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Cold rolling deformation and annealing behavior of a β-type Ti–34Nb–25Zr titanium alloy for biomedical applications

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\textbf{A B S T R A C T}

In this study, the microstructures and mechanical properties of a newly developed β-type Ti–34Nb–25Zr (TNZ) alloy after cold rolling at different reduction ratios and recrystallization annealing were investigated by optical microscopy, XRD, SEM, EBSD, hardness and tensile tests. The tensile strength of the TNZ alloys reached 1071 MPa after cold rolling, which is 1.4 times the tensile strength of the solution-treated alloy. The deformation mechanisms of the TNZ alloys were significantly affected by the cold rolling reduction ratio (CRRR). The dominant deformation mechanisms for the TNZ alloys cold rolled at 20% and 56% CRRR were the formation of kink bands and of stress-induced α′ martensite. With increases in CRRR to 76%, the TNZ alloys showed a combination of deformation mechanisms including the formation of shear bands and stress-induced α′ martensite, and (332) <113> β mechanical twinning. The TNZ alloy after cold rolling at 86% CRRR followed by annealing exhibited elongation at rupture of 18%, tensile strength of 810 MPa, Young’s modulus of 66 GPa, and toughness of 132 MJ/m\textsuperscript{3}, making it attractive for biomedical applications.

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1. Introduction

One of the issues associated with the mechanical compatibility of conventional metal implant materials during the past decades has been defined as ‘stress shielding’ [1], which results from a difference between the Young’s modulus (\(E\)) of the implant and that of the surrounding bone tissue [2]. When compared with stainless steels (\(E=190–210\) GPa) and cobalt-chromium (Co-Cr) alloys (\(E=210–250\) GPa), titanium (Ti) alloys (\(E=45–110\) GPa) are preferred metallic biomaterials for orthopedic implant applications due to their lower Young’s modulus, higher biocompatibility, and excellent corrosion resistance [3]. In addition to commercially pure Ti (CP-Ti), over seventy Ti alloys are currently commercially available for industrial applications including aeronautics, energy, chemical engineering, and biomedical engineering [4]. CP-Ti (an α-type Ti alloy) is frequently used as a dental implant material [5]. The Ti-6Al-4 V (Ti64) alloy may be used to replace CP-Ti in cases requiring higher mechanical strength [6–9], being a strong alternative to CP-Ti in biomedical applications [4,10].

However, CP-Ti and Ti64 are still substantially stiffer than natural bone (\(E=0.1–30\) GPa) [11,12]. Thus extensive research has been carried out on developing new Ti alloys, aiming at achieving a lower Young’s modulus so as to minimize or eliminate stress shielding [2,13–16]. It is of importance that orthopedic implant materials possess superior mechanical properties.
and biological compatibilities so that they can be used inside the human body without any problems [13,17]. Low Young’s modulus close to that of natural bone, high ductility, and high mechanical strength are prerequisites in the evaluating mechanical properties of potential orthopedic implant materials [13,18–20]. Metastable β-type Ti alloys are superior to α-type and α+β-type Ti alloys because they have even lower Young’s modulus (45–85 GPa) [21,22].

It is worth noting that Ti64 contains non-biocompatible alloying elements such as aluminum (Al) and vanadium (V). It has been reported that V is toxic [23] and Al is associated with neurological side effects [24] and genotoxicity [25]. Therefore, various β-type Ti alloys with low Young’s modulus, high mechanical strength, and high ductility were developed using biocompatible alloying elements such as niobium (Nb), zirconium (Zr), tantalum (Ta), molybdenum (Mo), and tin (Sn) in recent years for orthopedic implant applications [13,14,26–31].

β-type Ti alloys including Ti-Zr [32–34], Ti-Nb [35,36], Ti-Ta [37,38], Ti-Mo [39,40], Ti-Nb-Zr [33,14], Ti-Nb-Ta [41,42], Ti-Nb-Ta-Zr [43,44], Ti-Nb-Ta-Mo [43], and Ti-Nb-Mo-Zr [45] were investigated for biomedical applications. β-type Ti alloys are also reported to exhibit high fracture toughness [46]. In particular, of the abovementioned Ti alloys, Ti-Nb-Zr alloys are attracting increasing attention [13,14].

