Effect of Oxide Particles Formed through Addition of Rare-Earth Metal on Mechanical Properties of Biomedical β -Type Titanium Alloy

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In order to improve the mechanical properties of Ti-29Nb-13Ta-4.6Zr (TNTZ) alloy without increasing Young's modulus for application in bone prostheses, dispersion strengthening of TNTZ using yttrium oxide (Y_2O_3) particles was studied. The formation of well-dispersed Y_2O_3 particles inside grains of Y-added TNTZ is achieved through the reaction of added Y with the oxygen contained in TNTZ. The size and its standard deviation of obtained Y_2O_3 particles increased at Y concentrations of 0.2 and 0.5 mass%. The addition of Y led to a decrease in the grain size in Y-added TNTZ. Low Young's modulus was retained in the Y-added TNTZ subjected to cold rolling. The tensile strength and 0.2% proof stress slightly increased in Y-added TNTZ with Y concentrations below 0.1 mass%, whereas they decreased significantly in Y-added TNTZ with Y concentrations of 0.2 and 0.5 mass%. Large Y_2O_3 particles that formed in Y-added TNTZ with Y concentrations of 0.2 and 0.5 mass% worked as sources for the formation of voids during fracture, which resulted in a decrease in the tensile strength and 0.2% proof stress. Elongation tended to decrease in the Y-added TNTZ as compared to that of TNTZ without any Y addition. As a result, it is found that Y-added TNTZ with improved mechanical properties was obtained at a Y concentration of 0.05 mass% in this experiment. The fatigue strength of Y-added TNTZ was also improved at the Y concentration of 0.05 mass%. [doi:10.2320/matertrans.MF201308]

(Received February 13, 2013; Accepted April 11, 2013; Published May 31, 2013)

Keywords: β -type titanium alloy, rare-earth metal, oxide particles, dispersion strengthening, mechanical properties

1. Introduction

Ti-29Nb-13Ta-4.6Zr (TNTZ) is a biomedical β -type titanium alloy, which consists of nontoxic and non-allergenic elements.¹⁻³⁾ TNTZ has been developed for applications in bone prostheses because its Young's modulus (about 60 GPa) subjected to solution treatment is similar to that of human bone (10–30 GPa⁴⁻⁶⁾), thus preventing the stress shielding effect and the subsequent resorption and weakening of bone.⁷⁾ However, the mechanical strength of TNTZ subjected to solution treatment is inferior to that of the Ti-6Al-4V alloy, which is a conventional titanium alloy used in biomedical applications.⁸⁾ Although an aging treatment improves the mechanical properties of TNTZ, Young's modulus also increases by precipitation of an α phase.^{9,10)} Therefore, strengthening methods without causing a simultaneous increase in Young's modulus are required for producing improved TNTZ applicable in bone prostheses. Dispersion strengthening is a method, which improves the mechanical properties without increasing Young's modulus.¹¹⁻¹⁴⁾ Particles dispersed in a matrix inhibit the sliding of dislocations, which leads to the strengthening of the alloys.

In a previous study, dispersion strengthening of TNTZ was demonstrated through the addition of rare-earth oxide particles such as Y_2O_3 and TiB_2 to TNTZ.^{15,16)} The small amounts of oxide particles added to TNTZ improved the fatigue property without causing an increase in Young's modulus. However, an increase in the amount of oxide particles led to particle aggregation, which seemed to result in a decrease in the mechanical strength of TNTZ.

In this study, the formation of well-dispersed oxide particles was attempted through a reaction between rare-earth metals and the oxygen contained in TNTZ in order to

improve the mechanical properties of TNTZ through dispersion strengthening. Yttrium (Y) was employed to form the oxide particles in TNTZ. Y is an element that reacts with oxygen more easily than the elements contained in TNTZ. The concentration of Y added to TNTZ was changed in order to investigate the influence of its concentration on the size and volume fraction of oxide particles formed in Y-added TNTZ, and the grain size and the mechanical properties (Young's modulus, tensile strength, 0.2% proof stress, and elongation) of TNTZ. Finally, an appropriate concentration of Y for the improvement of mechanical properties was determined.

