Influence of Nb Addition on Phase Constitution and Mechanical Properties of Biomedical Ti-Zr Based Alloys

Yusuke Hisata1,*,1, Equo Kobayashi1,*,2 and Tatsuo Sato2

1Department of Metallurgy and Ceramics Science, Tokyo Institute of Technology, Tokyo 152-8552, Japan
2Precision and Intelligence Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan

The influence of Nb addition on phase constitution, microstructure and mechanical properties of biomedical equi-atomic Ti-Zr based alloys was investigated. Phase constitution of Ti-Zr based alloys containing Nb rapidly cooled from β single phase changed with Nb addition as follows: $\alpha' \rightarrow \alpha'' + \alpha + \beta \rightarrow \beta + \alpha'' \rightarrow \beta$. Young’s moduli of Ti-Zr based alloys subjected to water quenching initially decreased with increasing Nb content. The minimal value was obtained in the Ti-48Zr-4Nb (mol%) composition alloy. The Young’s moduli increased in relation to the phase constitution change. In the alloys containing over 4% Nb, their principal phase was changed by subsequent cold rolling, this is mainly because $\beta \rightarrow \alpha'$ and $\beta \rightarrow \alpha''$ stress-induced martensitic transformation occurred. This phase transformation resulted in a decrease of Young’s modulus. Furthermore, cold rolling imparted anisotropy to the Young’s modulus which caused the value to drop. The Ti-47Zr-6Nb alloy had the lowest value of Young’s modulus after cold rolling in this study, 59.5 GPa.

(Received March 24, 2015; Accepted June 12, 2015; Published July 31, 2015)

Keywords: Young’s modulus, titanium alloy, titanium-zirconium alloy, stress-induced martensitic transformation

1. Introduction

Recently, biomaterials market has become increasingly active with the advent of aging society. Especially, titanium (Ti) and its alloys are ideal metallic biomaterials for biomedical applications because of its excellent corrosion resistance and biocompatibility. CP Ti, which is used in orthopedic surgery, has high corrosion resistance and good biological stability. However, its mechanical strength is relatively low, hence CP Ti is mainly used for applications required high corrosion resistance, e.g. dental prostheses and implants. On the other hand, in the case for high strength, e.g. artificial hip joints or spinal fixations, Ti alloys are selected. Ti-6Al-4V is the typical titanium alloy widely used in not only biomedical fields but also other industrial fields. However, vanadium is known as a cytotoxic element and it is undesirable to design an alloy without using vanadium.1) Another important concern in clinical use is difference of Young’s modulus between human bone and metallic biomaterials. Young’s modulus of human cortical bone is around 103 GPa,2) whereas that of CP Ti and Ti-6Al-4V alloy are 103 GPa and 114 GPa, respectively,3) and this difference causes implant loosening and imbalance of bone-remodeling due to the stress shielding effect. Therefore, the new biomedical metallic materials, which composed only non-toxic elements and have good mechanical properties enough to use as biomedical applications, are emerged.

Titanium-Zirconium (Zr) based alloys were developed under this concept.4) Ti-Zr based alloys are composed of an equi-atomic composition of Ti and Zr. This alloy can achieve relatively high mechanical strength by solid solution strengthening between Ti and Zr. It is reported the highest value of hardness can be obtained in Ti-50 mol% Zr alloy in this binary system, and this value is 2 to 3 times larger than that of pure Ti and Zr.4) Moreover, this alloy system was investigated not only its mechanical properties but also biocompatibility for actual use in clinical field. Ti and Zr are both known to be non-toxic element in human body,1) and their corrosion resistance and biocompatibility are prior to that of CP Ti.5–7)

In this study, Ti-Zr based alloys containing small amount of niobium (Nb) were studied. Nb is also known to be non-toxic element and works as β phase stabilizer in Ti and Zr, and previous research revealed this ternary alloy can increase the hardness by heat treatment.3) Present study mainly focuses on further improvement of its mechanical properties, especially, lowering Young’s modulus. Now therefore, the objective of this research is to investigate the influence of Nb addition on phase constitution, microstructure and mechanical properties of Ti-Zr based alloys.

2. Experimental Procedure

Alloys with an equi-atomic composition of Ti and Zr with 0, 2, 4, 6 and 8 mol% Nb addition were selected. The alloys are named in the manner of TZnN, which is meant as Ti-Zr-Nb with n mol% Nb addition, hereafter. Button like ingots, weight approximately 18 g, were prepared from pure Ti (99.5 mass% purity), pure Zr (99.2 mass%) and pure Nb (99.9 mass%) rods and sheets using arc melting with a non-consumable tungsten electrode under high purity argon atmosphere. The ingots were turned over and re-melted four times in order to avoid chemical inhomogeneity of the alloys. Mass changes of all samples before and after melting were confirmed less than 0.3 mass%. The ingots then were homogenized at 1273 K for 86.4 ks under Ar flow condition, and followed by water quenching (as quenched). The samples were subsequently cold rolled. Reduction ratio was up to about 17% (as rolled).

