Effects of Silicon and Heat-Treatment on Microstructure and Mechanical Properties of Biomedical Ti-39Nb-6Zr Alloy

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Abstract: The cytotoxic tissue reactions of alloying elements (Al, V) of Ti-6Al-4V have been reported, whereas the Ti-39Nb-6Zr (TNZ40) alloy developed by adding β-phase stabilizing elements is known to have no cytotoxicity and exhibits excellent biocompatibility. In addition, there is a slight modulus difference between the TNZ40 alloy and human bones as the elastic modulus of the TNZ40 alloy is very low. This can inhibit detrimental effects such as osteoblast loss due to a stress-shielding effect. In this study, various Si contents were added and heat treatment under various conditions was performed to control the microstructure and mechanical properties of the TNZ40 alloy. In the β-type titanium alloy, the ω phase is commonly observed by quenching from the solution-treatment or aging-treatment temperature. These ω precipitates can typically increase the elastic modulus, hardness, and embrittlement of the β-type titanium alloy, which are important to control this phase. The correlation between Si content and precipitation and the effects of solution treatment and aging condition on the mechanical properties such as tensile strength, and hardness, were analyzed.

Keywords: Ti-39Nb-6Zr; silicon; biomedical materials; heat treatment; mechanical property

1. Introduction

Titanium and its alloys are generally used as high-value-added materials in the transportation equipment sector due to their excellent specific strength and corrosion resistance. They are also used in medical implants due to their superior biocompatibility [1,2]. The commercialized Ti-6Al-4V alloy has been reported to possibly cause various diseases, as alloy elements (Al, V) are released into the body when implanted. Therefore, it is necessary to develop bio-friendly titanium alloys that can replace the Ti-6Al-4V alloy [3,4]. These alloys also require good mechanical properties to increase the service life of the part, extend the dietary range, and make artificial implants lighter [5]. However, the elastic modulus generally increases with increasing strength. A stress-shielding effect will occur if the alloy has a high elastic modulus. The stress-shielding effect is a phenomenon in which a major portion of the force is transmitted to objects with high elastic modulus when an external force is applied to two objects with different elastic moduli [6]. Bones can grow by constantly being stimulated by external load. However, bones are not stimulated by the stress-shielding effects due to the application of implants with high elastic modulus; consequently, bones may deteriorate gradually, resulting in diseases such as osteoporosis [7].

The Ti-39Nb-6Zr (TNZ40) alloy was developed by adding the β-phase stabilizing element (Nb), which exhibits no cytotoxicity and excellent biocompatibility [8]. Particularly, as the difference between the elastic moduli of human bone and the TNZ40 alloy (~40 GPa in the case of β single phase [9]) is very small, the damage caused by the stress-shielding effects can be minimized. In the case of the β-titanium alloy, the amount, size, and distribution of precipitates are important factors for improving the mechanical properties through precipitation hardening. The temperature and duration of solution treatment and aging are important variables to control these factors [10]. Si, which is added in this study, is known to have good biocompatibility without cytotoxicity [11–13], and it improves the...
strength by limiting cross slip by reducing the stacking fault energy [14]. In this study, TNZ40 (Ti-39Nb-6Zr) alloys are manufactured using vacuum arc re-melting by adding various Si contents to improve the mechanical properties. Cold swaging, solution treatment at a temperature above β transus (approximately 810 °C), and aging are performed to control the mechanical properties of the TNZ40 + Si alloys. The correlation between the precipitation and Si content and the effects of heat-treatment conditions on the mechanical properties such as elastic modulus, hardness, and tensile strength are analyzed.

2. Experimental

With the addition of various Si contents (0, 0.1, 0.2 wt%) to Ti, Nb, and Zr elements with a purity of 99% or higher, ingots with the composition Ti-39Nb-6Zr (wt%) were manufactured via vacuum arc re-melting by ourselves. The initial size of the manufactured ingot was Φ16 mm, and cold swaging was performed using a swaging machine to improve the mechanical properties. The final bar size was Φ12 mm (hereafter referred to as the as-swaged specimen), and the reduction in the area was 43.8%.

The as-swaged specimens were heat-treated using an electric furnace (F6030CM-33-60, Thermo Scientific, Seoul, Korea). Solution treatment was performed at 830 °C for 1 h, followed by water quenching, and then aging treatment was performed at 380 °C for 16 h, followed by air-cooling (hereafter, referred to as solution treatment and aging (STA)-treated specimens).

