Original Article

Microstructure and elastic deformation behavior of β-type Ti-29Nb-13Ta-4.6Zr with promising mechanical properties for stent applications

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ABSTRACT

In this paper, an attempt was made to combine theoretical composition design and thermo-mechanical treatments to produce a metastable β-type titanium alloy with mechanical compatibility for self-expandable stent applications. Metastable β-type Ti-29Nb-13Ta-4.6Zr (wt.%) thin-wires with an elastic modulus of 46 GPa and a yield strength of 920 MPa were successfully fabricated by cold rolling and low temperature aging. This combination of high yield strength and comparatively low elastic modulus resulted in enhanced elastic recoverable strain of 1.9%, which is much higher than that of the conventional metallic stent materials. The microstructure responsible for the much sought-after mechanical properties was observed to be mainly consisted of a homogeneous distribution of nanometer-sized α'-precipitates in a β-phase matrix obtained via a spinodal decomposition of the pre-existing α'-martensite phase through α'' → α' lean + α' rich → α + β. The α'-precipitates increase the strength of the material by hindering the motion of dislocations (spinodal hardening) while the β-matrix with relatively low content of β-stabilizers gives rise to the observed low elastic modulus. More broadly, these findings could be extended to developing advanced metastable β-type titanium alloys for implant and other engineering applications.

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1. Introduction

Globally, the number of deaths per year due to cardiovascular diseases (CVDs) increased by 44% between 1990 and 2017, climbing from 12.3 million deaths to 17.7 million deaths. At the same time, efforts to prevent and treat CVDs appear to be working as the rise in deaths is slower than the overall growth of the population [1]. This includes the development of micro-traumatic surgeries with the implantation of stents, which is acknowledged to be one of the most effective approaches for CVDs. However, the most commonly used stent materials still face several questions about their mechanical performance and biocompatibility (e.g., local immune responses and...
inflammatory reactions induced by Ni and Cr ions released from 316L stainless steel, Co-Cr based and NiTi alloys [2–4], opening a path for innovation in this area.

Metastable β-type titanium alloys with non-toxic elements have become the most promising metallic materials in biomedical applications due to the excellent hemocompatibility together with good mechanical and corrosion properties, as well as cold forming ability [5]. Based on theoretical composition design and experimental verification, these alloys have been exploited with great perspective to pursue a concurrently ultralow modulus and high strength, which will minimize the “stress shielding” problem and enable application in soft tissue repair such as intravascular self-expandable (crush recoverable) stents [6]. In this context, Saito et al. first presented a new class of metastable β-type Ti-Nb-Ta-Zr-O alloys called “gum metal” with unique pseudosuperelastic properties in which application of cold work was demonstrated to unexpectedly decrease its elastic modulus and increase yield strength [7]. According to the authors, such behavior is only achieved when three critical electronic numbers are simultaneously satisfied: (i) a compositional average valence number (e/a) of about 4.24; (ii) a bond order (Bo value) of about 2.87; and (iii) a “d” electron-orbital energy level (Md value) of about 2.45 eV. Moreover, the alloy composition requires oxygen concentration to be restricted to a range between 0.7 and 3.0 at.%. Therefore, composition and oxidation control have become a central problem in manufacturing large amounts of gum metals, which often makes the process technically and economically unfeasible.

The design strategy of β-type Ti alloys is usually based on the “d-electron alloy design method” proposed by Morinaga et al. [8]. This approach provides a physical background to the phase stability and to the elastic modulus of titanium alloys by connecting the values of Bo (the covalent bond strength between Ti and alloying elements) and Md (the mean “d” electron-orbital energy level concerning electronegativity and elements radius) to the chemical stability of the phases. Therefore, “alloying vectors” on a Bo – Md diagram, originating from the Bo and Md values of pure Ti, represent the ability of each element to form either stable (α and β) or metastable (α’, α” and ω) phases. Moreover, since the bonding forces are not only related to the crystal structure, but also to the interatomic distances in the crystal lattice, the elastic modulus of β-phase is observed to be closely related to its total amount of β-stabilizers (e.g., Nb, Ta, Mo, etc.) and decreases monotonically with decreasing total content of β-stabilizers.