In order to identify phase constitution, X-ray diffraction analysis (XRD, RINT-2100, Rigaku) was conducted using Cu-Kα radiation at a diffraction range of 2θ = 30–42° and 48–56°. The voltage and current were 40 kV and 30 mA, respectively. Scanning speed was 0.05°/min to accurately identify the phase constitution.

---

1Graduate Student, Tokyo Institute of Technology. Present address: Kawasaki Heavy Industries, Ltd., Akashi 673-8666, Japan
2Corresponding author, E-mail: equo@mtl.titech.ac.jp
Microstructures of the samples were observed by an optical microscope. The samples were mechanically polished with emery paper (up to #4000 grid) and diamond powder, and then finally polished with colloidal silica. Most samples were non-etched and observed with a polarizing microscope, and the other samples were etched by HF-26 vol% HNO₃-66.6 vol% H₂O etchant and observed under non-polarized condition.

Electron back scattered diffraction (EBSD) analysis was carried out to get phase map and inverse pole figure (IPF) map. The samples were electro polished in a solution of perchloric acid and methanol.

Hardness measurement and Young’s modulus measurement were performed in order to measure mechanical properties. Micro Vickers hardness was measured after the samples were polished in the same manner with the microstructure observation. The measurement was conducted seven points for each sample, and calculated average value excluding maximal and minimal values. Young’s modulus, E were calculated by eq. (1).

\[ E = \rho V_S^2 \times \frac{3V_L^2 - 4V_S^2}{V_L^2 - V_S^2} \]  

Both surfaces of the samples were polished with emery paper (up to #4000 grid) and parallelized. Longitudinal and transversal sound velocities (\(V_L\) and \(V_S\), respectively) in the samples were measured by 2 point calibration mode. Density of the samples, \(\rho\) were measured by Archimedean method. The measurement was conducted seven times for each sample, and calculated average value excluding maximal and minimal values.

3. Results and Discussion

3.1 Phase constitution change with Nb addition

Figure 1 shows the XRD patterns of as quenched and as rolled samples. Due to the limited numbers of grains in the measurement area of the samples, it was difficult to get whole series of peaks each phase by the XRD. In as quenched samples, in TZ and TZ₂N alloys only martensite \(\alpha'(hcp)\) phase diffraction peaks were detected. TZ₄N alloy was composed of martensite \(\alpha'(orthorhombic)\) phase and \(\beta\) (bcc) phase. TZ₆N alloy consisted of \(\beta\) phase and \(\alpha'(bcc)\) phase, and TZ₈N alloy was composed of single \(\beta\) phase. According to a Ti-Zr equi-atomic isoplethal toward Nb corner in the Ti-Zr-Nb ternary phase diagram, all alloys in current research consisted of single \(\beta\) phase, that is \(\beta \rightarrow \alpha'\) or \(\beta \rightarrow \alpha''\) martensitic transformation were occurred in TZ to TZ₆N alloys, and around 6 mol% Nb addition, metastable \(\beta\) phase was retained. These results can be explained that the phase stability of these alloys was changed with Nb addition, which works as a \(\beta\) phase stabilizer for Ti and Zr. In the Ti-Nb binary alloy system, minimal concentration of Nb that metastable \(\beta\) phase can be retained at room temperature is about 22 mol%. In Ti-Zr based alloys system, however, metastable \(\beta\) phases can be present only about 6 mol% Nb addition, at room temperature. In other words, the amount of Nb which has high melting point, 2741 K can be reduced. Moreover, according to the Ti-Zr binary phase diagram, the lowest \(\beta\) transus temperature can be achieved at 875 K in Ti-50 mol% Zr alloy. Considering heat treatment process, heat treatment temperature can be decreased in Ti-Zr based alloys comparing to Ti and Zr alloys. Thereby Ti-Zr based alloys have an
advantage in cost of manufacturing. Zr is known to be neutral element for Ti, however, Abdel-Hady et al. reported that Zr works as a $\beta$-stabilizing element in $\beta$-type Ti-Zr-Nb alloys and the $\beta$ stabilizing effect of Zr increased with increasing Nb content in the Ti-Nb-Zr alloys. In current research, Ti-Zr based alloys contain 50 mol% Zr, this is quite unusual amount as additional element, therefore high amount of Zr contributes to emphasizing $\beta$ phase stabilization.