Ti alloys displaying high mechanical strength usually show high Young’s modulus. Recently, Xu et al. [47] reported that a cold rolling (CR) process on a β-type Ti-Nb-Ta-Zr-Fe alloy resulted in an increase in mechanical strength and a decrease in its Young’s modulus due to the formation of a stress-induced α” phase. On the other hand, increases in both mechanical strength and Young’s modulus were observed in Ti-Cr-O [48], Ti-Cr [49], and Ti-Mo [50] alloy systems after CR due to the formation of a stress-induced ω phase. The plastic deformation behavior of metastable β-type Ti alloys is complex and the deformation products that are generated as a result of plastic deformation affect both the strength and Young’s modulus of the material [19,20,26,48,49,51,52]. In addition, the intensity of plastic deformation is also reported to significantly affect the deformation mechanisms and deformation products [19,20]. In metastable β-type Ti alloys, ω, α’ and α” phases can be produced in the β matrix as a result of deformation [51].

The mechanical properties of an as-cast Ti-34Nb-25Zr (wt.%; hereafter) (TNZ) alloy were reported in our previous study [13]. The current study investigates the microstructural evolution and mechanical properties of the TNZ alloy after CR at different reduction ratios and annealing, through which we aimed to reveal the plastic deformation mechanisms of the thermomechanically processed alloy and to provide insight into achieving a combination of phases that display both high strength and low Young’s modulus in β-type Ti alloys.

2. Experimental procedures

The TNZ alloy with a nominal composition of Ti-34Nb-25Zr (wt.%.) was produced via a cold crucible levitation melting method using high purity Ti, Zr and Ti-Nb alloy [13]. The alloy ingot was re-melted five times to ensure the homogeneity of the chemical composition during casting. The TNZ alloy ingot was then subjected to solution treatment at 880 °C for 1 h and this group of specimens is hereafter denoted TNZ-S. The TNZ alloy underwent CR after solution treatment at different cold rolling reduction ratios (CRRR) of 20%, 56%, 76% and 86% and these specimens are denoted TNZ-A, TNZ-B, TNZ-C, and TNZ-D, respectively. The specimens that underwent CR at 86% CRRR were subsequently subjected to recrystallization annealing at 890 °C for 1 h and this group of specimens is denoted TNZ-R. The preparation steps of the thermomechanical processes for the TNZ alloy specimens are shown in Fig. 1.

Microstructural observation of the TNZ alloy specimens after the different thermomechanical processes was carried out using optical microscopy (OM) (Leica DM2500M with 3.1 MP CCD). The alloy specimens were ground and polished to a mirror finish, and etched using Kroll Solution (hydrofluoric acid 3 ml, nitric acid 5 ml and distilled water 100 ml) for OM examination. The phase constitutions of the alloys were analyzed using X-ray diffractometry (XRD; BrukerAXS D4 Endeavor). For the XRD analysis, specimens were scanned over the angular range of 30–90° using Cu- Kα radiation (λ = 0.154 nm) at a scanning rate of 0.02°/s. Stress-induced α” phases in the XRD patterns of cold rolled specimens were fitted using Peakfit. Electron backscatter diffraction (EBSD) analysis was conducted on the specimens after mirror-finish polishing using a field-emission scanning electron microscopy (FEI Nova NanoSEM).

Micro-hardness testing was carried out to measure the hardness of the TNZ alloy specimens and to analyze the work-hardening behavior of the specimens. A load of 300 g was applied for a period of 15 s during the Vickers micro-hardness tests. Eleven different measurements were made on each specimen and these measurements were averaged. Tensile tests were carried out on flat specimens with a gauge section with dimensions of 8 mm × 2 mm × 1 mm using an Instron 5567 testing system with advanced video extensometer at a strain ratio of 1 × 10⁻³ s⁻¹ at room temperature. Tensile strength, yield strength, Young’s modulus, resilience modulus, elongation at rupture and toughness values of the alloy specimens were obtained by calculating the average values obtained from five different tensile specimens. The toughness (MJ/m³) is defined as the energy absorbed by the TNZ alloy specimens until rupture during tensile testing and it is determined by calculating the area under the tensile curve. The fracture surfaces of tensile-tested specimens were examined using field-emission SEM (ZEISS SUPRA 40 VP).

The mechanical properties of the TNZ alloy specimens were analyzed via a one-way analysis of variance (ANOVA) method. Tukey’s HSD post hoc test was used to determine whether there were statistically significant differences between the specimen groups; differences between the specimen groups were considered significant when p < 0.05.

