High-Strength Metastable Beta-Titanium Alloys for Biomedical Applications

J.I. Qazi, B. Marquardt, and H.J. Rack

This investigation has shown that the strength of low-modulus metastable beta-titanium alloys can be increased by increasing their oxygen content and/or aging. Yield strength as high as 1,288 MPa along with reasonable ductility was obtained by aging Ti-35Nb-7Zr-5Ta-0.7O at 482°C for 8 h. Strengthening of these alloys is discussed in terms of ω- and α-phase precipitates.

INTRODUCTION

Most titanium alloys traditionally used for biomedical applications were originally developed for aerospace applications. In contrast, recently introduced low-modulus metastable β-Ti alloys were developed specifically for orthopedic applications, their aim being to decrease the elastic modulus difference between natural bone (10–30 GPa) and the implant material, thereby promoting load sharing between bone and implant.[1,2] This effort was undertaken in recognition of the fact that when insufficient load sharing occurs, for example as a result of either Ti-6Al-4V or cobalt implants being employed, natural bone resorption and loosening of the joint many occur. Indeed, this phenomenon, termed "stress-shielding induced bone resorption,"[2] is one of the main factors necessitating total hip replacement revision surgery.

Normally, low-modulus metastable β-Ti alloys are used in low-strength solution-treated condition. For example, Ti-35Nb-7Zr-5Ta in the solution-treated condition has an elastic modulus of 55 GPa, a yield strength of 530 MPa, and an elongation of 20%.[3] However, the strength of these alloys can be improved, albeit at some increase in elastic modulus, by increasing their oxygen content and/or by artificial aging.[3–11] These increases make them attractive candidates for other biomedical applications (e.g., bone plates and screws). This article provides an overview of an effort aimed at understanding the effect of oxygen content and aging on the phase transformations and tensile properties of Ti-35Nb-7Zr-5Ta. See the sidebar for experimental procedures.

RESULTS AND DISCUSSION

In the solution-treated condition, all the alloys examined in this investigation consisted of a single β-phase structure

EXPERIMENTAL PROCEDURE

Table A lists the chemical composition of three Ti-35Nb-7Zr-5Ta alloys containing varying oxygen contents. These alloys were produced by vacuum arc melting, and the differing oxygen contents were controlled through the addition of rutile (TiO_2). These materials were hot forged, rolled to 16 mm diameter rods, solution treated at 850°C (low oxygen), 840°C (medium oxygen), and 900°C (high oxygen) for 1 h, water quenched, and aged at 427°C, 482°C, 538°C, or 593°C for 8 h followed by air cooling. Additional samples were pre-aged at 260°C for 4 h prior to aging at 427°C for 8 h to examine what benefits might be accrued by duplex aging. The room-temperature tensile properties of the solution-treated and the solution-treated and aged conditions were determined at a strain rate of 0.5 s^{-1} per ASTM E8.

A microstructural analysis was also performed by optical, scanning, and transmission-electron microscopy (TEM). Samples for the former were prepared by standard mechanical polishing with final etching in a solution consisting of 8 vol.% HF, 15 vol.% HNO_3, and 77 vol.% distilled H_2O. Thin foils for TEM analysis were prepared by ion milling at an angle of 15° using a voltage of 4 kV and a current of 1 mA. Finally, phase analysis of the solution-treated as well as the solution-treated and aged samples was undertaken by x-ray diffraction using Cu-Ka radiation at 45 kV and 40 mA.

Table A. Chemical Composition of Ti-35Nb-7Zr-5Ta Alloys (wt.%)

Alloy	Ti	Nb	Zr	Ta	H	C	N	O
Low O	Bal.	35.3	7.2	4.9	0.001	0.013	0.002	0.06
Medium O	Bal.	34.6	7.3	5.6	0.005	0.046	0.009	0.46
High O	Bal.	34.6	7.1	5.6	0.006	0.048	0.012	0.68

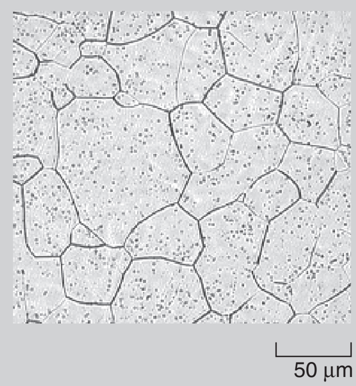

Figure 1. An optical photomicrograph showing the microstructure of solution-treated Ti-35Nb-7Zr-5Ta-0.06O.