The as-swaged and STA-treated specimens were ground from #100 to #2000 using a sand paper and were polished to the surface of a mirror using 6 µm, 1 µm, and 0.04 µm abrasives. The polished specimens were etched in Kroll solution (H2O 100 mL + HNO3 5 mL + HF 3 mL) and analyzed using an optical microscope (OM, BX53MRF-S, Olympus, Tokyo, Japan) to investigate their microstructural evolution with various Si contents and heat-treatment conditions. The grain sizes of the as-swaged and STA-treated specimens were measured by Image Analyzer software (LeopardTM 2009 iX, Zootos, Gyeonggi-do, Korea) based on circular intercept procedure (ASTM E112). An X-ray diffractometer (Brucker D8, XRD, Billerica, MA, USA) using Cu-Kα radiation at a diffraction angle (2θ) range of 30–90°, step size of 0.05°, and time-step of 3 s was used to identify the phase composition of the TNZ40 + Si alloys. A high-resolution transmission electron microscope (HR-TEM, TECNAI F20, FEI Company Hillsboro, Oregon, USA) was used to observe fine precipitates.

Hardness and room-temperature tensile tests were performed to evaluate the mechanical properties of the as-swaged and STA-treated specimens. The hardness test was performed using a Vickers hardness tester (HM-200, Mitutoyo, Takatsu, Japan), and 15 points were recorded from the side to the center region of the round specimens. Furthermore, tensile test specimens were fabricated according to ASTM E8/E8M, and the room-temperature tensile test was performed using a universal testing machine (UTM, BESTUTM-10MD, Ssaul Bestech, Seoul, Korea). The ultimate tensile strength (UTS), yield strength at 0.2% offset (YS), and elongation at fracture (El) were correspondingly determined.

3. Results and Discussion

3.1. Variation of Microstructural Characteristics

Microstructures of the Ti-39Nb-6Zr (TNZ40) alloys were observed using the OM to investigate their evolution with various Si contents and heat-treatment conditions. Figure 1 shows the optical microstructures of the as-swaged and STA-treated specimens. Nb is β-stabilized elements, and the manufactured TNZ40 alloy is a β-type titanium alloy with an equi-axed β phase (body-centered cubic crystal structure), as shown in Figure 1. The grain sizes of the as-swaged TNZ40, TNZ40 + 0.1 Si, and TNZ40 + 0.2 Si alloys were 383 µm (standard dev. 112 µm), 298 µm (standard dev. 178 µm), and 184 µm (standard dev. 91 µm), respectively, indicating a decrease with increasing Si content. In Figure 1d–f, as the solution treatment and aging were conducted after cold swaging, the grain was coarsened. A nano-sized ω phase was precipitated in the β matrix. The precipitated ω
phase was investigated using XRD and HR-TEM. The grain sizes of the aforementioned specimens after STA treatment were 425 µm, 367 µm, and 305 µm, respectively, indicating a decrease with increasing Si content, similar to the trend before the heat treatment. This phenomenon can be described in relation to the Si solution behavior within Ti [15–18]. The partitioning coefficient (k) for Si in Ti is 0.333; Si is rejected during the initial solidification, and constitutional under-cooling can activate adjacent nuclei. Consequently, the grain is refined by nuclei generation and growth through constitutional under-cooling.

Figure 1. Optical microscopy of as-swaged specimens (a–c) and solution treatment and aging (STA)-treated (d–f); (a,d) TNZ40, (b,e) TNZ40 + 0.1 Si, and (c,f) TNZ40 + 0.2 Si.

3.2. Effect of Si Content

To investigate the effect of Si content, XRD was used to identify the phase composition of the STA-treated specimens with varying Si contents. Figure 2 shows the XRD patterns of the STA-treated specimens after cold swaging, where (a), (b), and (c) correspond to the Si contents of 0%, 0.1%, and 0.2%, respectively. The β phase was mainly detected, and some α phase was also detected in all the specimens. However, ω particles in a beta matrix were developed in the specimen containing 0% Si (Figure 2a). As the TNZ40 alloy is a metastable β-Ti alloy, ω-solvus was formed between 400 °C and 430 °C, and both ω and α phases were developed during heat treatment at approximately 400 °C [5]. Some ω phase was also detected in the specimen containing 0.1% Si, and the continuous increase in Si content reduced the density of the ω phase. This reduction is attributed to the presence of Si as a β phase stabilization element. As the Si content increases, it interferes with the precipitation of the ω phase, which increases the strength of the β-Ti alloys [19,20].