An insufficient amount of β-stabilizers, however, might benefit the β to α’ martensitic transformation either by quenching or mechanical deformation at room temperature, leading to remarkable decrease in yield strength of the metastable β-Ti alloy. In this case, a precipitation hardening treatment could be used to restore the mechanical strength of the alloy, but its elastic modulus normally increases as well. However, recent studies have shown that these alloys can have a different behavior where a homogeneous distribution of ultrafine α precipitates in the parent β matrix of a metastable titanium alloy, after a series of thermo-mechanical treatments including swaging, cold rolling and low temperature aging, could be able to deliver both low elastic modulus and high yield strength [9–11]. As such, these results open a window for the development of metastable β-type titanium alloys with superelastic properties required for self-expandable stents and other biomedical applications.

In this work, an effort was made to combine theoretical composition design and thermo-mechanical treatments to fabricate β-type titanium thin-wires with mechanical compatibility for self-expandable stent applications. The alloy was produced by alloying, cold rolling and low temperature aging. The influence of the processing on microstructure and mechanical properties was investigated.

2. Materials and methods

Homogenized ingots (140 mm (length) × 25 mm (width) × 20 mm (thick)) of Ti-29Nb-13Ta-4.6Zr (wt.%) alloy produced by Ercata GmbH were hot swaged at 1273 K into rounded bars of 8 mm in diameter. The chemical composition of the as-received material is shown in Table 1. After swaging, samples were solution treated at 1073 K for 1 h under vacuum, followed by quenching into water (298 K). Some of the samples were then cold rolled to a final thickness of 0.9 mm without intermediate annealing, with a thickness reduction of 89%. The aim of this treatment is the formation of stress induced α’ martensite. Finally, these cold rolled samples were aged at 673 K for 20 min (in an atmosphere of argon to prevent oxidation of the samples) followed by quenching into water, as an attempt to reverse martensitic transformation from α’ to nano α + β.

Based on the d-electron alloy design method [12], the calculated average bond order and metal d-orbital energy level for the selected alloy is 2.878 and 2.462, respectively. Therefore, the alloy is located in the β + α’ region and close to the β/β + α’ phase boundary. Moreover, the alloy composition was intentionally chosen to have the same chemical composition of a gum metal, with levels of oxygen in a lower range.

Tensile specimens with a rectangular cross-section of 0.90 mm × 1.40 mm and a total length of 110 mm were cut from the aged samples with the rolling direction parallel to the loading axis. The elastic deformation behavior of the aged samples was then characterized by conventional loading-unloading tensile testing at a cross-head speed of 0.2 mm/min. An extensometer was used for accurate strain measurement.

A dynamic mechanical analyzer was employed to measure the storage modulus as a function of temperature, in a single cantilever mode with amplitude of 15 μm at dynamic stress frequency of 1 Hz and cooling rate of 5 K/min. The martensitic starting transformation temperature (Ms) of the specimens was determined from the recorded storage modulus-temperature curve.

Phase constitutions of both solution treated and aged samples were also examined by the X-ray diffraction (XRD) analysis using Cu Kα irradiation at an accelerating voltage of 40 kV and a current of 250 mA. Metallographic exam-

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<th>Table 1 – Chemical composition of the as-received titanium alloy (wt.%).</th>
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The results were initially conducted by optical microscopy. Subsequently, transmission electron microscopy (TEM) samples were mechanically polished and then milled using precision ion polishing system (PIPS). The thin foils were examined using a microscope equipped with energy dispersive X-ray spectroscopy (EDS) operated at 200 kV. Selected area electron diffraction (SAD) patterns were indexed using the Java Electron Microscopy Software (JEMS).

