Mechanical properties and microstructures of $\beta$ Ti–25Nb–11Sn ternary alloy for biomedical applications

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Abstract

The mechanical properties and microstructures of $\beta$ Ti–25%Nb–11%Sn ternary alloy rods were investigated for biomedical applications as a function of heat treatment temperature after swaging by an 86% reduction in cross-section area. An as-swaged rod consisting of a $\beta$ (bcc) single phase shows a low Young’s modulus of 53 GPa, which is interpreted in terms of both the metastable composition of the $\beta$ phase undergoing neither an athermal $\alpha$ transformation nor a deformation-induced $\alpha$ transformation and <110> texture development during swaging. Heat treatment at 673 K (400 °C) for 2 h leads to a high strength of approximately 1330 MPa and a high spring-back ratio of yield stress to Young’s modulus over $15 \times 10^{-3}$, with acceptable elongation. This high strength is attributable to needle-like $\alpha$ precipitates, which are identified by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and high-resolution electron microscopy (HREM).

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1. Introduction

Currently used orthopedic implant alloys such as Ti–6Al–4V and Co–Cr have Young’s moduli greater than 100 GPa [1], while bone moduli are 4–30 GPa, depending on the type of bone and the direction of measurement [2,3]. This large difference between implant devices and bone tissues causes bone resorption due to stress shielding [4], and it results in the loosening of devices, making total hip arthroplasty necessary. To overcome the critical issue of stress shielding, $\beta$ Ti–Nb based alloys for biomedical applications have recently attracted much attention, and many alloys with low Young’s modulus as well as high strength and good biocompatibility have been developed, e.g., Ti–13Nb–13Zr [5], Ti–35Nb–5Ta–7Zr [6], Ti–29Nb–13Ta–4.6Zr [7] and Ti–33.6Nb–4Sn [8], etc. These alloys possess low Young’s moduli of 40–80 GPa; thus, they have the potential to replace conventional implant alloys. Among them, $\beta$ Ti–Nb–Sn alloys have low melting temperature due to Sn alloying and no additional refractory element with a high melting temperature, such as Ta. This implies that large ingots can be easily made and the chemical homogenization of constituent elements is readily attained during melting and subsequent hot working. $\beta$ Ti–Nb–Sn alloys have been found to provide attractive mechanical properties, including low Young’s modulus [8–10], high strength [9,10] and good biocompatibility [11]. Moreover, $\beta$ Ti–Nb–Sn alloys are very ductile at ambient temperature, which enables cold die-forging to fabricate near-net-shaped implants [12]. These properties are achieved by optimizing the associated chemical compositions and thermo-mechanical processes. It is noted that Sn acts as a $\beta$ stabilizing element in the $\beta$ phase of Ti alloys in a manner similar to that of Nb [8,13]; hence, metastable $\beta$ Ti–Nb–Sn alloys can be designed to possess lower Young’s moduli over a wide composition range by balancing the Nb and Sn contents. For example, metastable Ti–33.6Nb–4Sn produces a slight $\alpha$ martensite phase in a $\beta$ matrix after quenching and noticeably after subsequent cold rolling [9]. Previously, Ti–22.3Nb–11Sn was shown to behave similarly as far as constituent phases and their volume fractions before and after cold rolling are concerned. Upon further increasing the Sn content to 12%, $\alpha$ is not detected, even after cold rolling in Ti–22Nb–12Sn. Matsumoto et al. [10] showed that the mechanical properties of thermo-mechanically processed Ti–33.6Nb–4Sn are greatly influenced by deformation-induced $\alpha$ with strong rolling texture. However, they did not clarify the effect of the texture of the bcc matrix phase on mechanical properties.