In as rolled samples, phase constitution of TZ and TZ2N alloys didn’t change from as quenched samples. On the other hand, TZ4N alloy was composed of mainly $\alpha''$ phase and $\alpha'$ phase, and no $\beta$ peak was detected. TZ6N alloy was composed of mainly $\alpha'$ phase, $\beta$ and $\alpha''$ phase. TZ8N alloy consisted of $\beta$ phase and small amount of $\alpha''$ phase. The phase constitution changed was considered to be occurred by stress-induced martensitic transformation together with following microstructure observation results.

Interestingly, main phase of TZ6N alloy changed from $\beta$ to martensite $\alpha''$ phase by cold rolling. In general, phase stability of each phase in Ti-TM binary alloy obtained by rapid cooling from $\beta$ single phase region changes with $\beta$ phase stabilizer elements; $\alpha' \rightarrow \alpha'' \rightarrow \beta$, and it corresponds to lowering $M_s$ temperature. In present study, $\beta \rightarrow \alpha'$ stress-induced martensitic transformation occurred, however, in this composition, $\alpha''$ phase is more stable than $\alpha'$ phase thermodynamically from results of as quenched alloys. Other possibility is $\alpha'' \rightarrow \alpha'$ transformation by cold rolling. Same results were reported by some investigators, however, its mechanism has been still unclear, and further investigation is required.

Microstructure of each alloy subjected to homogenization followed by water quenching are shown in Fig. 2(a). TZ to TZ4N alloys comprised fine acicular microstructure, while TZ6N and TZ8N alloys showed equiaxed grain microstructure, even though the very small portion of $\alpha''$ was observed in some limited area. From XRD analysis, it is considered that the acicular microstructure correspond to martensite $\alpha'$ and $\alpha''$ phase and the equiaxed microstructure, $\beta$ phase. No obvious difference of the morphology and size was observed among TZ, TZ2N and TZ4N alloys. Figure 2(b) shows the optical micrographs of each alloy subjected to cold rolling. Acicular microstructure similar to as quenched samples were observed in TZ to TZ4N alloys. On the other hand, TZ6N and TZ8N alloys comprised band and acicular microstructure in the equiaxed grain. It is not unclear the phases of these acicular and band-like microstructure yet.

Figure 3 shows phase maps of TZ6N and TZ8N as rolled alloys taken by EBSD technique. Acicular and band microstructures correspond to martensite $\alpha'$ or $\alpha''$ phases from Fig. 3(a) and (b). This results also clearly indicate that martensitic transformation occurred by cold rolling. IPF map of TZ6N as rolled alloy is shown in Fig. 3(c). Different orientation was observed inside of acicular microstructure composed of $\alpha'$ phase, and it corresponds to transformation twin, which is formed to suppress transformation strain increase.

In Ti-Nb alloy system, it’s well known that metastable athermal $\omega$ phase can be formed by rapid cooling from high temperature at the composition which $\alpha''$ phase can be stable. However, in Ti-Zr based alloy system containing Nb, no athermal $\omega$ phase was detected from XRD results. The phase constitution changes are summarized in Table 1 from XRD results and microstructural observation.

### 3.2 Hardness change with Nb addition

Hardness changes with Nb addition in as quenched and as rolled alloys are shown in Fig. 4. The hardness of as quenched samples gradually decreased with increasing Nb concentration. Generally, it is well-known that bcc crystal structure ($\beta$) is easy to deform comparing to hcp structure.
(α'). In the present case, the phase constitution (main phase) changed with Nb addition: α' → α'' → β. It is concluded that the hardness change corresponds to the phase constitution change, although it is not unclear the hardness difference between α' and α''.

TZ and TZ2N alloy subjected to water quenching were composed only martensite α' phase, but hardness were different. Compared with both microstructures, no clear difference in the size of acicular microstructures was observed. Therefore the reason of the difference of hardness can be explained by relaxation of lattice strain with Nb addition.9) The lattice misfit between Ti and Zr is relatively large, and this is the reason Ti-Zr based alloys can be achieved relatively high mechanical strength. On the other hand, atomic radius of Nb is quite close to that of Ti, hence it’s easy to assume that the hardness decrease with Nb addition.

Differences of hardness between as quenched and as rolled samples were very few, and this means effect of work hardening was small because small reduction ratio by cold rolling can’t introduce strain inside the grain enough to increase hardness.

### 3.3 Young’s modulus change with Nb addition

Figure 5 shows the Nb composition dependence of Young’s moduli (as quenched). From TZ to TZ4N alloys, Young’s moduli, E was gradually decreased. The minimal value of E was 83.0 GPa in TZ4N alloy. Then from TZ4N to TZ8N alloys, E was increased.