3. Results and discussion

3.1. Solution heat treated and water quenched specimens

Fig. 1 shows the microstructures of the solution heat treated and water quenched (ST/WQ) TNTZ alloy, in which a matrix embedded with a lath-shaped precipitates was observed. The XRD patterns presented in Fig. 2a provide evidence for the presence of parent β phase and the anα′-martensite. As previously mentioned, the β → α′ transformation can occur during the quenching of single β phase to room temperature due to low content of β-stabilizers in the alloy, suggesting that the martensitic transus temperature (Ms) is close to and above room temperature. Moreover, the alloy density is 5.7 g/cm³, representing a lower range among the metallic stent materials such as tantalum (16.6 g/cm³), Co–Cr alloy (9.2 g/cm³) and Nitinol (6.7 g/cm³).

Fig. 3 shows the conventional tensile stress–strain curve of the ST/WQ TNTZ specimen. The elastic deformation regime exhibits a nonlinear curve with a “double yielding” behavior. Several elastic mechanisms have been proposed for the nonlinear elasticity of the β titanium alloys, including stress-induced reversible α′ martensitic transformation [13], elastic strain energy [7] and extensive lattice distortion [14]. The XRD pattern of the ST/WQ specimens after tensile (Fig. 2b), which was performed near the ductile fracture surface, confirms the stress-induced β → α′ martensitic transformation as the peak’s intensity of α′ martensite was increased, evidencing the higher volume of this phase in the microstructure. Deformation at room temperature also produced α-phase, which has been previously shown to be a condition for omega formation in metastable titanium alloys. Therefore, based on the stress–strain curve, it can be stated that at stress levels as low as 88 MPa, the β-phase begins to undergo a transformation to α′. The α′ transformation accommodates the applied load by producing a tensile strain. After 4% strain, the transformational strain is exhausted, and the stress begins to rise again. This second rise goes on uninterrupted until the proper dislocation flow stress is reached.

Here, it is worth to point out that the observed extremely low yield strength makes the ST/WQ condition inadequate to be applied to self-expandable stents, although it does exhibit low Young’s modulus. On the other hand, the large elongation gives significant support to achieve thin-wires or thin-tubes by routine cold rolling, from which a large span of mechanical properties can be modulated by heat treatments, based on the diverse phase transformations between β and α phase as well as α′ martensite.

3.2. Cold-rolled, aged and water quenched specimens

Fig. 4b and c show the XRD patterns of the cold-rolled, aged and water quenched (CRA/AQ) specimens. In comparison to its room-temperature counterpart before aging (Fig. 4a), no diffraction peaks from α′-martensite can be observed, supporting the hypothesis that the β → α′-martensite transformation is fully reversed even for the relatively short aging times employed in this work. Comparing with other
biomedical β-type titanium alloys [15,16], the quenched α” martensite shows the lower stability and fast decomposition into equilibrium phases. It is important to observe that on subsequent cooling (after aging) the α” martensitic phase transformation was suppressed, indicating that the applied thermo-mechanical treatment lowered the martensitic transus temperature (Ms) below room temperature.

Fig. 5 shows the storage modulus measured by dynamic mechanical analyzer (DMA) during cooling for the ST/WQ and CRA/AQ (20 min aging time) specimens. From the curves it is possible to estimate the Ms temperature from β to α”. It is observed that the storage modulus of both specimens first decreases with decreasing temperature and then increases with further decrease in temperature. The martensitic starting transformation (Ms) temperatures of the ST/WQ and CRA/AQ (20 min aging time) specimens are estimated to be 74 and −19 °C, respectively. High density of dislocations and grain boundaries in the CRA/AQ (20 min aging time) specimen may be held responsible for retarding the shearing process associated with the martensitic transformation, which in turn lowers the Ms temperature. In agreement with the XRD results, it indicates that the martensitic transformation can be effectively retarded or even suppressed by cold rolling and subsequent aging.

