

Original Research

A β -type TiNbZr alloy with low modulus and high strength for biomedical applications

Qingkun Meng^a, Shun Guo^{b,*}, Qing Liu^a, Liang Hu^a, Xinqing Zhao^{a,**}

^aSchool of Materials Science and Engineering, Beihang University, Beijing 100191, China

^bInstitute for Advanced Materials, Jiangsu University, Zhenjiang 212013, China

Received 7 October 2013; accepted 13 January 2014

Available online 19 April 2014

Abstract

The effect of thermo-mechanical treatment on the mechanical properties of a novel β -type Ti–36Nb–5Zr (wt%) alloy has been investigated. The solution treated alloy consists of β and α' phases and exhibits a two-stage yielding with a low yield stress (around 100 MPa). After cold rolling at a reduction of 87.5% and subsequent annealing treatment at 698 K for 25 min, a fine microstructure with nanosized α precipitates distributed in small β grains as well as high density of dislocations was obtained to achieve a yield strength of 720 MPa and a ultimate tensile strength of 860 MPa. In spite of the formation of α precipitates, the β -stabilizers are not enriched in the parent β matrix due to the short duration and low temperature of the thermal treatment, resulting in a low chemical stability of β phase. The low stability of β phase and the small volume fraction of α precipitates produce a low Young's modulus of 48 GPa. Such an excellent combination of low elastic modulus and high strength in mechanical properties indicates great potential for biomedical applications.

© 2014 Chinese Materials Research Society. Production and hosting by Elsevier B.V. All rights reserved.

Keywords: β -type Ti alloy; Ti–Nb–Zr; Chemical stabilization; Young's modulus; Biomedical

1. Introduction

Titanium and its alloys have become one of the most attractive biomaterials for implant applications due to their excellent biocompatibility, high corrosion resistance, light weight and low modulus [1,2]. Nevertheless, the conventional implant Ti materials, e.g. pure Ti and Ti–6Al–4V, exhibit substantially higher Young's modulus (~ 110 GPa) than that of a human bone (~ 30 GPa) [3,4]. Such a large modulus mismatch causes insufficient loading of the bone adjacent to the implant, which can lead to potential bone resorption and eventual failure of the

implant device due to “stress shielding” effect [5,6]. The motivation to develop lower modulus orthopedic Ti alloys has led to an increased focus on β -type alloys which retain a single-phase β microstructure on rapidly cooling from high-temperature β phase field, because the β -type alloys exhibit relatively low moduli as compared to those of α and ($\alpha + \beta$) Ti alloys [7–10].

As is well known, the moduli of β -type Ti alloys are closely related to their phase constitution and chemical composition [11,12]. Previous studies have also showed that the modulus of β phase decreases monotonically with decreasing content of β -stabilizing elements, and thus the lowest modulus can be obtained at the composition containing the least amount of β -stabilizing elements while keeping the single β phase [13,14]. However, if the content of β -stabilizers is insufficient, a stress-induced martensitic transformation from β phase to α' martensite will take place during deformation, resulting in a very low yield stress [15,16]. Recent researches indicate that in addition to increasing the content of β -stabilizers, the stress-induced martensitic transformation can be suppressed by microstructure control achieved by severe cold rolling and subsequent annealing treatments [17–19]. This suggests

*Corresponding author. Tel.: +86 511 88783268; fax: +86 511 88797783.

**Corresponding author. Tel.: +86 10 82338559; fax: +86 10 82338200.

E-mail addresses: shunguo@ujs.edu.cn (S. Guo),

xinqing@buaa.edu.cn (X. Zhao).

Peer review under responsibility of Chinese Materials Research Society.



that the β phase can be strengthened by proper thermo-mechanical treatment, instead of simply increasing the chemical stability of the β phase. Obviously, this is beneficial for developing β -type Ti alloys with low modulus.