2. Experimental Procedures

2.1 Preparation of TNTZ and Y-added TNTZ

A hot forged TNTZ rod ($\phi 25$ mm) was used as the raw material in this experiment. Appropriate amounts of Y were added to TNTZ in order to prepare TNTZ ingots with Y concentrations of 0.05, 0.1, 0.2 and 0.5 mass% through levitation melting. Hereafter, these alloys are abbreviated as TNTZ-0.05Y, TNTZ-0.1Y, TNTZ-0.2Y and TNTZ-0.5Y, respectively, in tables and figures. A TNTZ ingot without the addition of Y was also prepared through levitation melting for comparison. The chemical compositions, as examined by induced coupled plasma optical emission spectroscopy for metallic elements and by an infrared absorption method for oxygen, and by a thermal conductivity method for nitrogen, are shown in Table 1. The TNTZ ingots with and without Y were homogenized at 1273 K for 21.6 ks, followed by water quenching. They were then subjected to hot forging at 1273 K, followed by air cooling in an argon atmosphere. Subsequently, solution treatment was performed to the hot-forged samples at 1063 K for 3.6 ks in vacuum, followed by water quenching. After the solution treatment, samples were cold rolled into plates at a reduction ratio of 87%.

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Table 1 Chemical compositions of TNTZ, and TNTZ–0.05Y, TNTZ–0.1Y, TNTZ–0.2Y and TNTZ–0.5Y.

Alloy	Composition						
	Ti	Nb	Ta	Zr	Y	O	N
TNTZ	Bal.	29.5	13.4	4.63	—	0.092	0.008
TNTZ–0.05Y	Bal.	29.4	13.4	4.65	0.05	0.091	0.007
TNTZ–0.1Y	Bal.	29.4	13.4	4.66	0.10	0.090	0.006
TNTZ–0.2Y	Bal.	29.6	13.4	4.65	0.19	0.094	0.006
TNTZ–0.5Y	Bal.	29.6	13.4	4.66	0.50	0.097	0.006

2.2 Microstructural observation

The phase constituents of the TNTZ samples were analyzed by X-ray diffraction (XRD) methods with Cu K α radiation at an accelerating voltage of 40 kV and a current of 40 mA. The samples for XRD analyses were polished using SiC abrasive papers of up to #4000 grit and buff-polished using a colloidal silica suspension. The analyzed surfaces were parallel to the rolling direction. The microstructures were observed using an optical microscope (OM) and a field emission scanning electron microscope (FE-SEM), fitted with an analyzer for electron probe microanalysis (EPMA), at an accelerating voltage of 15 kV. The shape and size of the obtained oxide particles formed in TNTZ with Y were observed by FE-SEM, and the composition of the oxide particles was analyzed by EPMA. The samples for the microstructural observation were wet polished using SiC abrasive papers of up to #1500 grit and then buff-polished using a colloidal silica suspension. After polishing, the samples were etched with 5% hydrofluoric acid for 120 s to obtain mirror surfaces.

2.3 Evaluation of mechanical properties

Young's moduli of the samples were measured by the free resonance method. The size of the samples for the measurement of Young's modulus was $10 \times 40 \times 1.5 \text{ mm}^3$, and the measurements were performed on sample surfaces parallel to the rolling direction. The samples were polished using SiC abrasive papers of up to #1500 grit. Mechanical properties (tensile strength, 0.2% proof stress, and elongation) were evaluated by tensile tests using an Instron-type tensile testing machine. Samples with a thickness of 1.5 mm, a width of 3 mm, and a gage length of 13 mm were used for tensile tests. The longitudinal direction of the samples was parallel to the rolling direction. The samples for tensile tests were polished using SiC abrasive papers of up to #1500 grit. The tensile tests were performed at a crosshead speed of $0.5 \times 10^{-6} \text{ m} \cdot \text{s}^{-1}$ at room temperature in air. After tensile tests, the fracture surfaces of the samples were observed using a FE-SEM. Fatigue tests were performed on the samples of TNTZ and Y-added TNTZ at a frequency of 10 Hz with a stress ratio (R) of 0.1 under tension mode at room temperature in air. The same size samples as those used for the tensile tests were employed for the fatigue tests.

3. Results

Figure 1 shows the XRD patterns of TNTZ and Y-added TNTZ with Y concentrations of 0.05, 0.1, 0.2, and 0.5 mass%

Fig. 1 XRD patterns of TNTZ and TNTZ–0.05Y, TNTZ–0.1Y, TNTZ–0.2Y, and TNTZ–0.5Y (a) before and (b) after cold rolling.