The objective of this paper was to investigate the mechanical properties of a metastable $\beta$ Ti–Nb–Sn alloy undergoing no deformation-induced $\alpha$ transformation for comparison with the properties of a less stable $\beta$ Ti–Nb–Sn alloy, Ti–25Nb–11Sn alloy with a low Nb content was selected to meet this objective because the expensive Nb content is reduced to retain the metastable $\beta$ single phase for future commercial applications. Yield stress, ultimate tensile strength, elongation and Young’s modulus were examined in tensile tests as a function of heat treatment temperature after cold swaging for the development of $\beta$ Ti alloy implants with low Young’s modulus and high strength. Microstructures...
were investigated mainly by transmission electron microscopy (TEM) to understand the effects of heat treatment on the mechanical properties of the materials studied.

Once a low Young's modulus with a high yield stress is obtained, an alloy can be applied not only in orthopedic implants but also orthodontic devices because a large elastic recovery strain arising from Hooke's law is expected. This paper also discusses the effect of heat treatments on the recovery of elastic strain by evaluating the spring-back ratio.

2. Experimental procedure

A Ti–Nb–Sn alloy ingot weighing 15 kg was prepared by high-frequency induction melting in a vacuum using a water-cooled copper hearth, followed by vacuum arc melting. The nominal composition of the alloy was Ti–25Nb–11Sn (compositions in this paper are denoted by mass% in the style of Ti–25Nb–11Sn unless otherwise noted). The ingot was hot forged at 1373 to 1173 K (1100 to 900 °C) to a 30 mm diameter rod, hot rolled at 1173 K (900 °C) to an 8 mm diameter rod and swaged at room temperature to a 3 mm diameter rod after removing surface oxide layers by scalping. The swaging reduction was 86% in cross section. The chemical composition after swaging was Ti–25.4%Nb–11.2%Sn, with impurities of 0.07%M, 0.068C, 0.007%Mn and 0.02%Fe. The alloy will be referred to as Ti–25Nb–11Sn hereafter. Tensile samples with the gage portion of 15 mm in length and 2 mm in diameter were prepared. Tensile tests at an initial strain rate of 5.6 × 10^{-4} s^{-1} were carried out at 297 K (25 °C) after heat treatments at 473 to 1173 K (200 to 900 °C) for 2 h. At least 3 specimens were heat treated at each temperature and tensile tested. Young's modulus was measured by recording tensile strain using a video extensometer.

Constituent phases after swaging were determined by X-ray diffraction (XRD) with Cu–Kα radiation. The microstructures of the ingot were investigated using an optical microscope (OM), a scanning electron microscope (SEM) and a transmission electron microscope (TEM). Transverse texture was determined by the differential scanning calorimetry coupled with microstructural observations. Using a JEOL JEM-3010 with a LaB6 gun operating at 300 kV, electron diffraction patterns were taken from a selected area of approximately 80 nm in diameter. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were acquired using an FEI Titan 80–300 TEM operating at 300 kV with a field emission gun and a detector with an inner angle greater than 55 mrad. To prepare TEM samples, disks perpendicular to the longitudinal direction of a swaged bar were ground to less than 80 μm in thickness and electro-polished in a solution of 10 vol% nitric acid in methanol at 243 K (−30 °C) with a DC voltage below 10 V. Finally, thin foils were prepared using a low-angle ion milling machine, Fischione Instruments Model 1010, with an argon ion beam accelerated at 3 kV.