The elastic deformation behavior of the CRA/AQ (20 min aging time) specimens was evaluated by cyclic loading-unloading tensile tests (Fig. 6). In the first cycle (to strain of 1.0%), loading and unloading curves were overlapped due to the occurrence of only reversible elastic deformation. The second cycle (to strain of 2.0%) is almost completely recovered in spite of a very small residual strain of about 0.1%, for example, the recoverable strain keeps 1.9%, which is far greater than that of Ti-6Al-4 V (0.8%), 316L SS (0.17%) and Nitinol (0.23–0.83%), and similar to those of bulk metallic glasses such as Vitreloy1 (2%) and metallic glass matrix composites such as Ti-18Zr-12V-5Cu-17Be (1.7%) [6]. Meanwhile, the alloy is significantly strengthened, presenting a yield strength in the order of 920 MPa (admitting a plastic deformation of 0.2%) and also exhibits an elastic modulus of only 46 GPa. Based on these observations, apart from being promising for applications in metallic stent materials, the CRA/AQ (20 min aging time) condition also possesses high potential to be widely used in the fields of sporting equipment, electronics, other medical devices and defense applications.

A nonlinear elastic deformation is also observed for the CRA/AQ (20 min aging time) stress–strain curve. However, different from the SQ/WT specimens, which presented a well-defined plateau, the stress–strain curves slightly deviate from the linear elastic behavior after the strain exceeded the limit of a linear elastic range of 0.5%. A similar behavior was observed for cold-rolled β-type Ti-25Nb–3Zr–3Mo–2Sn alloy [2], although no sufficient evidence was found to illustrate the origin of particularly nonlinear elasticity. The authors considered that the pre-existed metastable phases could play a role in enlarging elastic range and causing continuous elastic softening during later tensile loading.

In order to understand the microstructure evolution during the proposed thermo-mechanical treatment, bright field TEM images were taken from CRA/AQ (20 min aging time) specimen (Fig. 7). Fig. 7a shows an apparent contrast caused by dislocation tangles near grain boundaries due to the severe cold rolling prior to annealing. At higher magnifications (Fig. 7b), the microstructure is observed to be mainly composed by a homogeneous distribution of nanometer-sized precipitates with lenticular morphology embedded in a β matrix, known as the most favorable microstructure from a high strength application perspective. The particles have, on average, minor axis
in projection of 5 nm and a major axis of 25 nm, for an aspect ratio that is on average 0.2. Also, it is possible to observe some larger white particles (indicated by the yellow arrows in Fig. 7c and identified as the original $\alpha''$ phase) decomposing near their edge and forming the matrix. Fig. 7d shows the SAD pattern corresponding to Fig. 7b. Indexing of the SAD pattern indicates that these ultrafine precipitates are $\alpha$-phase, which was also detectable via XRD.

In most cases the presence of an intermediate metastable phase, such as omega precipitates, is seen as the only means to achieve such homogeneous distribution of alpha precipitates. These metastable phases are believed to play a role as heterogeneous nucleation sites for precipitation of stable alpha phase. In addition to precipitation on heterogeneous nucleation sites, other different mechanisms for alpha precipitation have also been proposed. The first mechanism involves the phase separation of $\alpha''$ phase into two solid solutions, one rich with beta stabilizing elements while the other being lean of it [17]. The solute rich and solute lean phases are thought to be conducive for the precipitation of beta and alpha phases, respectively. Another and more recent mechanism that has been proposed requires no intermediate phase or heterogeneous sites and enables homogeneous alpha precipitation by small compositional fluctuations in the beta matrix when the composition of the alloy is close to the co(T) composition for alpha and beta phases. The co(T) composition is marked by the intersection of the free energy curves for the two phases [18,19].

Therefore, from the TEM observations, the microstructure of the CRA/AQ (20 min aging time) TNTZ alloy is observed to be primarily formed via a spinodal decomposition of the pre-existing $\alpha''$ martensite phase through $\alpha'' \rightarrow \alpha''$ lean + $\alpha''$ rich $\rightarrow \alpha + \beta$. The $\alpha$ nanometer-precipitates are believed to be responsible for increasing the strength of the material by hindering the motion of dislocations (spinodal hardening) while the $\beta$-matrix with relatively low content of $\beta$-stabilizers gives rise to the observed low elastic modulus. Fig. 8 outlines the interrelation between the three lattices as represented in the orthorhombic system. It is no surprise that as more $\beta$ stabilizers are added, the orthorhombic parameters of $\alpha''$-phase change and become closer to the bcc dimensions. Likewise, a lower content of $\beta$-stabilizers changes the crystal structure from orthorhombic to hexagonal close packed (hcp).

