Variation in Mechanical Properties of Ti-13Nb-13Zr Depending on Annealing Temperature

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Abstract: Ti-13Nb-13Zr alloy is an orthopedic implant material possessing good mechanical properties, corrosion resistance, and biocompatibility. An international standard suggests a heat treatment known as “capability aging” for this alloy. This study provides extensive data of mechanical properties under a wide temperature condition built around the capability-aging process. Specifically, it investigates the effect of annealing temperature (573–973 K) on mechanical properties (i.e., yield strength, tensile strength, hardness, Young’s modulus, and mechanical compatibility) of Ti-13Nb-13Zr alloys. Although these mechanical properties showed similar trends with respect to the annealing temperature, Young’s modulus exhibited the highest value at 873 K in contrast to those of the other properties shown at 773 K. Such a disparity was discussed in light of static spheroidization and phase decomposition based on microstructural characteristics of the annealed Ti-13Nb-13Zr alloys.

Keywords: Ti-13Nb-13Zr; annealing; static spheroidization; phase transformation; mechanical properties

1. Introduction

Titanium alloy is a promising candidate among various metallic materials for biomedical applications, particularly as an orthopedic implant material. This arises from its high resistance to fatigue fracture and corrosion, relatively low Young’s modulus, and biocompatibility [1]. Materials scientists and biomedical engineers first paid attention to the two most frequently used titanium alloys for biomedical applications: commercially pure titanium (CP-Ti) and Ti-6Al-4V alloy. However, CP-Ti has a disadvantage of low mechanical strength [2], while Ti-6Al-4V has an issue of toxicity owing to Al and V alloying elements [3]. In addition, both alloys possess an excessive Young’s modulus (>100 GPa), and thus are vulnerable to the stress-shielding effect. These drawbacks of CP-Ti and Ti-6Al-4V gave rise to the development of various alternative titanium alloys with high strength, low Young’s modulus, and superior biocompatibility.

Ti–Nb–Zr ternary system has attracted great attention for this purpose due to their less toxic alloying elements as well as enhanced mechanical properties [4]. Furthermore, Ti-13Nb-13Zr alloy, one of the earlier developed materials, has already resolved the biocompatibility issue by being listed in the ASTM international standard for implant applications [5]. The standard introduces two methods of heat treatment, namely solution treatment (ST) and capability aging (CA). The ST process is composed of a heat treatment above the beta-transus temperature (i.e., 1008 K, [6]) and subsequent rapid cooling to room temperature. The CA process refers to a subsequent annealing of ST Ti-13Nb-13Zr performed at 768 K for 6 h.

In addition to the ST and CA processes, previous studies have suggested a variety of alternative thermomechanical processes to increase a biomaterial performance of Ti-13Nb-13Zr alloy [7–12]. For example, Majumdar et al. [8] tried several combinations of hot-working, ST, and cooling conditions to optimize mechanical performance. Park et al. [9] introduced a warm cross-rolling to cause an ultrafine-grained structure in Ti-13Nb-13Zr. Lee et al. [10,11] suggested improved mechanical properties
of this alloy through a multipass caliber rolling for the first time. He recently succeeded in enhancing the process to confer the lowest Young’s modulus reported ever for Ti-13Nb-13Zr [12]. However, these studies paid less attention to the simple annealing of Ti-13Nb-13Zr alloys, except for the aforementioned CA process. Gathering such data becomes more important nowadays due to the recent emergence of machine learning [13]. Hence, this study investigated the variation in mechanical properties (i.e., strength, hardness, and Young’s modulus) of Ti-13Nb-13Zr alloys depending on the annealing temperature in the (α + β) domain. The mechanisms under these variations are interpreted on the basis of their microstructural characteristics.

2. Materials and Methods

Extruded Ti-13Nb-13Zr rods with a diameter of 28 mm were used for this study. The chemical composition of main alloying elements was measured to be 13.0 wt.%Nb, 12.1 wt.%Zr, 0.086 wt.%O, 0.009 wt.%N, 0.0012 wt.%H, and balance Ti. These rods were soaked in a furnace at 1073 K for 1 h, followed by quenching in a water bath based on the ST process in the ASTM standard. Afterwards, they were soaked in a furnace again set to a given annealing temperature for 1 h, followed by the second water quenching. The employed annealing temperatures ranged from 573 to 973 K with an interval of 100 K.