3. Results and discussion

Swaging from 8 to 3 mm diameter was easily carried out at room temperature without intermediate annealing, indicating the excellent ductility of the alloy. Fig. 1 shows XRD patterns taken from cross sections perpendicular and parallel to the longitudinal direction of the swaged rod, which are denoted as ‘perpendicular’ and ‘parallel’ in the figure, respectively. It can be seen that all the reflections are referred to as bcc structure and 110 reflection in the perpendicular is very strong, as compared to other reflections such as 220 and 211. Therefore, Ti–25Nb–11Sn consists of a β (bcc) single phase with a strong <110>β texture along the swaging direction. Fig. 2 shows the peak yield stress. A β (bcc) grain boundary and its Young's modulus was explained in terms of a strong anisotropy in the Young's modulus of deformation-induced orthorhombic α', with preferred deformation texture developing during rolling [10]. Inamura et al. [15] have drawn the same conclusion from experiments and the calculation of the orientation dependence of Young's modulus in Ti–Nb alloy. Quite recently, Zhang et al. [16] measured Young's moduli of 27.1, 56.3 and 88.1 GPa for <100>, <110> and <111>, respectively, using single crystals of Ti–24Nb–4Zr–8Sn. These results are consistent with each other, and it is interesting to note that the Young's modulus of Ti–11Sn was reported to decrease to less than 45 GPa by cold rolling at ambient temperature. The low modulus was explained in terms of a strong anisotropy in the Young's modulus of deformation-induced orthorhombic α', with preferred deformation texture developing during rolling [10]. However, the current Ti–25Nb–11Sn exhibits no detectable deformation-induced α'. Tane et al. [14] demonstrated that a β′ Ti–Nb–Ta–Zr single crystal shows an anisotropy in its Young's modulus, and experimentally measured values are on the order of [100] < [110] < [111]. Inamura et al. [15] have drawn the same conclusion from experiments and the calculation of the orientation dependence of Young's modulus in Ti–Nb alloy. Quite recently, Zhang et al. [16] measured Young's moduli of 27.1, 56.3 and 88.1 GPa for <100>, <110> and <111>, respectively, using single crystals of Ti–24Nb–4Zr–8Sn. These results are consistent with each other, and it is interesting to note that the Young's modulus of <110> in Ti–
24Nb–4Zr–8Sn with the composition similar to Ti–25Nb–11Sn in this study is 56.3 GPa. The observed Young’s modulus of 53 GPa after swaging will be associated with the strong <110>\text{β}, texture development observed experimentally (Fig. 1). On the other hand, in Ti–33.6Nb–4Sn, the preferred rolling textures of <110>\text{β}, for \(β\) and <020>\text{α}\text{′} for \(α\text{′}\) were observed along the rolling direction, and a Young’s modulus lower than 50 GPa was measured [10]. Therefore, the lower Young’s modulus of Ti–33.6Nb–4Sn versus that of Ti–25Nb–11Sn is considered to be apparent values originating from the anisotropic \(α\text{′}\) formation in the former alloy.

It is widely accepted that a low Young’s modulus in \(β\) Ti alloys is obtained at the composition containing the least amount of \(β\) stabilizing element to form a single phase [13,17–19]. This is the case in Ti–25Nb–11Sn, whose composition was experimentally determined by referring to a previous paper [12]. The composition of the prepared alloy is in good agreement with the theoretical prediction of phase stability in Ti alloys made by Morinaga et al. [13,20]. These researchers revealed that there is a general correlation between the phase stability and the elastic properties of \(β\) Ti alloys by delineating the \(β\)/phase boundary in the \(β\)–MD diagram. \(β\) is the bond order, which is a measure of the covalent bond strength between Ti and an alloying element. MD is the metal d-orbital energy level of an alloying transition metal, which correlates well with the electronegativity and metallic radius of elements. The average values of MD and MD are defined by taking the compositional average of each parameter. Ti–25Nb–11Sn, which is calculated to have \(β\) = 2.811 and MD = 2.424, is located near the MS = RT curve in the \(β\)–MD diagram, while MS = RT denotes that the alloy has martensitic transformation start temperature around room temperature. Therefore, the low Young’s modulus of approximately 53 GPa in Ti–25Nb–11Sn can be explained by the low stability of the \(β\) phase.