In addition to low elastic modulus, Ti alloys used for implants should have high yield strength due to the complicate cyclic loading applied to the implants. However, β -type Ti alloys with low modulus usually possess lower yield strength than that of ($\alpha + \beta$) type Ti–6Al–4V alloy [20]. In order to enhance the yield strength of β -type Ti alloys, precipitation hardening is frequently employed through annealing treatment [4,21]. However, the stable α or metastable ω precipitation introduced by annealing treatment exhibits higher modulus than the β phase. Meanwhile, the precipitation of α or ω phase causes the enrichment of β -stabilizers in the residual β matrix, resulting in an increase in the modulus of the β phase [22–24]. In such a case, the conventional annealing treatment will lead to a significant increase in the modulus of Ti alloys, which is not suitable to achieve simultaneously both low Young's modulus and high strength. Therefore, it is important to develop a thermo-mechanical process to strengthen β -type alloys without sacrificing low Young's moduli.

Ti–Nb–Zr alloy system has been proved to be a good candidate for developing absolutely safe biomedical β -type Ti alloys, because Ti, Nb and Zr are non-toxic elements and thus can minimize adverse tissue reactions originating from the release of metal ions from the implant [25,26]. However, most of the present Ti–Nb–Zr alloys possess low yield stress less than 400 MPa due to stress-induced martensitic transformation [27,28]. On the other hand, the elastic moduli will increase to more than 80 GPa if the alloys are strengthened by precipitation hardening [29]. The mechanical properties of Ti–Nb–Zr alloys are yet to be further enhanced so as to achieve an optimal combination of high strength and low modulus.

In this paper, a novel β -type Ti–Nb–Zr alloy consisting only of nontoxic elements was fabricated through alloying and thermo-mechanical treatment, with the aim of achieving an excellent combination of high strength and low modulus. Also, the influence of microstructures and phase stability on the mechanical properties of Ti–Nb–Zr alloy was briefly discussed.

2. Experimental

The ternary Ti–36Nb–5Zr (wt%, all chemical compositions are denoted in weight percent hereafter) alloy was prepared by arc melting in an argon atmosphere using high purity Ti (99.99%), Nb (99.95%) and Zr (99.95%) as raw materials. The ingot was re-melted four times in order to ensure chemical homogeneity. The arc-melted ingot was first forged to billet with a cross-section of $8 \times 60 \text{ mm}^2$, and then homogenized at 1223 K for 5 h in vacuum, followed by quenching in water. The homogenized billet was cold rolled (CR) to a thickness of 1 mm at a reduction of 87.5%. Some CR specimens were solution treated (ST) at 1073 K for 1 h in an evacuated quartz tube, while the others were annealed (CRA) at 698 K for 25 min; both the ST and CRA specimens were quenched in water after the heat treatment.

Specimens for tensile test with a gage length of 30 mm and a cross section of $1 \times 1.46 \text{ mm}^2$ were spark cut along the rolling

direction. Tensile tests were conducted on an Instron 8801 machine at a strain rate of $1 \times 10^{-4} \text{ s}^{-1}$. To ensure the accuracy of Young's modulus, an extensometer with a gage length of 25 mm was used to measure the strain. Phase constitutions were determined by X-ray diffraction (XRD) with Cu $K\alpha$ radiation at an accelerating voltage of 40 kV and a current of 250 mA. The microstructural evolutions during thermo-mechanical treatments were characterized on a FEI Quanta 200F transmission electron microscope (TEM) operating at a voltage of 200 kV. Local chemical compositions were determined via scanning transmission electron microscopy (STEM) equipped with energy dispersive X-ray spectroscopy (EDS). TEM specimens were prepared by a twin-jet electro-polishing technique in a solution of 9% perchloric acid, 21% *n*-butyl alcohol and 70% methanol at about 243 K.