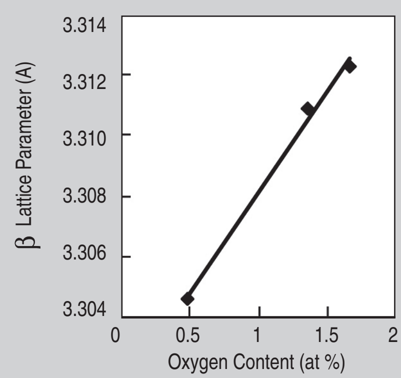

Figure 2. The dependence of β-phase lattice parameter of Ti-35Nb-7Zr-5Ta on oxygen content in the solution-treated condition.

Table I. Tensile Properties of Ti-35Nb-7Zr-5Ta-0.06O

Heat Treatment	YS (MPa)	UTS (MPa)	El. (%)	RA (%)
Solution treated	530	590	21	69
427°C/ 8 h	630	686	17	42
482°C/ 8 h	503	534	20	46
538°C/ 8 h	493	537	21	52
593°C/ 8 h	508	549	26	63
260°C/ 4 h/ 427°C/8 h	693	753	15	35

Table II. Tensile Properties of Ti-35Nb-7Zr-5Ta-0.46O

Heat Treatment	YS (MPa)	UTS (MPa)	El. (%)	RA (%)
Solution treated	937	1,014	19	55
427°C/ 8 h	1,007	1,055	12	27
482°C/ 8 h	1,060	1,149	9	17
538°C/ 8 h	806	929	11	22
593°C/ 8 h	765	861	15	22
260°C/ 4 h/ 427°C/8 h	1,202	1,244	8	16

Table III. Tensile Properties of Ti-35Nb-7Zr-5Ta-0.68O

Heat Treatment	YS (MPa)	UTS (MPa)	El. (%)	RA (%)
Solution treated	1,081	1,097	21	50
427°C/ 8 h	1,222	1,252	9	13
482°C/ 8 h	1,288	1,362	8	9
538°C/ 8 h	1,036	1,180	9	11
593°C/ 8 h	893	1,036	10	12
260°C/ 4 h/ 427°C/8 h	1,234	1,260	7	9

with an average grain size of 60 μm, 23 μm, and 28 μm, respectively (Figure 1). The black spots seen in this figure are common to all and represent etch pits that develop during the rather lengthy etching time required. An x-ray analysis also revealed that the lattice parameters of the β phase increased with increasing oxygen content (Figure 2).

The tensile properties of the solution-treated and the solution-treated and aged specimens are listed in Tables I to III for Ti-35Nb-7Zr-5Ta-0.06/0.46/0.68O, respectively. With an increase in the oxygen content in the solution-treated condition, the yield and ultimate tensile strength increased while the elongation remained unaffected. This increase in strength can be attributed to the oxygen interstitial solid-solution strengthening of the β phase.

Initial analysis of Ti-35Nb-7Zr-5Ta-0.06O indicated that aging at 427°C for 8 h had little effect on the microstructure when compared to the solution-treated condition. In contrast, examination of Ti-35Nb-7Zr-5Ta-0.46/0.68O revealed the presence of fine α precipitates, as illustrated in Figure 3 for Ti-35Nb-7Zr-5Ta-0.46O. However, the presence of an ω phase in Ti-35Nb-7Zr-5Ta-0.06/0.46O after aging at 427°C for 8 h was detected by x-ray diffraction analysis (Figure 4) and confirmed by TEM. The dark-field photomicrograph in Figure 5 illustrates the almost circular ω phase morphology observed in Ti-35Nb-7Zr-5Ta-0.06O. These and other TEM observations (to be reported later) suggested that increasing oxygen content tended to suppress ω formation while enhancing α phase formation.

