTZ-0.14O (Fig. 4) indicate that they have a strong β (110) texture. Grain refinement strengthening is associated with a mismatch of grain orientations. Therefore, the orientation unit can be considered an effective grain. Even though grain refinement is caused by the cold swaging process and the subsequent heat-treatment, the strong β (110) texture suggests that the effective grain diameters of the TNTZ-0.06O and TNTZ-0.14O are significant larger than those determined using the OM images.

The 0.2% proof stresses for the heat-treated and solutionized TNTZ-0.06O are significantly lower than one-half of the corresponding tensile strengths. The ratios of the 0.2% proof stresses to the tensile strengths ($\sigma_{0.2}/\sigma_B$) are in the range of 38–43%. On the other hand, except solutionized TNTZ-0.14O, the 0.2% proof stresses of the heat-treated TNTZ-0.14O are higher than half their corresponding tensile strengths. The ratios of the 0.2% proof stresses to the tensile strength ($\sigma_{0.2}/\sigma_B$) are in the range of 70–74%. Duerig *et al.*

Fig. 8 Typical electron diffraction patterns of the $[110]_{\beta}$ zone of fractured sections of (a) heat-treated TNTZ-0.06O, (b) solutionized TNTZ-0.06O, (c) heat-treated TNTZ-0.14O and (d) solutionized TNTZ-0.14O after subjected to a tensile test.

have reported that the 0.2% proof stresses of Ti alloys decrease when a stress-induced α'' martensite phase is formed.¹⁶⁾ Therefore, the microstructures of the fractured sections of the TNTZ-0.06O and TNTZ-0.14O were evaluated by TEM. Figure 8 shows typical electron diffraction patterns of the $[110]_{\beta}$ zone of the fractured sections of the (a) heat-treated TNTZ-0.06O, (b) solutionized TNTZ-0.06O, (c) heat-treated TNTZ-0.14O and (d) solutionized TNTZ-0.14O after subjected to the tensile test. The electron diffraction patterns of the fractured sections of the heat-treated and solutionized TNTZ-0.06O as well as that of the solutionized TNTZ-0.14O show spots attributable to the β and α'' martensite phases (Figs. 8(a), 8(b) and 8(d)). Moreover, a double yielding is observed in the stress-strain (S - S) curves of the heat-treated and solutionized TNTZ-0.06O and the solutionized TNTZ-0.14O (not shown here). These results indicate that a stress-induced martensite phase transformation occurs in the heat-treated and solutionized TNTZ-0.06O and in the solutionized TNTZ-0.14O during tensile loading. On the other hand, the electron diffraction pattern of the fractured section of the heat-treated TNTZ-0.14O shows spots attributable only to the β phase (Fig. 8(c)). Geng *et al.* have reported that oxygen can suppress the formation of the stress-induced α'' martensite phase in TNTZ.¹⁴⁾ Moreover, Niinomi *et al.* have reported that the stress-induced α'' martensite phase forms more readily in solutionized TNTZ than in heat-treated ones.¹⁷⁾ Together, these results and reports suggest that the stress-induced martensite phase transformation does not occur in the heat-treated TNTZ-0.14O during tensile loading. Therefore, the ratios of the 0.2% proof stresses to tensile strengths ($\sigma_{0.2}/\sigma_B$) of the heat-treated TNTZ-0.14O are

Fig. 9 S - N curves of TNTZ-0.06O heat-treated at 923 K for 3.6 ks, the solutionized TNTZ-0.06O specimen and the TNTZ-0.14O specimen heat-treated at 923 K for 3.6 ks. The previously reported S - N curve for a solutionized TNTZ alloy is also shown.

relatively higher than those of the heat-treated and solutionized TNTZ-0.06O and the solutionized TNTZ-0.14O.

3.2.3 Fatigue properties

The S - N curves of the TNTZ-0.06O heat-treated at 923 K for 3.6 ks, the solutionized TNTZ-0.06O and the TNTZ-0.14O heat-treated at 923 K for 3.6 ks are shown in Fig. 9; the previously reported S - N curve for a solutionized TNTZ (Ti: bal, Nb: 31.5, Ta: 11.6, Zr: 4.7, O: 0.14 mass%) is also shown. As can be seen from the Fig. 9, the difference in the fatigue strengths of the heat-treated and solutionized TNTZ-0.06O is very small in the low-cycle fatigue life region ($<1 \times 10^5$ cycles). This result is in agreement with the results of the tensile tests of the heat-treated and solutionized TNTZ-0.06O. As shown in Fig. 6(a), the difference in the tensile properties of the heat-treated and solutionized TNTZ-0.06O is very small. On the other hand, the fatigue strength of the heat-treated TNTZ-0.06O is higher than that of the solutionized TNTZ-0.06O in high-cycle fatigue life region ($>1 \times 10^5$ cycles). Moreover, the fatigue strength of the heat-treated TNTZ-0.14O is much higher than that of previously reported solutionized TNTZ. The fatigue limits of the heat-treated and solutionized TNTZ-0.06O are approximately 290 and 230 MPa, respectively. In addition, the fatigue limits of the heat-treated TNTZ-0.14O is 540 MPa, while the value previously reported for solutionized TNTZ-0.14O is 330 MPa. These results indicate that the gain refinement caused by cold swaging and a subsequent heat-treatment can improve the high-cycle fatigue life properties of TNTZ.