3. Results and discussion

Fig. 1 shows the XRD patterns of the solution treated, cold rolled and cold rolled plus annealed specimens. A dual ($\beta + \alpha'$) phase can be identified in the ST specimen, suggesting that the martensitic transformation start temperature (M_s) of the ST Ti–36Nb–5Zr alloy is above room temperature. After the cold rolling, the Ti–36Nb–5Zr alloy exhibits the same phase constitution as observed in the solution treated specimen, i.e. martensite and β phase. Interestingly, upon the following annealing at 698 K for 25 min, α' martensite completely transformed to β phase and does not form during the subsequent cooling, indicating that the M_s of the CRA specimen drops below room temperature. In addition, a small amount of α precipitates was observable in the annealed specimen, as evidenced by relatively weak α diffraction peaks. It is worth noting that the precipitation of few α phases does not lead to the shift of β diffraction peaks. This implies that the present annealing does not lead to significant repartition of β -stabilizers and the residual β phase still possesses relatively low chemical stability. Therefore, there exist some other factors rather

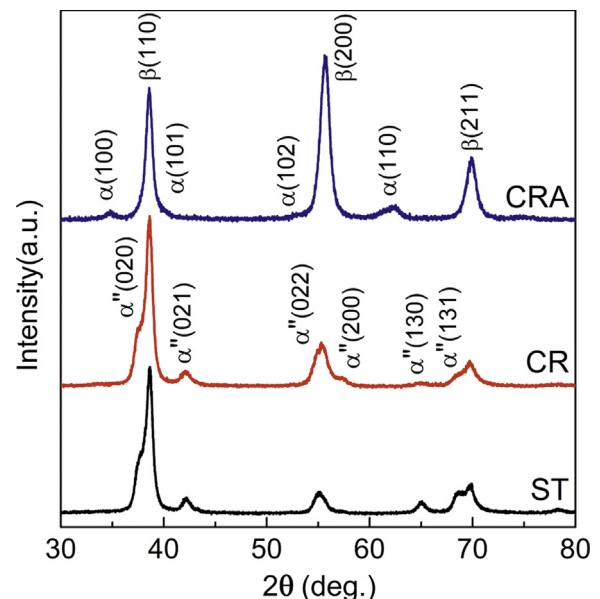


Fig. 1. XRD patterns of solution treated (ST), cold rolled (CR) and cold rolled plus annealed (CRA) Ti–36Nb–5Zr specimens.

than the enrichment of β -stabilizers in the parent β matrix contributing to the stabilization of β phase in the annealed specimen, which will be discussed later.

The TEM images of ST, CR and CRA specimens are shown in Fig. 2. The bright-field micrograph in Fig. 2(a) shows that the lath-shaped α'' martensite distributes within the β grains in the ST specimen. The presence of α'' martensite can be confirmed from the $[111]\beta$ zone axis selected area diffraction (SAD) pattern shown in Fig. 2(a), where the reflections near the $1/2\{112\}\beta$ positions are attributed to α'' phase. Upon severe cold rolling, numerous irregular dark areas caused by dislocation tangles are observed in the CR specimen, as shown in the bright-field image of CR specimen in Fig. 2(b). Fig. 2(b) also represents the SAD pattern of the CR specimen. It can be observed that the severe cold rolling does not exert a substantial effect on the phase constitution, and that the phase constitution of CR specimen is still β and α'' martensite phases. However, the SAD pattern of CR specimen exhibits near-continuous diffraction rings indicating that the cold rolling leads to significant grain refinement, irrespective of the β phase or martensite.

Fig. 2(c) shows the bright-field micrograph and the corresponding SAD pattern of the CRA specimen. Fine scale precipitates with

a width of several nanometers, marked by white arrows, are observed within β matrix. According to the SAD pattern shown in Fig. 2(c), the lath precipitates distributed within the β matrix are recognized to be of α phase. In addition, it can be clearly seen that numerous irregular dark areas caused by dislocation tangles still exist after annealing treatment, suggesting that the alloy is not completely recrystallized from the as-rolled state. From the SAD pattern, it is noticed that the process combining cold rolling and short-time annealing leads to a considerable reduction in the β grain size, as evidenced by the near-continuous diffraction rings. Easy deformation-induced grain refinement has been found in many β -type Ti alloys with low stability [30]. It is proposed that the martensitic transformation and the reversible transition from α'' martensite back to β phase play a significant role in grain refinement [31,32]. Referring to the present alloy, experimental results from the XRD and TEM have shown that the Ti-36Nb-5Zr alloy exhibits low β phase stability against martensitic transformation. Therefore, it is reasonable to conclude that the grain refinement in the annealed Ti-36Nb-5Zr specimen can be attributed to stress-induced martensitic transformation during cold rolling and its reverse transformation during subsequent annealing.