3. Results and discussion

3.1. Optical microstructure

Fig. 2 shows optical micrographs of the TNZ alloy specimens after the different thermomechanical processes. Equiaxed grains with an average grain size of 275 μm were observed.
in the microstructure of the solution-treated alloy samples TNZ-S (Fig. 2a). The grain size was determined using the intercept method. It was found that deformation products emerged in the microstructures of the cold-rolled samples of TNZ-A, B, C, and D (Fig. 2b–e). Furthermore, after undergoing CR at 86% CRRR, the TNZ-D specimens exhibited a fibrous structure (Fig. 2e). Clear recrystallized grains free from deformation products were observed in the annealed specimens of TNZ-R (Fig. 2f), which exhibited an averaged grain size of 125 μm. It is not possible via OM examination to conclusively identify the deformation products that appeared in the microstructures of the cold-rolled TNZ alloy specimens. To this end, EBSD analysis was carried out to identify.

3.2. Phase constitutions analyzed by XRD

Fig. 3 shows XRD diffraction patterns of the TNZ alloy specimens. It can be seen that TNZ-S and TNZ-R exhibited peaks only belonging to a β phase. Peaks belonging to athermal α” martensite were not observed in the XRD patterns of TNZ-R and TNZ-S. Previous studies [53-55] reported that an athermal α” martensite phase emerged in β Ti alloys as a result of water quenching. Hu et al. [56] reported that the concentration of Nb required for the stability of the β phase in binary Ti-Nb alloys was 38%. The TNZ alloy in this study contained 34% Nb in addition to a high concentration of Zr (25%). The absence of an athermal α” martensite phase in the TNZ alloys after solution and annealing treatment may be due to the combined stabilization of the β phase by the high concentrations of Nb and Zr elements, as reported elsewhere [19,20]. As can be seen in Fig. 3, a (200)α” peak belonging to an α” martensite phase was observed in the XRD patterns of the cold-rolled TNZ alloy specimens (TNZ-A, TNZ-B, TNZ-C, and TNZ-D) along with the peaks belonging to a β phase. The stress-induced α” martensite phase disappeared in the TNZ-R specimens, which were cold rolled at 86% CRRR followed by a recrystallization annealing, indicating that a stress-induced α” phase with an orthorhombic crystal lattice structure transformed into a body centered cubic (BCC) β phase during annealing. No correlation between the increase in the intensity of the (200)α” peaks and the increase in CRRR was observed. The TNZ-S showed the highest (110)β peak intensity and this intensity was decreased in the cold-rolled TNZ alloy specimens. For the specimens after annealing, TNZ-R displayed the highest intensity of (211)β peaks with a value of 917 a.u., and the (211)β peak intensity values for the TNZ-S, TNZ-A, TNZ-B, TNZ-C and TNZ-D specimens were measured to be 74, 324, 96, 106 and 127 a.u., respectively. It is well known that the distortion of crystal lattices and the dislocation density increase with an increase in CRRR. Recrystallization annealing is a thermal process that is intended to relieve the deformation stress resulting from CR. The width of the β-phase peaks of in TNZ-R was decreased in comparison to the cold-rolled specimens TNZ-A, TNZ-B, TNZ-C, and TNZ-D, confirming that the crystal lattice structure was transformed into a more stress-relieved state, similar to the results reported elsewhere [19]. Notably, sub-grain boundaries were found to occur inside the grains as seen in Fig. 2e and f, causing the grains to become finer and relevant peaks wider. As seen in Fig. 2f, the sub-grain boundaries were transformed into large-angle boundaries after the annealing treatment. No XRD patterns of the TNZ alloy specimens showed peaks of an ω phase. This might be due to the small dimension of the ω phase, as reported elsewhere [14,18–20,57,58].

3.3. Crystal structure and crystal orientation of phases analyzed by EBSD

EBSD analysis was performed to determine the local crystal structures and crystal orientations of the phases in the
TNZ alloy specimens, thus revealing the deformation mechanisms of the alloy specimens during CR. The inverse pole figure (IPF) maps and corresponding misorientation profiles of the TNZ specimens are shown in Fig. 4. Notably, the IPF maps of TNZ-R (Fig. 4a) and TNZ-S (Fig. 4b) show that these alloy specimens were in an as-quenched state without deformation product existing in their microstructures. The IPF maps of TNZ-A (Fig. 4c), TNZ-B (Fig. 4e), and TNZ-C (Fig. 4g) use the different colors for the deformation products and the β matrix, and the corresponding misorientation profiles are shown in Fig. 4d, f and h.