Fig. 2 Intensity ratios of (200)/(110) as a function of Y concentration in the TNTZ and TNTZ–0.05Y, TNTZ–0.1Y, TNTZ–0.2Y, and TNTZ–0.5Y before and after cold rolling.

before [Fig. 1(a)] and after cold rolling [Fig. 1(b)]. The peaks corresponding to the body-centered cubic (bcc) β phase are identified on the XRD patterns of all specimens before and after cold rolling. The intensities of the peaks corresponding to the (110) plane are higher than those of peaks corresponding to other planes of the β phase in the XRD patterns of all specimens before cold rolling. After cold rolling, the peaks corresponding to the (200) plane increases in the XRD patterns of TNTZ and Y-added TNTZ with a Y concentration of 0.5 mass%, whereas the intensities of the peaks corresponding to the (110) plane are higher for Y-added TNTZ with Y concentrations of 0.05, 0.1 and 0.2 mass%. Figure 2 shows the intensity ratios of (200)/(110) as a function of Y concentration in the TNTZ and in Y-added TNTZ with Y concentrations of 0.05, 0.1, 0.2 and 0.5 mass% before and after cold rolling. The intensity ratios

Fig. 3 Microstructures of (a) TNTZ and (b) TNTZ-0.05Y, (c) TNTZ-0.1Y, (d) TNTZ-0.2Y, and (e) TNTZ-0.5Y subjected to solution treatment.

of (200)/(110) significantly increase in the TNTZ and Y-added TNTZ with a Y concentration of 0.5 mass% after cold rolling as compared with those before cold rolling. These results indicate that the change in orientation of the β phase caused by cold rolling was suppressed through the addition of Y with concentrations of 0.05, 0.1 and 0.2 mass%.

Figure 3 shows the microstructures of TNTZ and Y-added TNTZ with Y concentrations of 0.05, 0.1, 0.2 and 0.5 mass% subjected to solution treatment. Equiaxed grain structures are observed in the microstructures of TNTZ and Y-added TNTZ with different Y concentrations. The XRD patterns and microstructural images obtained by OM revealed that TNTZ and Y-added TNTZ with different Y concentrations consist of a single β phase. Many particles are observed in the grains of Y-added TNTZ with a Y concentration of 0.5 mass%. The average grain diameters of the β phase of TNTZ and Y-added TNTZ with Y concentrations of 0.05, 0.1, 0.2 and 0.5 mass% are shown in Fig. 4. The average grain diameters of the β phases of TNTZ and Y-added TNTZ with Y concentrations of 0.05, 0.1, 0.2 and 0.5 mass% are $75.8 \pm 16.8 \mu\text{m}$, $44.8 \pm 5.9 \mu\text{m}$, $48.5 \pm 6.0 \mu\text{m}$, $53.1 \pm 6.7 \mu\text{m}$ and $48.8 \pm 13.9 \mu\text{m}$, respectively. The average grain diameters of the β phase in Y-added TNTZ with Y concentrations of 0.05, 0.1, 0.2 and 0.5 mass% decrease as compared with that of TNTZ because of the pinning effect of the oxide particles formed in Y-added TNTZ. The amount of decrease in grain diameter is found to be independent of the Y concentration.

Figure 5 shows the SEM images of Y-added TNTZ with Y concentrations of 0.05, 0.1, 0.2 and 0.5 mass% subjected to solution treatment. Well-dispersed particles are observed in each SEM image. The diameters of the dispersed particles in the β phase at Y concentrations of 0.05, 0.1, 0.2 and 0.5 mass% are $0.52 \pm 0.43 \mu\text{m}$, $0.45 \pm 0.42 \mu\text{m}$, $0.62 \pm 0.79 \mu\text{m}$ and $2.80 \pm 2.72 \mu\text{m}$, respectively. EPMA analysis

Fig. 4 Average grain diameters of the β phase of TNTZ and TNTZ-0.05Y, TNTZ-0.1Y, TNTZ-0.2Y, and TNTZ-0.5Y.

result shown in Fig. 6 reveals the composition of the particles to be Y_2O_3 , which is formed by a reaction between the added Y and the oxygen contained in TNTZ.

Figure 7 shows Young's moduli of TNTZ and Y-added TNTZ with Y concentrations of 0.05, 0.1, 0.2 and 0.5 mass% after cold rolling. Young's modulus of TNTZ subjected to cold rolling is approximately 60 GPa. The Young's moduli of Y-added TNTZ with Y concentrations of 0.05, 0.1, 0.2 and 0.5 mass% subjected to cold rolling remains approximately 60 GPa. Slightly lower Young's moduli are obtained in TNTZ and Y-added TNTZ with a Y concentration of 0.5 mass% as compared with those of Y-added TNTZ with Y concentrations of 0.05, 0.1 and 0.2 mass%.