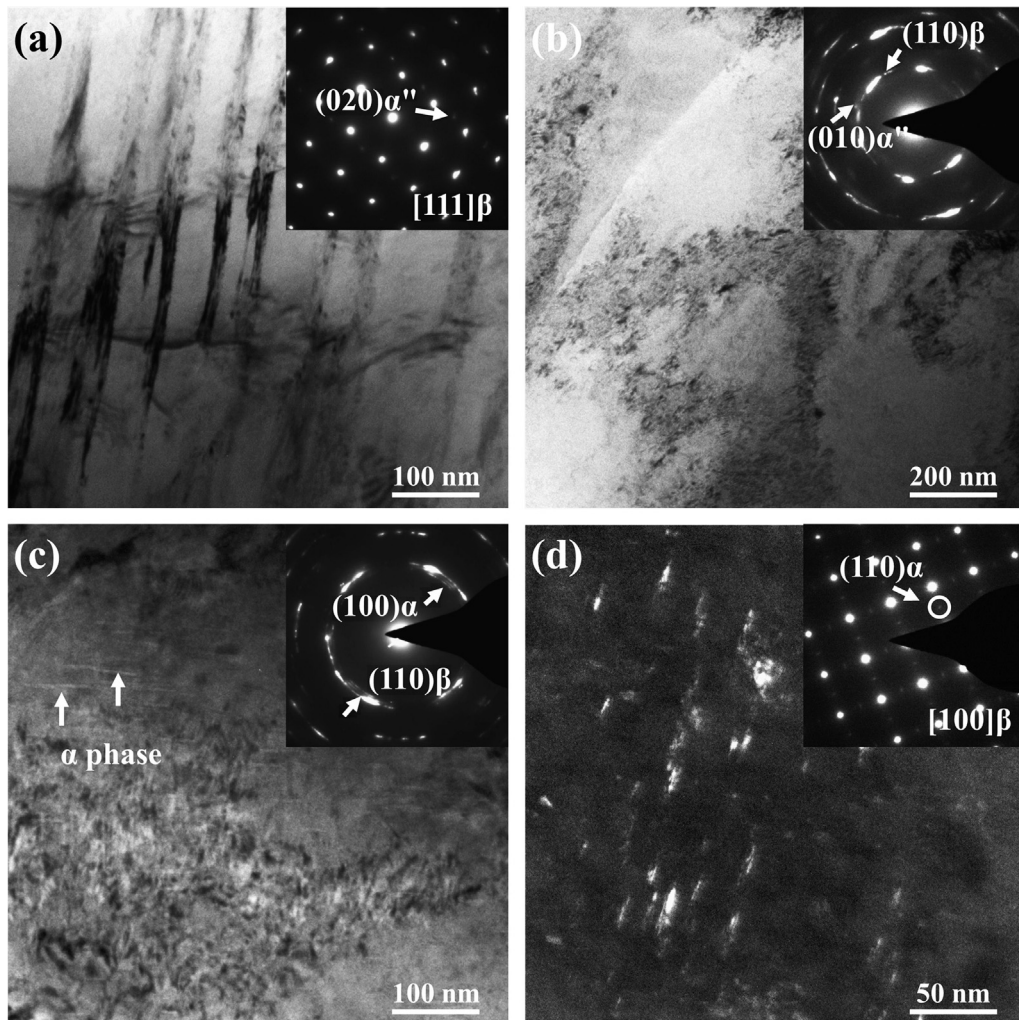


Fig. 2. Bright-field TEM micrographs of the solution treated (a), cold rolled (b) and cold rolled plus annealed (c) specimens and dark-field micrographs of the cold rolled plus annealed specimen. Inset: the corresponding SAD patterns.