It should be noted that the \(β\) value of Ti – 25Nb alloyed with Sn with a low Bo value is much smaller than that of Ti – 50Ta – 20Zr (Bo = 2.934) or Ti – 30Zr – 10Nb – 10Ta (mol%, Bo = 2.945), although Abdel-Hady et al. predicted that alloying with elements with high Bo values is preferable to reduce Young’s modulus [13]. This inconsistency is not clearly understood, but the cluster model of bcc Ti and hcp Ti used in the calculation by Morinaga et al. [20] may be unapplicable to the Ti alloys including so high solute contents. In addition, some experimental problems may be involved in it as follows: 1) \(β\) Ti alloys exhibit a crystallographic anisotropy with respect to Young’s modulus as described above [14 –16], while they easily develop recrystallization texture or deformation texture [10]. 2) Young’s modulus in metastable \(β\) Ti alloys shows a significant temperature dependence at ambient temperature when they possess Ms just below room temperature [15]. 3) The static Young’s modulus measured by tensile tests is significantly reduced when the formation of a martensite phase is induced during testing. 4) Young’s modulus may be influenced by the content of unintentionally introduced interstitial impurity elements such as oxygen and carbon. 5) Young’s modulus depends on the measurement methods employed; the static Young’s modulus determined by tensile testing is not always equal to the dynamic one, e.g., via the resonance vibration method. Accordingly, the comparison of Young’s moduli at room temperature using different polycrystalline alloys must be performed using the same measurement method after preparing the samples, through which the above uncertainties are avoided as much as possible.

Zener [21] first pointed out thatbcc phase stability is associated with the shear modulus \(c′ = (c_{11} - c_{12})/2\) for \(<110><110>\) shear. Fisher and Dever [22] showed that \(c′\) decreases with decreasing electron-atom ratio (e/a), thereby decreasing the bcc phase stability. Very recently, Lee et al. [23] have revealed that low Young’s modulus appears when \(β\) Ti alloys possess a low value of e/a and \(α\) phase is not included, based on the measurements of the elastic moduli in \(β\) Ti–Mo–Zr–Al alloy single crystals and the modulus data of other \(β\) Ti alloy single crystals in references. The examined \(β\) Ti alloys had e/a ratios ranging from 4.1 to 4.8. They found that low Young’s modulus of 44.4 GPa along the \(<100>\) direction is obtained in \(β\) Ti–Mo–Zr–Al with the lowest e/a of 4.10. \(β\) Ti–25Nb–11Sn alloy in this study has a low e/a of 4.16. Therefore, the low Young’s modulus will result from the low stability of \(β\) phase.

Fig. 3 shows the elongation to fracture and spring-back ratio (yield stress at 0.2% plastic strain to Young’s modulus) of as-swaged and heat-treated Ti–25Nb–11Sn. The elongation is 16% after swaging and decreases to approximately 8% at 623 and 673 K (350 and 400 °C); it increases to 30% upon further increasing the temperature. The failure of the as-swaged specimen was accompanied with considerable necking before fracture, as shown in Fig. 4(a). The SEM fracture surface corresponding to the white line square in Fig. 4(a) is completely composed of dimples (Fig. 4(b)), although the core is different from the rim in contrast and dimple size. The macroscopic fracture plane is roughly perpendicular to the tensile direction at the core, while it is inclined to the tensile direction at the rim. The SEM fractographs shown in Fig. 4(c and d) for a sample fractured at 673 K (400 °C), indicating different fracture modes at the core and the rim, are similar to those shown in Fig. 4(a and b). These observations suggest that final fracture occurs by void coalescence under tensile stress at the core and under shear stress at the rim. These fractographic features nearly disappeared when the sample was fractured at 923 K (650 °C) and completely disappeared at 1073 K (800 °C), as shown in Fig. 4(e, f). Grain growth after recrystallization was observed by OM, and no apparent change in average grain sizes was observed from the rim to core of the rod. Therefore, the characteristic fractographs shown in Fig. 4(a–d) cannot currently be unambiguously explained. Further investigation is necessary. The measured grain size after recrystallization is plotted in Fig. 5, indicating a gradual increase from 40 μm for 923 K to 117 μm for 1173 K with heat treatment temperature above \(β\) transus of 925 K (652 °C). The \(β\) grain growth is considered to contribute to the decrease in strength observed at high temperatures (Fig. 2). Thus, it was found that the \(β\) Ti–25Nb–11Sn alloy is extremely ductile and significantly strengthened by heat treatment at approximately 673 K (400 °C) after swaging.