The misorientation angles between the deformation bands and the β matrix in TNZ-A, TNZ-B, and TNZ-C were measured to determine the type of deformation products. As indicated by the white arrows in Fig. 4c, the misorientation angles between the β matrix and the deformation product in TNZ-A varied in the range of 10–30°, as shown in Fig. 4d. Yang et al. [59] reported that the misorientation angles between kink bands and β matrix in a Ti-22.4Nb-0.73Ta-2Zr-1.34O alloy during compression straining varied in the range of 10–30°. It can be deduced that the band-type deformation products in TNZ-A (cold rolled at 20% CRRR) were kink bands. The IPF map of TNZ-B is shown in Fig. 4e, where the misorientation angles between the deformation bands and the β matrix are marked by white arrows, and the corresponding misorientation profile shown in Fig. 4f indicates misorientation angles ranging from 20 to 32°, confirming the formation of kink bands. The formation of kink bands was still the dominant deformation mechanism in TNZ-B (cold rolled at 56% CRRR). It can be concluded that the dominant deformation mechanisms for the TNZ alloys after cold rolling at 20% and 56% CRRR were the formation of kink bands as indicated by the white dashed arrows in Fig. 4c and e. The misorientation angles between the β matrix and the twin bands in TNZ-C (cold rolled at 76% CRRR), as indicated by the white arrows in Fig. 4g, were in the range of 52–56°, which is verified by the corresponding mis-
The orientation profile in Fig. 4h. Furuta et al. [60] reported that the misorientation angle between \{332\} <113> β mechanical twins and the β matrix was 50.5° in the <110> β direction. The misorientation angle between the β matrix and the twin bands in TNZ-C is slightly higher than 50.5°, which is due to the high CRRR (76%). Similar results are found in the misorientation angle with an increase in plastic deformation were reported in β Ti alloys [19,20]. In addition, unlike the TNZ-A and TNZ-B specimens, the formation of shear bands as indicated by the white dashed arrows was observed in TNZ-C (Fig. 4g). Formation of shear bands were reported to occur in severely cold-deformed β-type titanium alloys [59,61]. Shear bands were considered to originate from rotated and severely distorted crystals due to a mass of shear stress localization on a slip plane [59]. Notably, a decrease in the phase stability of β-type Ti alloys leads to an alteration of the main deformation mechanisms, namely, formation of stress-induced martensite and mechanical twinning substituting the dislocation glide mechanism [62]. In this study, kinking, \{332\}<113> β mechanical twinning, stress-induced α" and shear band formations were found to be the deformation mechanisms during CR of the TNZ alloy. Furthermore, the \{332\}<113> β mechanical twining and shear band formation became dominant with increasing CRRR of the TNZ alloys.

3.4. Micro-hardness evaluation

The micro-hardness of the TNZ alloy specimens was measured to be 229 ± 5 HV, 243 ± 11 HV, 274 ± 7 HV, 275 ± 9 HV, 275 ± 4 HV, and 244 ± 5 HV for TNZ-S, TNZ-A, TNZ-B, TNZ-C, TNZ-D and TNZ-R, respectively. It can be seen that all the cold-rolled specimens (TNZ-A, TNZ-B, TNZ-C, and TNZ-D) exhibited a higher micro-hardness than that of the solution-treated specimen TNZ-S, while the annealed specimen TNZ-R exhibited a higher micro-hardness than the solution-treated specimen TNZ-S. This increased micro-hardness in TNZ-R compared to TNZ-S is attributed to its finer grain size after recrystallization. The higher micro-hardness of the cold-rolled TNZ alloy specimens in comparison to the TNZ-S specimen is due to the increased dislocation density and tangles resulting from CR. However, CR at 56%, 76% and 86% CRRR did not lead to a significant change in the micro-hardness value, indicating that limited work hardening was taking place in the TNZ alloy after CR at a CRRR ≥ 56.