The tensile results indicate that aging at 427°C for 8 h increased the yield strength of all the alloys examined when compared to the solution-treated condition. The largest percentage increase in yield strength, approximately 19%, occurred in Ti-35Nb-7Zr-5Ta-0.06O and was associated with the aforementioned precipitation of fine ω phase precipitates. In contrast, the ω+α and α precipitate microstructures observed, respectively, in Ti-35Nb-7Zr-0.46O and Ti-35Nb-7Zr-5Ta-0.68O resulted in an increase of approximately 7.5% and 13% in their respective yield strength vis-a-vis the solution-treated condition. In all cases, these increases in strength were accompanied by a decrease in tensile ductility, the elongation and reduction in area decreasing for all three alloys after aging at 427°C for 8 h. However, the percentage decrease in tensile ductility was dependent on the oxygen content, the largest percentage decrease being observed in Ti-35Nb-7Zr-5Ta-0.68O.

Aging at 482°C and above had little effect on either the microstructure or tensile properties of Ti-35Nb-7Zr-5Ta-0.06O. In contrast, the aging of Ti-35Nb-7Zr-5Ta-0.46/0.68O at 482°C for 8 h resulted in the formation of fine α precipitates with some evidence for precipitate-free zones associated with

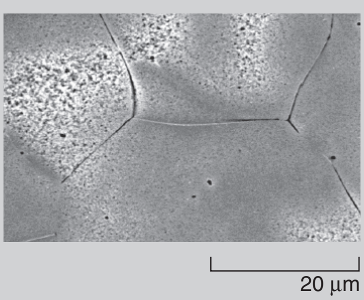

Figure 3. A scanning-electron micrograph showing fine α precipitates in Ti-35Nb-7Zr-5Ta-0.460 aged at 427°C for 8 h.

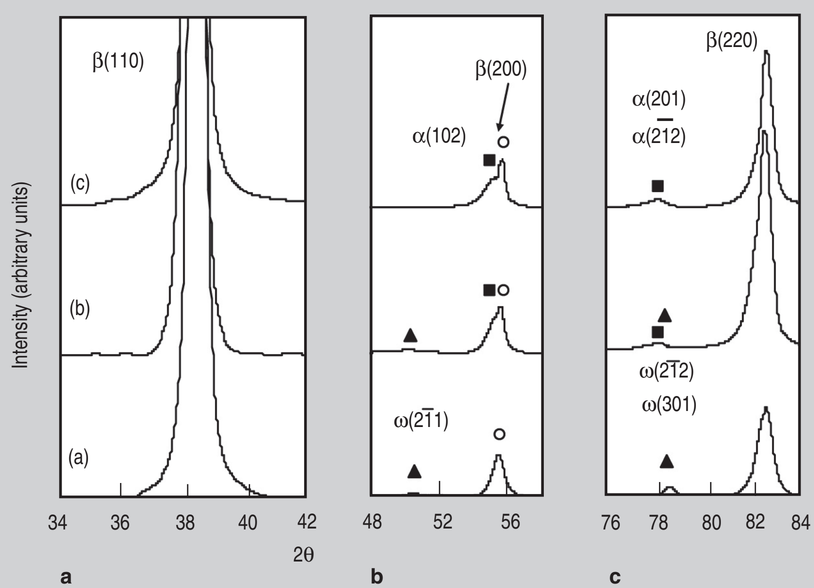

Figure 4. X-ray diffraction patterns for Ti-35Nb-7Zr-5Ta containing (a) 0.06%, (b) 0.46%, and (c) 0.68% oxygen aged at 427°C for 8 h.

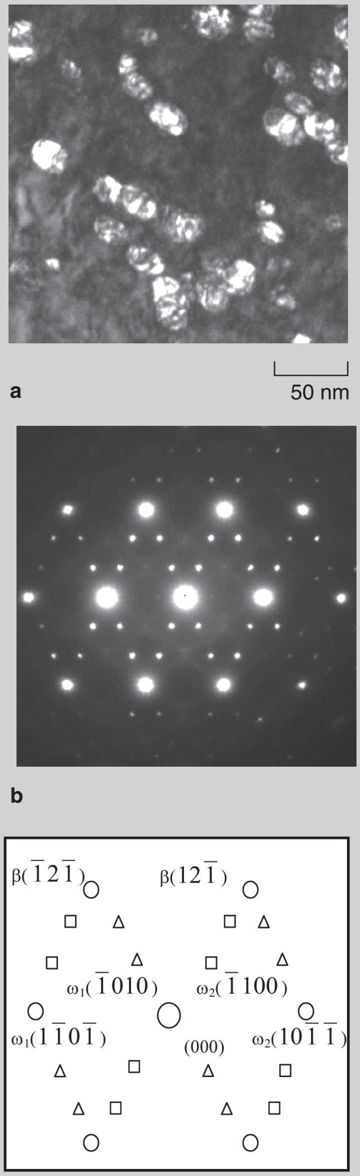

Figure 5. Transmission electron micrographs of Ti-3Nb-7Zr-5Ta-0.06O aged at 427°C for 8 h; (a) a dark field showing ω precipates; (b) the corresponding selected area diffraction pattern; (c) a key diagram for the selected area diffraction pattern in (b).