Mechanical properties of the investigated alloys were evaluated using a quasi-static uniaxial tensile test, Vickers hardness test, and ultrasonic measurement. The tensile tests were carried out at a strain rate of $5 \times 10^{-3}$ s$^{-1}$ with a 25-mm extensometer. Tensile specimens were machined with a gage meter of 25 mm and a gage diameter of 6 mm. The tests were repeated three times per condition, yielding an average and standard deviation. The Vickers hardness test was conducted 10 times under a force of 500 gf with dwell time of 10 s. The ultrasonic measurement was employed to measure Young’s modulus based on the velocities of ultrasonic waves along longitudinal and transverse directions, separately [14]. The specimens for the last two experiments were mechanically polished using #400, #800, #1200, and #2400 emery paper before commencing a test.

Microstructures of the alloys were investigated using X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM), and electron backscatter diffraction (EBSD) analysis. All samples were water-abraded using the emery paper from #400 to #2400. XRD analysis was performed immediately after this procedure to minimize the effect of surface corrosion. SEM samples were additionally subjected to a chemical etching in an aqueous solution of 3% fluoric acid and 5% nitric acid. EBSD samples were prepared by an electropolishing at 22 V for 20 s in a solution of 6% perchloric acid, 35% 2-butoxy ethanol, and 59% methanol. EBSD data with a high confidence index ($\geq 0.1$) were processed using TSL OIM Software Ver. 7.

3. Results and Discussion

Figure 1 shows the microstructure of ST alloy (i.e., the initial microstructure) composed of fine laths with a submicron thickness. These laths are known to α’ martensite with the hexagonal close-packed (hcp) structure. ST Ti-13Nb-13Zr is transformed into the full-β structure in the first step of the ST process (i.e., the heat treatment in the β domain), which is converted into the full α’-martensitic structure in the second step (i.e., the rapid cooling) due to the martensite-starting temperature of 823 K and the martensite-finishing temperature of 758 K, respectively [15].

Figure 2 demonstrates the variation in mechanical properties of the investigated Ti-13Nb-13Zr alloys including yield strength (YS), ultimate tensile strength (UTS), Vickers hardness, Young’s modulus, and mechanical compatibility. ST Ti-13Nb-13Zr exhibited YS of 478 ± 22 MPa, UTS of 666 ± 15 MPa, hardness of 219 ± 6 HV, Young’s modulus of 63 GPa, and mechanical compatibility of $7.5 \times 10^{-3}$. These results are highly consistent with values in the literature [16], ensuring the data reliability of this study. All mechanical properties of the annealed alloys increased with increasing temperature up to an intermediate temperature, above which they showed a negative correlation with the temperatures. Specifically, an increasing temperature of annealing from 573 K to 773 K gave rise to...
to an increment in YS (507 ± 29 MPa for 573 K, 623 ± 11 MPa for 673 K, and 672 ± 7 MPa for 773 K, respectively), UTS (674 ± 19 MPa, 746 ± 9 MPa, and 762 ± 8 MPa), and hardness (220 ± 4 HV, 258 ± 4 HV, and 277 ± 5 HV). However, the annealing at the higher temperatures resulted in decreasing mechanical properties with increasing temperature. YS values were measured to be 560 ± 1 MPa for 873 K and 366 ± 47 MPa for 973 K. UTS also decreased with increasing temperature as 718 ± 11 MPa for 873 K and 658 ± 11 MPa for 973 K, while hardness decreased as 250 ± 5 HV and 218 ± 3 HV.

Figure 1. Scanning electron microscopy (SEM) image of the initial Ti-13Nb-13Zr alloy fabricated through the solution treatment (ST).

Figure 2. Mechanical properties of Ti-13Nb-13Zr alloys depending on the annealing temperature: (a) strength, (b) hardness, (c) Young’s modulus, and (d) mechanical compatibility.