3.5. Tensile properties

Fig. 5 shows the representative tensile stress-strain curves for the TNZ alloy specimens. It can be seen that there were three deformation stages for the TNZ specimens during tensile tests. The TNZ specimens initially experienced an elastic deformation stage, followed by a plastic deformation stage, before a fracture. The tensile strength (σt), yield strength (σy), and elongation at rupture (ε), as well as the Young's modulus (E), and elastic admissible strain (δ) of the TNZ specimens are summarized in Table 1. The elastic admissible strain is calculated as the ratio of the yield strength over the Young's modulus of the material (δ = σy/E) [13,14,19,20,22,63].

Tensile properties are crucial for implant materials. As can be seen in Table 1, the tensile strength was measured to be 747,
Fig. 4 – (a) Inverse pole figure (IPF) map of TNZ-S, (b) IPF map of TNZ-R, (c) IPF map of TNZ-A, (d) misorientation profile along white arrows in (c), (e) IPF map of TNZ-B, (f) misorientation profile along white arrows in (e), (g) IPF map of TNZ-C, (h) misorientation profile along white arrows in (g).

788, 895, 1015, and 810 MPa, and the yield strength was measured to be 723, 738, 983, 1030 and 786 MPa for TNZ-S, TNZ-A, TNZ-B, TNZ-C, TNZ-D, and TNZ-R, respectively. It can be seen that the tensile strength and yield strength of all the cold-rolled TNZ alloy specimens (TNZ-A, TNZ-B, TNZ-C, and TNZ-D) were higher than those of the solution-treated specimen TNZ-S and these properties increased with an increase in CRRR. It can be deduced that a higher CRRR resulted in a higher dislocation density and finer grains, leading to an increase in the tensile strength of the cold-rolled TNZ alloy specimens. Notably, stress-induced $\alpha''$ phase was reported to be effective in grain refining, thus leading to an increase in the
Table 1 – Tensile properties of TNZ alloy specimens.

<table>
<thead>
<tr>
<th>Ti alloy</th>
<th>σYS (MPa)</th>
<th>σUT (MPa)</th>
<th>ε (%)</th>
<th>E (GPa)</th>
<th>δ</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNZ (as-cast)</td>
<td>810 ± 48</td>
<td>839 ± 32</td>
<td>15 ± 2</td>
<td>62 ± 4</td>
<td>1.31</td>
<td>[13]</td>
</tr>
<tr>
<td>TNZ-S</td>
<td>723 ± 28</td>
<td>747 ± 9</td>
<td>12 ± 3</td>
<td>61 ± 3</td>
<td>1.18±0.02</td>
<td>[This study]</td>
</tr>
<tr>
<td>TNZ-A</td>
<td>738 ± 7</td>
<td>788 ± 39</td>
<td>8 ± 0</td>
<td>68 ± 5</td>
<td>1.08±0.08</td>
<td>[This study]</td>
</tr>
<tr>
<td>TNZ-B</td>
<td>840 ± 30</td>
<td>895 ± 20</td>
<td>7 ± 1</td>
<td>65 ± 2</td>
<td>1.32±0.02</td>
<td>[This study]</td>
</tr>
<tr>
<td>TNZ-C</td>
<td>983 ± 34</td>
<td>1015 ± 20</td>
<td>10 ± 0</td>
<td>74 ± 2</td>
<td>1.33±0.01</td>
<td>[This study]</td>
</tr>
<tr>
<td>TNZ-D</td>
<td>1030 ± 21</td>
<td>1071 ± 14</td>
<td>8 ± 1</td>
<td>75 ± 1</td>
<td>1.37±0.04</td>
<td>[This study]</td>
</tr>
<tr>
<td>TNZ-R</td>
<td>786 ± 15</td>
<td>810 ± 21</td>
<td>18 ± 3</td>
<td>66 ± 1</td>
<td>1.20±0.05</td>
<td>[This study]</td>
</tr>
</tbody>
</table>

![Fig. 5 – Typical tensile stress-strain curves for the TNZ alloy specimens.](image)

![Fig. 6 – Young's modulus, toughness, and elastic energy of the TNZ alloy specimens.](image)