The EDS elemental mapping results for Ti, Nb, Ta and Zr covering the matrix and the larger particles of $\alpha''$-phase of the CRA/AQ (20 min aging time) specimens are presented in Fig. 9. Obvious compositional changes can be observed from the non-decomposed particles of $\alpha''$-phase and the matrix, which.
Fig. 8 – An illustration of how the lattices of the α, β and α’ phases are interrelated. Also shown are the transformation strains for β→α and β→α’ [20].

corroborates to the hypothesis of spinodal decomposition and hardening. Intriguingly, no compositional change is observed in the matrix within the nanometer-sized α-precipitates, suggesting a small composition difference between precipitates/matrix or a possible overlapping of EDS spots due to the extremely small size and distribution of these precipitates.

Finally, it is also important to point out that the CRA/AQ TNTZ alloy can be further strengthened by extending aging time. Fig. 10 shows the elastic modulus and Vickers hardness as function of three different aging times: 1, 20 and 100 min. Comparing the 1 min and 20 min aging conditions, it is possible to note a significant strengthening of the alloy accompanied by a lower increase in elastic modulus, corroborating to the high recoverable strain observed for the CRA/AQ (20 min aging time) specimens previously discussed. In the case of the 100 min aging condition, a high strength can be obtained at the expense of a similar increase of elastic modulus. Clearly, in comparison to high strength, a low elastic modulus is also important to ensure a large elastic limit. The XRD pattern of the CRA/AQ (100 min aging time) specimen is shown in Fig. 4c, revealing that the material strengthening is obtained due to the formation of more α precipitates and also to the presence of ω precipitates—which are known for decreasing the elastic strain regime. Previous investigations have shown that ω-phase could form within regions of matrix compositionally depleted with respect to β-stabilizing elements [16]. As such, on subsequent or continued isothermal aging, this phase can grow and coarsen by rejecting the β-stabilizing alloying elements into the surrounding matrix, which is eventually replaced by the equilibrium α-phase in titanium alloys. Therefore, based on these observations, short-time aging at low aging temperature, that is, aging at 673 K

Fig. 9 – Energy dispersive spectroscopy (EDS) elemental mapping results for Ti, Nb, Ta and Zr covering the matrix and the larger particles of α’-phase (white particles) of the CRA/AQ (20 min aging time) specimen.

Fig. 10 – Elastic modulus and Vickers hardness as function of three different aging times: 1, 20 and 100 min.
for 20 min, was confirmed to be best aging condition for self-expansible stent applications as it limits the precipitation of both \(\beta\) and \(\alpha\) phases.

4. Conclusions

In this study, the microstructure and elastic deformation behavior of metastable \(\beta\)-type Ti-29Nb-13Ta-4.6 Zr (wt.\%) with promising mechanical properties for stent applications were investigated. Considering the results and discussions, the following conclusions can be drawn:

- Thin-wires of metastable \(\beta\)-type Ti-29Nb-13Ta-4.6 Zr can be successfully fabricated by routine cold rolling based on its good ductility after hot-forging, annealing and water quenching.
- High yield strength (920 MPa) and ultralow elastic modulus (46 GPa) can be obtained for the cold rolled thin-wires after low temperature and short time aging, giving rise to an elastic (recoverable) strain higher than that of the conventional metallic stent materials.
- The microstructure responsible for the much sought-after mechanical properties is consisted of a homogeneous distribution of nanometer-sized \(\alpha\)-precipitates in a \(\beta\)-phase matrix obtained via a spinodal decomposition of the pre-existing \(\alpha''\). By extending aging time, a higher strength is reached at the expense of an undesirable increasing in elastic modulus.
- These findings might have far-reaching consequences by expanding the application range of \(\beta\)-stabilized Ti-alloys and by opening up new opportunities to improve their mechanical and functional behavior.

Acknowledgments

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References