The tensile properties of TNTZ and Y-added TNTZ with Y concentrations of 0.05, 0.1, 0.2 and 0.5 mass% subjected to cold rolling are shown in Fig. 8. The tensile strength of TNTZ is approximately 740 MPa in this experiment. No change in tensile strength is observed in Y-added TNTZ with a Y concentration of 0.05 mass%. The tensile strength slightly increases in Y-added TNTZ with a Y concentration of 0.1 mass%, whereas it tends to decrease in Y-added TNTZ with Y concentrations of 0.2 and 0.5 mass%. The maximum value of tensile strength of 800 MPa can be achieved, by taking into account the maximum value of the error bar in Y-added TNTZ with a Y concentration of 0.1 mass%. As compared to the tensile strength of TNTZ, the tensile strength of Y-added TNTZ with a Y concentration of 0.1 mass% improves by 11%. The 0.2% proof stress significantly increases with increasing Y concentration below 0.1 mass%. An increase of approximately 16% is achieved in the 0.2% proof stress in Y-added TNTZ with Y concentration of 0.05 and 0.1 mass%. At Y concentrations higher than 0.2 mass%, the 0.2% proof stress decreases in a manner similar to that of tensile strength. Elongation tends to decrease in Y-added TNTZ with Y concentrations of 0.05, 0.1, 0.2 and 0.5 mass% as compared to that of TNTZ.

The fracture surfaces of TNTZ and Y-added TNTZ with Y concentrations of 0.05, 0.1, 0.2 and 0.5 mass% subjected to cold rolling after tensile tests are shown in Fig. 9. The size of the dimples in the Y-added TNTZ is smaller than that of TNTZ, and many Y_2O_3 particles are found inside the dimples in the fracture surfaces of Y-added TNTZ with Y concentrations of 0.2 and 0.5 mass%. These large oxide

Fig. 5 SEM images of (a) TNTZ-0.05Y, (b) TNTZ-0.1Y, (c) TNTZ-0.2Y, and (d) TNTZ-0.5Y subjected to solution treatment.

Fig. 6 EPMA analysis of particles formed in TNTZ-0.5Y.

Fig. 7 Young's moduli of TNTZ and TNTZ-0.05Y, TNTZ-0.1Y, TNTZ-0.2Y, and TNTZ-0.5Y.

Fig. 8 Tensile properties of TNTZ and TNTZ-0.05Y, TNTZ-0.1Y, TNTZ-0.2Y, and TNTZ-0.5Y.

Fig. 9 SEM fractographs of (a) TNTZ and (b) TNTZ-0.05Y, (c) TNTZ-0.1Y, (d) TNTZ-0.2Y, and (e) TNTZ-0.5Y subjected to cold rolling after tensile tests.

particles, formed by the oxidation of Y added to TNTZ, are the cause of the decrease in the tensile strength and the 0.2% proof stress because they work as sources of voids generated during fracture.

Taking into account the strength and elongation balance, fatigue tests of TNTZ and Y-added TNTZ with a Y concentration of 0.05 mass% were carried out. S-N curves of TNTZ and Y-added TNTZ with a Y concentration of 0.05 mass% are shown in Fig. 10. The fatigue limit of Y-added TNTZ with a Y concentration of 0.05 mass%, which is the maximum cyclic stress where a material can endure for

10^7 cycles without breaking, is about 470 MPa, which is higher than the value for TNTZ. The fatigue strength of Y-added TNTZ with a Y concentration of 0.05 mass% is considerably improved in both the low- and high-cycle fatigue life regions.

4. Discussion

From the above results, it is found that Y, which added to TNTZ, produces well-dispersed Y_2O_3 particles in the grains through a reaction between Y and the oxygen contained in

Fig. 10 Fatigue properties of TNTZ and TNTZ-0.5Y.

TNTZ. The average diameter and its standard deviation of the Y_2O_3 particles generated in Y-added TNTZ increased at Y concentrations of 0.2 and 0.5 mass%. The Y_2O_3 particles formed by the addition of Y suppressed the orientation change in texture caused by cold rolling. This pinning effect occurred in TNTZ with Y concentrations of 0.05, 0.1 and 0.2 mass%. At a Y concentration of 0.5 mass%, large Y_2O_3 particles with an average diameter of approximately 3 μm did not work as pins against the change in orientation. Y-added TNTZ with Y concentrations of 0.05, 0.1, 0.2 and 0.5 mass% retained low Young's moduli similar to that of TNTZ. The slightly smaller Young's moduli of TNTZ and Y-added TNTZ with a Y concentration of 0.5 mass% could be attributed to the change in orientation of the texture. Young's modulus depends on the textures of TNTZ. For example, the $\langle 111 \rangle$ and $\langle 110 \rangle$ directions exhibit relatively high Young's moduli in TNTZ.¹⁷⁾ It is supposed that planes with low Young's moduli were orientated by cold rolling in TNTZ and Y-added TNTZ with the Y concentration of 0.5 mass%.