The typical XRD profiles of the fractured sections of the heat-treated and solutionized TNTZ-0.06O as well as that of the heat-treated TNTZ-0.14O after subjected to a fatigue test are shown in Fig. 10. Diffraction peaks attributable to the α'' (020) and α'' (021) phases can clearly be observed in the profiles of the heat-treated and solutionized TNTZ-0.06O. It should be noted that the stress-induced α'' martensite phase does not appear in the previously reported solutionized TNTZ after tensile loading. Li *et al.* have reported that the fatigue strength of β -Ti alloys decreases when stress gets concentrated at the interface between the stress-induced α'' martensite phase and the β phase.¹⁸⁾ Therefore, controlling the formation of the stress-induced α'' martensite phase during cyclic loading is also important for improving the fatigue properties of TNTZ. As above mentioned, oxygen can suppress the formation of the stress-induced α'' martensite

Fig. 10 Typical XRD profiles of fractured sections of heat-treated and solutionized TNTZ-0.06O and heat-treated TNTZ-0.14O after subjected to a fatigue test.

phase in TNTZ. Moreover, solid solution strengthening owing to oxygen is expected to improve the fatigue properties of these alloys. Therefore, the fatigue properties of the heat-treated TNTZ-0.14O and the previously reported solutionized TNTZ are better than those of the heat-treated and solutionized TNTZ-0.06O. In particular, because the heat-treated TNTZ-0.14O is subjected to grain-refinement strengthening and solid-solution strengthening and because the formation of the stress-induced α'' martensite phase is suppressed in it, it exhibits better fatigue properties than the heat-treated and solutionized TNTZ-0.06O and the previously reported solutionized TNTZ-0.14O.

The results of this study indicate that grain refinement caused by cold swaging and a subsequent heat-treatment, and the addition of oxygen in the amount of 0.14 mass% can improve the tensile and fatigue properties of TNTZ without increasing their Young's moduli.

4. Conclusions

- (1) After the TNTZ-0.06O and TNTZ-0.14O subjected to cold swaging and a subsequent heat-treatment at 923 K for 3.6 ks, their grain diameters decrease from 27 μm (as-received) to 1.7 μm and from 33 μm (as-received) to 1.0 μm , respectively. In addition, the grain diameters of these TNTZ increase with an increase in the heat-treatment time and temperature. However, the grain diameters of the heat-treated TNTZ-0.06O and TNTZ-0.14O remained smaller than those of the as-received and solutionized TNTZ-0.06O and TNTZ-0.14O.
- (2) The XRD profiles of cross sections of the as-received, as-cold swaged, heat-treated and solutionized TNTZ-0.06O and TNTZ-0.14O bars indicate that these TNTZ-0.06O and TNTZ-0.14O consist of a single β phase. Moreover, the β (110) texture develops as a

result of cold swaging.

- (3) Young's moduli of the as-cold swaged, heat-treated and solutionized TNTZ-0.06O and TNTZ-0.14O are within the range of 61–68 GPa. The differences of the Young's moduli between low and high oxygen contents and before and after the heat-treatment are very small.
- (4) The tensile strengths and elongations of the as-cold swaged, heat-treated and solutionized TNTZ-0.14O are approximately 30% higher and 20% lower, respectively, than those of the corresponding TNTZ-0.06O.
- (5) The values of the Hall-Petch constant (k) for TNTZ-0.06O ($k_{\text{TNTZ-0.06O}} = 0.02$) and TNTZ-0.14O ($k_{\text{TNTZ-0.14O}} = 0.005$) are much smaller than those for pure Ti ($k_{\text{CP-Ti}} = 0.2$) and another β -type Ti alloy (Ti-15.2Mo, $k_{\text{Ti-15.2Mo}} = 0.4$).
- (6) The heat-treated TNTZ-0.14O has significantly better fatigue properties (its fatigue limit is 540 MPa) than heat-treated, solutionized TNTZ-0.06O and a previously reported solutionized TNTZ-0.14O.

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