Young’s modulus exhibited similar trends but different position of the peak. The value increased from the annealing temperature of 573 K to 873 K, not 773 K as shown in the other mechanical properties, and then decreased at 973 K. The measured values were 63 GPa for 573 K, 67 GPa for 673 K, 71 GPa for 773 K, 83 GPa for 873 K, and 66 GPa for 973 K. Thus, the highest values of mechanical strength
and hardness were obtained after the annealing at 773 K for 1 h, whereas that of elastic modulus was confirmed at 873 K for 1 h. Such a disparity is discussed below in more detail.

Mechanical compatibilities were determined as $8.0 \times 10^{-3}$ for 573 K, $9.4 \times 10^{-3}$ for 673 K, $9.5 \times 10^{-3}$ for 773 K, $6.7 \times 10^{-3}$ for 873 K, and $5.5 \times 10^{-3}$ for 973 K. Their correlation with the annealing temperature is similar to those found in strength and hardness. This is understood by the definition of mechanical compatibility, which is a ratio of YS to Young’s modulus. In other words, the highest Young’s modulus of the 873 K specimen decreased its mechanical compatibility.

Figure 3 shows the XRD line profile of the investigated Ti-13Nb-13Zr alloys. The annealed alloys presented three XRD peaks at $2\theta \approx 35^\circ$, $38^\circ$, and $40^\circ$. These peaks correspond to (100)$\alpha/\alpha'$, (002)$\alpha/\alpha'$, and (101)$\alpha/\alpha'$, respectively [12]. In addition, the annealing at 873 K and 973 K gave rise to the formation of an additional XRD peak at $2\theta \approx 38.5^\circ$, as marked by the arrows in Figure 3. This peak indicates the precipitation of $(110)\beta$ in these samples [12].

![Figure 3. X-ray diffraction (XRD) line profile of Ti-13Nb-13Zr alloys depending on the annealing temperature.](image)

Kobayashi et al. [17] and Lee et al. [18] reported five types of phase transformations during an annealing of Ti-13Nb-13Zr alloy. Two of them are stable phases: hcp $\alpha$ and body-centered cubic $\beta$. The other three are unstable phases: hcp $\alpha'$, orthorhombic $\alpha''$, and hcp $\omega$. $\alpha'$ and $\alpha''$ are also called a martensite. The full $\alpha'$-martensitic structure of ST Ti-13Nb-13Zr tends to be decomposed into the dual phase of $\alpha$ and $\beta$ during the tempering due to the thermal equilibrium. The $(110)\beta$ peak shown in the alloys annealed at 873 K and 973 K provided clear evidence for such a decomposition.

The annealing at the lower temperatures (i.e., 573–773 K) showed the absence of $(110)\beta$ peak. This does not indicate the absence of $\beta$ phases but rather the low fraction insufficient for being measured through the XRD analysis. Indeed, Lee et al. [18] reported an appearance of $(110)\beta$ peak even after the annealing at 773 K for sufficient periods. In their work, the peak was not confirmed after the annealing up to 1 h, as is consistent with the present study, but emerged after 3 h. Furthermore, the peak intensity was significantly increased when the annealing time was increased to 6 h, suggestive of the increasing $\beta$ fraction with increasing annealing periods.

The separation of $\alpha$ and $\alpha'$ phases is difficult through XRD measurement, because both phases have the same hcp structure. Nevertheless, it is rational in terms of thermodynamics that the $\alpha$ fraction increases with increasing annealing temperature and/or time. It is noted that $\alpha$ phase is harder than $\alpha'$ martensite [19]. In other words, the decomposition of $\alpha'$ into $(\alpha + \beta)$ increases YS, UTS, hardness, and Young’s modulus simultaneously. It well explains the tendency for mechanical properties to increase after the annealing at 573–773 K (i.e., the positive correlation with the annealing temperature), as presented in Figure 2.