There are a lot of previous reports about composition dependence of Young’s modulus in Ti-TM binary alloy (Ti-Nb, Ti-V, Ti-Mo etc.),14,19–23 and many of the results show similar composition dependence corresponding to phase constitution change: Firstly Young’s modulus decrease, then composition dependence shows two minimal value and one maximal value. Maximal values appear near the composition α'' can be stable, and this is due to the formation of athermal ω phases in competition with α'' phase by rapidly cooling from high temperature. Interestingly, however, no maximal value was observed in Ti-Zr based alloys system. The reason has been unclear, however, several investigators reported that formation of athermal ω phase can be suppressed with a few addition of Sn and Zr.21,24 In this alloys system, high amount of Zr contains and this is one of the striking feature or difference as compared to other Ti alloys. Considering ω phase peaks wasn’t confirmed from XRD results in this study, it cloud be attributed to containing a large amount of Zr. It is known that each consistent phase has different Young’s modulus, ω phase shows the highest, second is α phase, and β phase shows the lowest value.25 On the contrary, however, the magnitude relation of Young’s modulus among α', α'' and β metastable phases has been unclear.26,27 In current research, composition dependence of Young’s modulus indicates that the order of Young’s modulus is following in increasing order: α' phase, β phase and α' phase. And, composition dependence of Young’s modulus in Ti-TM alloys are often discussed in stability of each phase and lattice softening resulted from phase stability change with concentration of β phase stabilizer element,13 and the lowest value can be achieved in most instable composition of martensitic phase, i.e., Mf temperature is close to R.T. The current results shows similar tendency.

On the other hand, in as rolled specimen, Nb composition dependence of Young’s modulus was changed as compared to as quenched samples (Fig. 6). There is no change in TZ and TZ2N alloys before and after cold rolling, by contrast, in TZ4N, TZ6N and TZ8N alloys, Young’s modulus decreased as compared to as quenched alloys, especially in TZ6N alloy Young’s modulus was significantly reduced. And intriguingly as rolled specimen had anisotropy of Young’s modulus except for TZ and TZ2N alloys, which means that different values of sound velocity were obtained depending on the measured orientation of transversal wave amplitude. Young’s modulus measured by parallel to rolling direction was lower than by vertical to rolling direction. Alloys changed phase
contribution by cold rolling decreased Young’s modulus, this can be due to increasing volume fraction of martensite α” phase which is formed by stress-induced martensitic transformation and has relatively low Young’s modulus. On the other hand, Ti-Cr and Ti-Mo β type alloys systems show different results from present study. Nakai et al. reported Young’s modulus of Ti-12Cr alloy increases by cold rolling, and this is derived from the deformation-induced α phase transformation.28 Combined with above results, it could be suggested that Ti-Zr based alloys system is resistant to form α phase.

Other reason Young’s modulus changed and anisotropy appeared by cold rolling can be considered besides above consistent phases change. Matsumoto et al. reported in Ti alloys consisting of fully α’ martensite, Young’s modulus decreases after cold groove rolling, and this decrease is reasonably explained in relation to the texture formation.29 However in the present case, maximal reduction ratio by cold rolling was less than or comparable to 17%, hence it’s unlikely that main reason for decreasing Young’s modulus is due to the formation of texture. It is well known that a few martensite variants can be preferentially formed on deformation, dependent on applied stress direction.30 Although the main reason anisotropy in Young’s modulus occurs is not certain, one of the reason is attributed to this phenomena. Besides, TZ6N alloy subjected to cold rolling had the lowest value of Young’s modulus in this study, 59.5 GPa even though the main phase changed to not α” phase but α’ phase. Thus it is now concluded that the Ti-Zr based alloys containing Nb, which have quite lower value in Young’s modulus as compared to existing CP Ti and Ti-6Al-4V alloy, are good candidate of new metallic biomaterials for biomedical applications.

4. Conclusion

The influence of Nb addition on phase constitution, microstructure and mechanical properties of new biomedical equi-atomic Ti-Zr based alloys was investigated. The results obtained are summarized as follows:

1. Phase constitution of Ti-Zr based alloys containing Nb rapidly cooling from β single phase changed with increasing Nb content as follows: $\alpha' \rightarrow \alpha'' + \alpha' + \beta \rightarrow \beta + \alpha'' \rightarrow \beta$, and Young’s moduli of as quenched samples changed with Nb composition, and they correspond to their phase constitution.

2. β → α’ and β → α” stress-induced martensitic transformation were occurred in TZ4N, TZ6N and TZ8N alloys subjected to cold rolling, and this phase transformation resulted in decreasing Young’s modulus. Furthermore, as rolled specimen had anisotropy of E, and this also contributed to lowering Young’s modulus. TZ6N alloy subjected to cold rolling had the lowest value of E in this research, 59.5 GPa.

REFERENCES