The microstructures of the STA-treated specimens were closely observed using a TEM to investigate the size, shape, and distribution of the precipitates with the addition of Si. Figure 3 shows the optical microstructures of the STA-treated TNZ40 + 0.2 Si alloy observed using the TEM. It was observed that fine spherical compounds grown to a size of 0.1 µm were precipitated, mainly along the grain boundaries. Crystal structure analysis was performed to investigate the precipitations. Figure 4b,c show the diffraction pattern of the matrix and the precipitations shown in Figure 4a. Figure 4b shows the selected-area diffraction (SAD) pattern of the β-Ti matrix from Z = <111>. Figure 4c shows the SAD pattern from Z = <011> of the fine α phase precipitated at a size of approximately 0.5 µm in the β-matrix (Figure 4a). Figure 4d shows the SAD pattern from Z = <100> of the finer Ti silicide precipitated at a size of 0.1 µm along the β grain boundaries (Figure 4a). The form of the Ti silicide is reported to be stabilized through the TiSi$_2$→TiSi→Ti$_3$Si$_4$→Ti$_5$Si$_3$
transformation process [16]. In this study, the crystal structure of the precipitates was identified as Ti₅Si₄ (tetragonal, \(a = 12.174 \, \text{Å}, \ b=6.702 \, \text{Å}\)), corresponding to the metastable intermediate phase.

![X-ray diffraction patterns obtained from STA-treated TNZ40 alloys](image)

**Figure 2.** X-ray diffraction patterns obtained from STA-treated TNZ40 alloys: (a) TNZ40, (b) TNZ40 + 0.1 Si, and (c) TNZ40 + 0.2 Si.

![TEM microscopy of STA-treated TNZ40 alloy containing 0.2% Si](image)

**Figure 3.** TEM microscopy of STA-treated TNZ40 alloy containing 0.2% Si.
3.3. Variation of Mechanical Properties

Room-temperature tensile test and hardness measurement were performed to evaluate the mechanical properties according to the microstructures. Figures 5 and 6 show the stress-strain curves of all the specimens, and Table 1 shows the room-temperature tensile characteristics (YS, UTS, El) obtained from the stress-strain curves. The cold-swaged specimens (Figure 5, (a) 0%, (b) 0.1%, and (c) 0.2%) showed increases in the YS (895→910 MPa) and UTS (900→912 MPa) and a decrease in the El (12.3%→4.2%) with increasing Si content (0%→0.2%). The YS and UTS showed no significant increase because the work hardening effect by cold swaging is considerably more dominant than the effect of grain refinement hardening. El decreased due to the effect of Ti silicide with increasing Si content. As shown in Figure 7, the as-swaged specimens were principally characterized by the brittle intergranular fracture mode with increasing Si content.

The STA-treated specimens (Figure 6, (a) 0%, (b) 0.1%, and (c) 0.2%) showed a decrease in the El (5.5%→4.3%→2.9%) with increasing Si content (0%→0.2%). The YS (753→731 MPa) and UTS (788→758 MPa) decreased with the increase in Si content from 0% to 0.1%. The YS and UTS decreased overall after STA. This is due to the greater reduction in the work hardening effects by grain growth [21], and the decrease in dislocation density and plastic deformation energy [22], despite a hardening effect by the precipitates of the ω phase after the aging treatment [23].
Figure 5. Tensile engineering stress-strain curves of as-swaged TNZ40 alloys; (a) TNZ40, (b) TNZ40 + 0.1 Si, and (c) TNZ40 + 0.2 Si.

Figure 6. Tensile engineering stress-strain curves of STA-treated TNZ40 alloys: (a) TNZ40, (b) TNZ40 + 0.1 Si, and (c) TNZ40 + 0.2 Si.