The tensile strength of the cold rolled specimens [64]. The higher mechanical strength of the cold-rolled TNZ alloy is considered to be originated from the formation of sub-grain boundaries. Furthermore, the tensile strength and yield strength of TNZ-R were higher than those of TNZ-S. Taking the average grain size into consideration (275 and 125 μm for TNZ-S and TNZ-R, respectively), it can be interpreted that the increase in tensile strength and yield strength are attributable to the grain refinement resulting from the recrystallization during annealing. The elastic admissible strain was calculated to be 1.18%, 1.08%, 1.32%, 1.33%, 1.37%, and 1.20% for TNZ-S, TNZ-A, TNZ-B, TNZ-C, TNZ-D, and TNZ-R, respectively. The elastic admissible strain values of the TNZ alloy specimens also increased with an increase in CRRR. The increase in yield strength with increasing CRRR resulted in an increase in the elastic admissible strain. Although the Young’s modulus of TNZ-C and TNZ-D was measured to be higher than those of TNZ-A and TNZ-B, the elastic admissible strain values of TNZ-C and TNZ-D were calculated to be significantly (μ<0.05) higher than those of TNZ-A and TNZ-B; indicating that the increase in yield strength is more dominant than the increase in Young’s modulus. It is worth noting that the difference between the tensile strength and the yield strength of the TNZ alloy specimens is small, indicating that little strain hardening occurred during tensile testing.

The elongation at rupture of TNZ-S, TNZ-A, TNZ-B, TNZ-C, TNZ-D and TNZ-R was measured to be 12%, 8%, 7%, 10%, 8% and 18%, respectively. It can be seen that TNZ-R exhibited significant ductility during tensile testing and its elongation at rupture was 1.5 times that of TNZ-S. The higher ductility of TNZ-R is attributed to its uniform microstructure with a fine grain size (Fig. 2f). The elongation at rupture of TNZ-D (cold rolled at 86% CRRR) was lower by 33% when compared to TNZ-S. The recrystallization annealing process was designed and carried out to eliminate the deformation effects of CR on the microstructure and to improve the ductility of the cold-rolled specimens. The elongation at rupture of TNZ-R reached 18%, which is 2.5 times greater than that of TNZ-D, as a result of the recrystallization annealing.

Fig. 6 shows the Young's modulus, modulus of resilience and toughness values of the TNZ alloy specimens. The Young's modulus was measured to be 61, 68, 65, 74, 75, and 66 GPa for TNZ-S, TNZ-A, TNZ-B, TNZ-C, TNZ-D, and TNZ-R, respectively. The differences between the Young's modulus of the TNZ alloy specimens after the different thermomechanical processes is attributed to the different phases and textures generated in the specimens, as reported elsewhere [65]. The Young's modulus of orthopaedic implant materials is an important parameter because a higher stiffness compared to the adjacent bone leads to stress shielding. It has been reported that stress-induced α and ω phases may occur during cold rolling of metastable β-type Ti alloys [19]. The Young’s modulus of these phases are different from the β phase, thus the β-type Ti alloys exhibited different Young’s moduli after cold rolling [19,20,26]. A decrease in Young's modulus was observed when the stress-induced α” phase occurred during cold rolling of
the metastable β-type Ti alloys, which is attributed to the fact that the Young’s modulus of the stress-induced α” phase is lower than that of the β phase [64]. In the case of the formation of stress-induced ω phase, whose Young’s modulus is higher than that of the β phase [66,67], an increase in Young’s modulus was observed during CR [39,26]. If both phases are present together, the Young’s modulus of the metastable β-type alloy depends on the fractions of the phases [19,68]. Notably, cold rolling process may also result in a decrease of atomic distance between atoms, leading an increase in Young’s modulus [26]. It is worth noting that the Young’s modulus of TNZ-C and TNZ-D was measured to be significantly (p<0.05) higher than those of the rest of specimens. It is considered that both the formation of stress-induced ω phase and decrease in atomic distance occurred in the heavily cold-rolled TNZ alloys, leading to an increase in their Young’s modulus.

An increase in the Young’s modulus was observed for the TNZ alloy specimens after CR (Fig. 6). The XRD patterns of the cold-rolled TNZ alloy specimens exhibited peaks belonging to stress-induced α” martensite phase (Fig. 3). Matsumoto et al. [64] reported that a decrease in Young’s modulus was observed in cold-rolled β Ti-Nb-Sn alloys because a (100)_ω texture was developed during CR.