Fig. 6 shows a TEM bright-field image of the as-swaged sample observed along the longitudinal direction. Most of the fine grains measuring 100 to 500 nm exhibit remarkable strain contrasts, most likely due to a high density of dislocations. All of the grains observed were determined to possess a bcc structure (lattice parameter, a = 0.331 nm) by indexing the selected area diffraction patterns (an example is inserted in Fig. 6), consistent with the XRD result described above (Fig. 1). It is noted in the diffraction pattern of Fig. 6 that neither a diffraction spot nor diffuse scattering related to the \(α\) phase is observed. The formation of athermal \(α\) or deformation-induced \(α\) is well known to increase Young’s modulus. Therefore, the low Young’s modulus of the as-swaged alloy will be related to metastable \(β\) Ti alloy containing no \(α\) phase with \(<110>\) deformation texture.

![Fig. 3. Temperature dependence of elongation and spring-back ratio of Ti–25Nb–11Sn heat treated after swaging.](image-url)
TEM images obtained at the peak strength are shown in Fig. 7, where Fig. 7(a) is a bright-field image and Fig. 7(b) and (c) are typical selected area diffraction patterns at incident beams of [001]_β and [110]_β. All grains in Fig. 7(a) contain fine needle-like products as well as strain contrasts, most likely arising from a high density of dislocations. The diffraction patterns in Figs. 7(b) and (c) show weak reflections, together with strong fundamental spots from bcc structure. The weak reflections are from α phase with a distorted hcp structure (a = 0.297 nm, c = 0.471 nm) as indexed in the figures and streaks seen in Fig. 7(c) are probably due to a shape-effect by thin needle α phase. The arrowed reflection maxima are close to, but slightly displaced from the expected positions of ω diffraction maxima. The reflections would come from α precipitates with other variants, although they were not identified unambiguously because of weak reflections. It has been revealed that the ω transformation is retarded or suppressed by adding a small amount of elements such as Sn, Al, Zr and O to metastable β Ti alloys [13,17,24–30]. Therefore, the suppression of thermal ω phase precipitation in the present alloy may be due to the relatively high Nb and/or Sn content. Fig. 8(a) shows a high-magnification TEM bright-field image at the peak strength. Fine needle-like precipitates of the α phase, measuring 20–100 nm in length, can be observed along two ≈111> directions. Fig. 8(b) shows a HAADF-STEM image, where precipitates are manifested as the dark contrast. Z contrast images obtained by HAADF-STEM are known to result from the thermal diffuse scattering of atoms which is approximately proportional to the square of the atomic number. It is evident from a comparison of the atomic number of Nb with that of Ti and Sn that the Nb content in the precipitates is lower than that of the β matrix. Hence, the HAADF-STEM result is consistent with the above conclusion from the electron diffraction analysis that the precipitates are composed of the α phase formed by the decomposition of the metastable β phase.
Fig. 9 shows a HREM image taken from the [110]β zone axis in an area containing precipitates at the peak strength. The image shows that the precipitates with incoherent α/β interface possess a hexagonal structure whose [0001]α is parallel to the zone axis and $b_{11\overline{2}}$α is parallel to $b_{11\overline{1}}$β of the β matrix. Fast Fourier Transform (FFT) images taken from the selected regions of β and α phases are shown in Fig. 9(b) and (c), respectively. The FFT analysis of the HREM image confirms that the Burger’s orientation relationship between β and α, $\{110\}_\beta//\{0001\}_\alpha$ and $<1-120>\alpha//<11-20>\alpha$, is satisfied in the present alloy as in many β Ti alloys with α precipitates. It has been reported that metastable β Ti–Nb-based alloys are significantly strengthened by the decomposition of β to α, ω or β′, depending sensitively on the alloy composition and heat treatment condition [25,28,31–36]. Moreover, some alloys have been found to be strengthened by B2 ordering.
According to the diffraction patterns shown in Fig. 7(b,c), no detectable reflections can be observed at the 1/2 {200} positions arising from B2 ordering. Additionally, the splitting of {110} reflections evidencing the coexistence of two phases β and β’ is not observed in the FFT of Fig. 9(b). Therefore, both β phase separation and B2 ordering can be ruled out as strengthening mechanisms for age-hardening in β-Ti–25Nb–11Sn. The preferential precipitation of α over ω, which is related to the stability of the β phase, is not clearly understood at the moment, but two factors seem to be involved. One is the high density of dislocations acting as α nucleation sites in heavily swaged samples prior to aging; otherwise ω/β interfaces may be needed as α nucleation sites for fine distribution in β grains. The other is the high alloying content of Sn, which acts as an element suppressing or retarding ω transformation, as described above.