Table 1. Comparison of the tensile mechanical properties of the TNZ40 + x Si alloys: yield stress ($\sigma_y$), ultimate tensile strength ($\sigma_{\text{max}}$), and elongation (El).

| Sample Conditions | Si Contents | $\sigma_y$ (MPa) | $\sigma_{\text{max}}$ (MPa) | El (%) |
|-------------------|-------------|------------------|-----------------------------|--------|
| As-swaged         | 0%          | 895 ± 6          | 900 ± 3                     | 12.3 ± 1.5 |
|                   | 0.1%        | 907 ± 4          | 910 ± 3                     | 7.0 ± 1.2  |
|                   | 0.2%        | 910 ± 4          | 912 ± 5                     | 4.2 ± 2.3  |
| STA               | 0%          | 753 ± 7          | 788 ± 6                     | 5.5 ± 1.6  |
|                   | 0.1%        | 731 ± 6          | 758 ± 8                     | 4.3 ± 1.7  |
|                   | 0.2%        | 915 ± 8          | 942 ± 12                    | 2.9 ± 1.9  |
In the case of the TNZ40 + 0.2 Si alloy, the YS (915 MPa) and UTS (942 MPa) increased after the heat treatment, due to the precipitation hardening effects of the Ti silicides by over-aging. $\text{Ti}_5\text{Si}_4$ observed via TEM (Figure 3) coheres to the $\beta$-Ti matrix and precipitates finely, inhibiting grain growth and resulting in increases in the YS and UTS [24]. The reasons for the initial decrease in the YS and UTS (0.1% Si) and subsequent increase (0.2% Si) with increasing Si content in the STA-treated specimens are as follows. Because the specimen containing 0.1% Si was mainly reinforced by the $\omega$ phase, rather than the effect of precipitation hardening by Ti silicides with the addition of Ti, the UTS decreased due to a reduction in the fraction of the $\omega$ phase precipitation by Si. In contrast, the UTS of the specimen containing 0.2% Si was higher than that of the specimen containing 0% Si due to the grain refinement and Ti silicide precipitation, even if the fraction of the $\omega$ phase was significantly reduced, as the precipitation hardening effect by Ti silicides was predominant. Figure 8 shows the results of the Vickers hardness measurements. The hardness values of the STA-treated specimens with various added Si contents showed the same tendency as the tensile test results. In other words, the as-swaged specimens have higher overall hardness values than the STA-treated specimens due to the greater work hardening effect and grain refinement by swaging.

The El of the STA-treated TNZ40 alloys decreased compared with that of the as-swaged TNZ40 due to the high brittleness of the $\omega$ phase and the grain growth by the solution treatment and over-aging. For the STA-treated TNZ40 + 0.1 Si alloy, the El reduction effect due to the inhibition of the $\omega$ phase growth by the addition of Si was reduced, but the overall El decreased due to grain coarsening and Ti silicides. For the STA-treated
TNZ40 + 0.2 Si alloy, as shown in the XRD results (Figure 2), no ω phases were observed, but the overall El decreased because the El reduction effect due to the precipitation of Ti silicides considerably increases with increasing Si content. In addition, as Ti₅Si₄ exists along the grain boundaries of a relatively soft β phase, it acted as the crack initiation site during the room-temperature tensile test. The specimen containing 0.2% Si was principally characterized by the brittle intergranular fracture mode with low plastic deformation and no ductile fracture (Figure 7). Consequently, it was determined that the El decreased sharply with increasing Si content.

4. Conclusions

The influences of Si contents and heat-treatment conditions on the microstructure and mechanical properties of the as-swaged Ti-39Nb-6Zr (TNZ40) alloy were investigated, and the following conclusions were drawn:

(1) For the as-swaged alloys, the work hardening effect by cold swaging was much more dominant than the effect of grain refinement hardening. For the decrease in El, the specimens were principally characterized by the brittle intergranular fracture mode with increasing Si content.

(2) ω particles in a beta matrix were precipitated in the STA-treated specimen containing no Si content. The continuous increase in Si content interfered with the precipitation of the ω phase, which increased the strength of the β-Ti alloys.

(3) For the STA-treated alloys, the specimen containing 0.1% Si was mainly reinforced by the ω phase rather than the effect of precipitation hardening by Ti silicides. The specimen containing 0.2% Si was mainly reinforced by the precipitation hardening effect by Ti silicides.

(4) Fine spherical Ti silicides (Ti₅Si₄) grown to a size of 0.1 µm were precipitated along the grain boundaries of the STA-treated specimen containing 0.2% Si. Ti silicides inhibited the grain growth and increased the YS and UTS, but acted as the crack initiation site during the room-temperature tensile test.

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