The Y_2O_3 particles generated in Y-added TNTZ led to a decrease in the grain diameter of Y-added TNTZ. This grain refinement and dispersion of Y_2O_3 particles improved the tensile strength of Y-added TNTZ with a Y concentration of 0.1 mass%. When the large Y_2O_3 particles were formed in Y-added TNTZ with Y concentrations of 0.2 and 0.5 mass%, distances of particles increased and did not work as an inhibitor against the sliding of dislocations introduced by cold rolling. In addition, the Y_2O_3 particles worked as sources of voids generated during fracture, which caused a significant decrease in the tensile strength of Y-added TNTZ with Y concentrations of 0.2 and 0.5 mass%. Consequently, in order to improve the tensile strength and 0.2% proof stress, 0.1 mass% of Y addition is an appropriate concentration. However, the elongation significantly decreased in Y-added TNTZ with the Y concentration of 0.1 mass%. Taking into account of the balance of tensile strength, 0.2% proof stress and elongation, mechanical properties of Y-added TNTZ with a Y concentration of 0.05 mass% may be more superior than that of Y-added TNTZ with a Y concentration of 0.1 mass%. As compared with the results in a previous study,¹⁵⁾ which was a study on the dispersion strengthening of TNTZ through the addition of Y_2O_3 particles, Y-added TNTZ exhibited different tendencies from that of the Y_2O_3 -added TNTZ in terms of the mechanical properties. A slight increase in

tensile strength occurred in both Y-added TNTZ and Y_2O_3 -added TNTZ. Although the well-dispersed Y_2O_3 particles were obtained in Y-added TNTZ with Y concentrations of 0.05, 0.1, 0.2 and 0.5 mass%, the tensile strength decreased in Y-added TNTZ with Y concentrations of 0.2 and 0.5 mass% because of the large Y_2O_3 particles. The 0.2% proof stress of the Y-added TNTZ increased considerably at Y concentrations below 0.1 mass%, whereas that of the Y_2O_3 -added TNTZ decreased as compared to that of TNTZ. Song *et al.* have reported that debonding of Y_2O_3 particles causes the decrease of 0.2% proof stress due to weak bonding of interface between TNTZ and Y_2O_3 particles added to TNTZ in previous study.¹⁵⁾ It is supposed that the interface between TNTZ and Y_2O_3 particles formed in TNTZ by a reaction of Y and the oxygen contained in TNTZ is stronger than that in Y_2O_3 -added TNTZ. Therefore, the 0.2% proof stress of Y-added TNTZ increased with Y concentrations of 0.05 and 0.1 mass%. The elongation of Y-added TNTZ decreased with increasing Y concentration. On the other hand, the elongation of Y_2O_3 -added TNTZ was the same as that of TNTZ. It is supposed that the difference in the interface between the particles and TNTZ led to such differences in the mechanical properties.

5. Conclusions

The formation of dispersed Y_2O_3 particles in TNTZ was intended in order to improve the mechanical properties of TNTZ through a reaction of the Y added to TNTZ and the oxygen contained in TNTZ. The following results were obtained in this study:

- (1) Well-dispersed Y_2O_3 particles are formed by a reaction between Y added to TNTZ and the oxygen contained in TNTZ. The diameter and its standard deviation of the obtained Y_2O_3 particles increases in Y-added TNTZ with Y concentrations of 0.2 and 0.5 mass%.
- (2) The addition of Y leads to a decrease in grain size in Y-added TNTZ after solution treatment.
- (3) Young's moduli of Y-added TNTZ with Y concentrations of 0.05, 0.1, 0.2, and 0.5 mass% subjected to cold rolling remain approximately 60 GPa, i.e., there is no significant difference from that of TNTZ.
- (4) The tensile strength and the 0.2% proof stress increase in Y-added TNTZ with Y concentrations below 0.1 mass%, whereas these properties decrease significantly in Y-added TNTZ with Y concentrations of 0.2 and 0.5 mass%. The Y_2O_3 particles work as sources of voids generated during fracture, which causes a decrease in the tensile strength.
- (5) The addition of 0.05 mass% of Y provides Y-added TNTZ with improved mechanical properties (tensile and fatigue properties).

Acknowledgement

This study was supported in part by Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (Grant Number 24246111 and Grant Number 24656401) and the Global COE program "Materials Integration International Center of Education and Research,

Tohoku University”, Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan; the Tohoku Leading Women’s JUMP UP Project, Tohoku University; the inter university cooperative research program “Innovative Research for Biosis-Abiosis Intelligent Interface”, MEXT; and the cooperative research program of the Advanced Research Center of Metallic Glasses, Institute for Materials Research, Tohoku University.

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