As shown in Figs. 7, 8 and 9, a high density of fine α needles leads to a decrease in spacing between the needles, which effectively hinders dislocation movement. Young’s modulus of Ti alloys is sensitive to constituent phases and their volume fraction. α phase has higher Young’s modulus than β phase [39]. Thus, the remarkably increases of Young’s modulus and tensile strength in Fig. 2 can be ascribed to fine needle-like α precipitation.

Fig. 3 also shows the temperature dependence of elastic strain estimated by the spring-back ratio. A relatively large spring-back ratio over $15 \times 10^{-3}$ is obtained by aging at 473 K (200 °C) to 723 K (450 °C). Verstrynge et al. [40] evaluated the mechanical properties, including the spring-back ratio, of orthodontic archwires produced by β Ti alloys and compared them to those of stainless steel archwires. They demonstrated spring-back ratios of $(11-14) \times 10^{-3}$ for β Ti alloys and $(9-10) \times 10^{-3}$ for stainless steel and reported the advantage of β Ti archwires with respect to their high spring-back ratio, low stiffness and good formability. Compare to their results, the results of this study indicate that Ti–25Nb–11Sn exhibits a better balance of yield strength and Young’s modulus. However, for a reasonable comparison with their results, the mechanical properties of Ti–25Nb–11Sn should be investigated using thin wires of the same size as those they employed.

Fig. 10 shows a bright-field image after heat treatment at 923 K (650 °C), indicating grain growth by recrystallization and a decrease in dislocation density, compared with Fig. 7. Some grains include weak strain contrast elongated along $<111>_{β}$, which may be associated with the α phase, suggesting that β transus temperature is just above 923 K (650 °C). These microstructural changes in substructure may be closely related to the decrease in strength at high temperatures.

As described above, β Ti–25Nb–11Sn alloy has excellent ductility and low Young’s modulus at ambient temperature, and its strength is remarkably increased by α precipitation during heat treatment after...
cold swaging. Therefore, this alloy is adaptable to cold-working or plastic-forming techniques such as cold rolling, drawing, swaging or die-forging in the fabrication of biomedical devices. Moreover, the mechanical properties can be controlled by heat treatment after cold working over the wide range of 900 to 1300 MPa for tensile strength and 53 to 86 GPa for Young’s modulus.

4. Summary

β-Ti — 25Nb — 11Sn ternary alloy was developed for easy making of a bulk ingot and easy homogenization of chemical composition, as compared to multicomponent β-Ti alloys. The alloy is so ductile at ambient temperature that it can be readily swaged to a highly reduced cross section without intermediate annealing. An as-swaged rod has a low Young’s modulus of 53 GPa along the longitudinal direction. The low Young’s modulus is derived from both metastable β phase and preferred [110] texture development. With increasing heat treatment temperature, the yield stress and tensile strength increase and exhibit a peak approximately 673 K (400 °C), with a yield stress of 1300 MPa and tensile strength of 1330 MPa. Large elastic strain (spring-back ratio) is obtained by aging around the peak temperature. HAADF-STEM and HREM revealed that strengthening is due to fine needle-like α precipitates.

It is suggested that biomedical devices with attractive mechanical properties are easily fabricated by conventional cold working or plastic forming processes followed by heat treatment.

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References