The Young’s modulus, yield strength, and elongation at rupture of the TNZ alloy specimens were in the ranges of 61–75 GPa, 723–1030 MPa, and 7–18%, respectively. Another promising β-type Ti-Nb-Zr alloy developed for biomedical applications is the Ti-13Nb-13Zr [69]. The Young’s modulus, yield strength, and elongation at rupture of a thermomechanically processed Ti-13Nb-13Zr alloy were reported to be in the ranges of 79–84 GPa, 836–908 MPa, and 10–16%, respectively [70]. It can be seen that TNZ-R showed a significantly higher ductility (ε = 18%) than Ti-13Nb-13Zr. Also, the Young’s modulus of TNZ-R (E = 66 GPa) was lower than that of aged Ti-13Nb-13Zr (79–84 GPa) [70], annealed Ti–15Mo (78 GPa) [9], mill annealed Ti-6Al-4V ELI (110 GPa) [9], and CP-Ti (103 GPa) [20]. It can be concluded that the mechanical properties of these TNZ alloy specimens are particularly suitable for biomedical applications.

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**Fig. 7** – Fracture surfaces of TNZ alloy specimens: (a) TNZ-S, (b) TNZ-A, (c) TNZ-B, (d) TNZ-C, (e) TNZ-D, and (f) TNZ-R.
The toughness values of the TNZ-S, TNZ-A, TNZ-B, TNZ-C, TNZ-D and TNZ-R specimens were measured to be 73, 53, 49, 81, 73 and 132 MJ/m², respectively. Although the tensile strength of TNZ-R was lower than those of TNZ-B, TNZ-C, and TNZ-D resulting from recrystallization annealing, its toughness increased significantly due to the increase in its ductility. The elastic energy (MJ/m²) absorbed by the TNZ alloy specimens during elastic deformation was determined by calculating the elastic area under the tensile curve and the elastic energy values of TNZ-S, TNZ-A, TNZ-B, TNZ-C, TNZ-D and TNZ-R were measured to be 6, 5, 7, 9, 9, and 6 MJ/m², respectively. It has been revealed that the elastic energy of the TNZ alloy specimens increased with an increase in CRRR.

Fig. 7 shows the SEM micrographs of the fracture surfaces of the TNZ specimens after tensile testing. It can be seen that the fracture surfaces were very rough with many dimples, revealing that the specimens were fractured in a ductile manner. Intergranular fracture did not occur in any of the fracture surfaces. It is worth noting that shallow vein patterns along with cleavage facets were observed in the fracture surfaces of the cold-rolled TNZ alloy specimens TNZ-A, TNZ-B, TNZ-C, and TNZ-D (Fig. 7b–e). However, a higher number of dimples with deeper morphology occurred in the fracture surface of the TNZ-R alloy specimen (Fig. 7f), which is very consistent with the ductile fracture manner along with the highest ductility (an elongation at rupture value of 18%). In particular, a cup-and-cone type ductile fracture surface was observed in TNZ-R, indicating a micro-void coalescence mechanism during deformation.

4. Conclusions

In this study, the microstructure and mechanical properties of a β-type TNZ alloy after cold rolling and recrystallization annealing have been examined. The main conclusions are as follows:

1) XRD analysis has revealed that the cold-rolled TNZ alloy specimens exhibited peaks belonging to the stress-induced α′ and β phases. Both TNZ-S and TNZ-R exhibited only peaks belonging to a β phase.
2) Plastic deformation mechanisms during cold rolling in the TNZ alloy specimens were revealed to be the formation of kink bands, shear bands, stress-induced α′ martensite, and ⟨332⟩<113> β mechanical twins.
3) It has been revealed that cold rolling at a reduction ratio in the range of 56–86% did not result in an increase in the micro-hardness of the specimens, indicating the significant deformation capability of the TNZ alloy.
4) The tensile strength, elongation at rupture, and Young's modulus of the thermomechanically processed TNZ alloy specimens were in the ranges of 747–1071 MPa, 7–18%, and 61–75 GPa, respectively.
5) TNZ-R showed the most ductile behaviour, with an elongation at rupture of 18% during tensile testing, along with other excellent mechanical properties including tensile strength of 810 MPa, Young's modulus of 66 GPa, and toughness of 132 MJ/m². The TNZ alloys after cold rolling at an 86% reduction ratio followed by annealing at 890 °C for 1 h exhibited attractive mechanical properties for biomedical applications.

Conflicts of interest

The authors declare that there are no conflicts of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jmrt.2019.12.062.

References