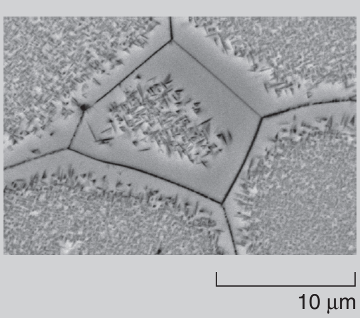

Figure 6. A scanning-electron micrograph showing α phase precipitates and precipitate-free zone in Ti-35Nb-7Zr-5Ta-0.46O aged at 538°C for 8 h.

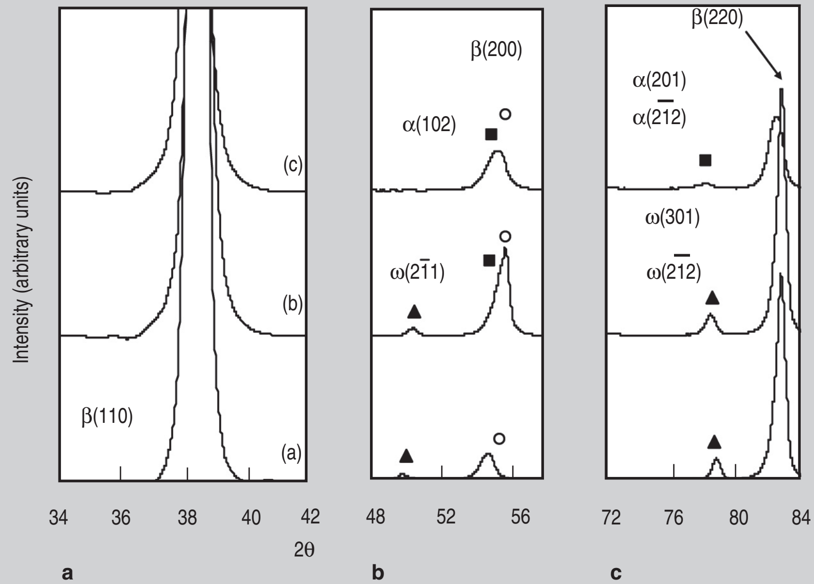

Figure 7. X-ray diffraction patterns for Ti-35Nb-7Zr-5Ta containing (a) 0.06%, (b) 0.46%, and (c) 0.68% oxygen aged at 260°C for 4 h/427°C for 8 h.

prior β grain boundaries. These conditions resulted in an approximate 13% and 19% increase in yield strength when compared to the solution-treated condition. Indeed, aging at 482°C for 8 h resulted in the highest yield strength (1,288 MPa) observed for Ti-35Nb-7Zr-5Ta-0.68O with the tensile ductility still remaining within acceptable limits (i.e., 8% elongation). Further increases in aging temperature to 538°C or higher led to coarsening of the lenticular α phase, as illustrated in Figure 6 for Ti-35Nb-7Zr-5Ta-0.46O. In addition, increased aging temperature led to an increase in the width of the precipitate-free zones. Ultimately, the yield strength as well as the tensile ductility of Ti-35Nb-7Zr-5Ta-0.46/0.68O decreased after aging at these higher temperatures.

Finally, duplex aging resulted in a higher volume fraction of ω in comparison to a single aging treatment in both the Ti-35Nb-7Zr-5Ta-0.06O and Ti-35Nb-7Zr-5Ta-0.46O, where previous study showed an $\omega+\beta$ and $\omega+\alpha+\beta$ structure, respectively. This increase is most easily seen by considering the increase in the integrated intensity of $(2\bar{1}1)$, (301), and $(2\bar{1}2)$ ω peaks in Figure 7. This increase also resulted in the largest increases in tensile yield strength observed in this study, approximately 31% and 28%, when compared to the solution-treated condition, although with some sacrifice in tensile elongation.

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