It is interesting to note that the annealing temperature for the highest strength and hardness (i.e., 773 K in Figure 2a,b) was different from that for the highest Young’s modulus (873 K in Figure 2c). Figure 4 compares the microstructures after the annealing at each temperature to elucidate the mechanisms under such a disparity. SEM observation showed a shorter length of laths in the 873 K
specimen as compared to that of the 773 K specimen. EBSD observation presented a higher β fraction of the former (3.0%) than the latter (1.4%).

![Figure 4. SEM micrograph and electron backscatter diffraction (EBSD) phase map of Ti-13Nb-13Zn alloys annealed at (a) 773 K and (b) 873 K. Red and green areas indicate α/α’ and β phase, respectively.](image)

Static spheroidization (often called “globularization”) of titanium alloys consists of two discrete steps of (i) boundary splitting and (ii) termination migration [20]. The boundary-splitting step occurs by the initiation of grooves at subgrain boundaries and their propagation in the early stage of spheroidization. The termination-migration step did not occur for the investigated alloys due to the relatively short annealing period adopted in this work (i.e., 1 h). For example, Park et al. [21] proposed that a static spheroidization of Ti-6Al-2Sn-4Zr-2Mo-0.1Si alloy at 1228 K required 1.4 h of boundary splitting and then 23.5 h of termination migration. Such time requirements may increase for the present case considering the significantly lower annealing temperatures. Therefore, the different characteristics between 773 K and 873 K specimens were determined by the boundary splitting.

The time for boundary splitting is proportional to grain size and temperature, whereas it decreases with an increase in solute concentration, surface energy of phase interface, α fraction, and solute diffusivity [22]. Increasing temperature from 773 K to 873 K changed the α fraction, solute diffusivity, and the temperature itself towards the accelerated boundary splitting. This is experimentally confirmed as well [21]; a small decrease in annealing temperature (25 K) increased the time for boundary splitting from 0.5 to 2 h. Thus, the higher annealing temperature considerably accelerated the boundary splitting that mostly accounted for the static spheroidization for the present annealing conditions.

Meanwhile, Young’s modulus is not affected by grain boundaries but by phase compositions. For example, Hao et al. [23] confirmed a consistent Young’s modulus of 67 GPa for Ti-29Nb-13Ta-4.6Zr alloys with average grain sizes of 25–75 μm. A phase mixture model [24] also suggests a negligible positive correlation between Young’s modulus and grain size when the latter is higher than 20 nm, which is applicable to the present case. Therefore, the reduced lath size in the 873 K specimen barely contributed to its Young’s modulus. In contrast, the increasing α fraction due to the martensitic decomposition gave rise to increasing Young’s modulus in comparison to that of the 773 K specimen.

As a final note, the Young’s moduli obtained in this work could not break the known lower boundary for Ti-13Nb-13Zr (i.e., 60 GPa). The measured mechanical compatibilities, as shown in Figure 2d, rarely exceeded the reported values as well [7–12]. It is thus deduced that a novel approach other than the simple annealing is required to attain the combination of high strength and low Young’s
modulus for an enhanced orthopedic application. Exploiting a dual-phase martensitic structure can be a good example [12].

4. Conclusions

The present study investigated the effect of annealing temperature in the \((\alpha + \beta)\) domain on YS, UTS, Vickers hardness, Young’s modulus, and mechanical compatibility of Ti-13Nb-13Zr alloys. The mechanical properties, except for Young’s modulus, increased with increasing temperature up to 773 K and then decreased at the higher temperatures. That is, the highest values were confirmed at 773 K for these mechanical properties. Such trends arose from the lath refinement as a part of static spheroidization and the phase decomposition of \(\alpha'\) into the \((\alpha + \beta)\) structure. \((110)\beta\) XRD peak confirmed at the high annealing temperatures (i.e., 873 K and 973 K) stemmed from the accelerated phase decomposition. In contrast to the other mechanical properties, Young’s modulus showed the highest value at 873 K, although it presented similar trends with an increase in the annealing temperature. Such a disparity is ascribed to the fact that grain refinement does not affect Young’s modulus but affects the other mechanical properties. As a result, refined laths in 873 K rarely made a contribution to the reduction of Young’s modulus, thereby leading to the highest value among the investigated.

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