Fig. 2(d) shows the dark-field micrograph using α reflection in the corresponding SAD pattern marked with a circle. The α phase exhibits lenticular morphology, about tens of nanometers in length and several nanometers in width. It is well known that α phase always preferentially nucleates at defects in β matrix, e.g. dislocations and grain boundaries [33]. As shown in Fig. 2(c), a large amount of dislocations and grain boundaries can be observed in the annealed specimen. These dislocations and grain boundaries provide sufficient heterogeneous nucleation sites for the α precipitation. On the other hand, the short-time annealing treatment hinders the coarsening of precipitates. In such a case, nanosized α phase can be obtained in the CRA specimen. Note that the α'' martensite is not observed in annealed specimen, as shown in Fig. 2(c) and (d), which agrees well with the corresponding XRD result. Previous investigations have suggested that martensitic transformation can be considerably affected by microstructures [17–19]. On the basis of the above TEM results, one can conclude that grain refinement, high density of dislocations and nanosized α precipitates play a key role in suppressing martensitic transformation of the CRA specimen.

The tensile stress–strain curves of ST, CR and CRA specimens are shown in Fig. 3. The ST specimen exhibits a remarkable

two-stage yielding, which is the typical deformation characteristic of metastable β -type Ti alloys, as shown in Fig. 3(a). The first yielding is related to the induction of martensite and the rearrangement of martensite variants, and the second yielding to the initiation of permanent plastic deformation.

Upon cold rolling at a reduction of 87.5%, the ultimate tensile strength increases significantly from 480 MPa to 662 MPa, as shown in Fig. 3(b). The remarkable strengthening of the alloy can be attributed to the interaction between fine α'' martensite and dislocation tangles introduced by cold rolling deformation, as evidenced in Fig. 2(b). Interestingly, the CR specimen exhibits nonlinear elasticity with an incipient Young's modulus of 40 GPa. Our previous studies suggest that this peculiar deformation behavior originates from the stress-induced martensitic transformation and/or the reorientation of martensite variants due to an initial dual ($\beta + \alpha''$) microstructure in the CR alloy (see Fig. 1) [34]. In addition, it can be observed from Fig. 2(b) that cold rolling leads to a considerable decrease in modulus as compared with that of the ST specimen (56 GPa), which is attributable to the formation of $(200)_{\alpha''}[010]_{\alpha''}$ texture and the crystallography anisotropy of α'' phase [35]. Although the CR specimen exhibits a low Young's modulus of 40 GPa, it is not a good candidate for biomedical applications, because the alloy possesses a low yield strength (flow stress at 0.2% plastic strain) of 413 MPa due to the nonlinear deformation behavior.

In comparison to nonlinear deformation of the CR specimen, the tensile stress–strain curve of the CRA specimen shown in Fig. 3(b) indicates that the annealed specimen shows a linear elastic deformation behavior. This suggests that the β phase in CRA specimens is fully stabilized and no stress-induced martensitic transformation takes place on tensile loading. As mentioned above, this can be attributed to the inhibitory effect of grain refinement, high density of dislocations and nanosized α precipitates on the martensitic transformation. The tensile test of the annealed specimen also indicates that upon this annealing treatment, the Ti–36Nb–5Zr alloy is significantly strengthened, with an ultimate tensile strength of 860 MPa which is comparable to the widely used Ti–6Al–4V ELI alloy. Combining with the microstructural observation shown in Fig. 2, it is reasonable to conclude that the precipitation of nanosized α phase as well as the dislocations plays a crucial role in the strengthening of the alloy. The fine α precipitates could pin the dislocations and obstruct the dislocation motion, resulting in high ultimate tensile strength of the CRA specimen. In spite of significant improvement in strength, the alloy still retained a relatively low modulus of 48 GPa after the annealing treatment.

Generally, Young's modulus of a two-phase alloy is determined by the volume fraction and moduli of the individual phase [36]. It has been well accepted that α phase exhibits a higher modulus than that of β phase [37]. For example, Bowen reported that Young's modulus of α phase is two times as high as that of β phase [38]. From Fig. 2(c) and (d), it can be seen that the volume fraction of α phase is very low in the CRA specimen. Thus, the contribution of α precipitation to the modulus of the annealed alloy is quite limited. In such a case, one has the reason to believe that the low modulus of the CRA

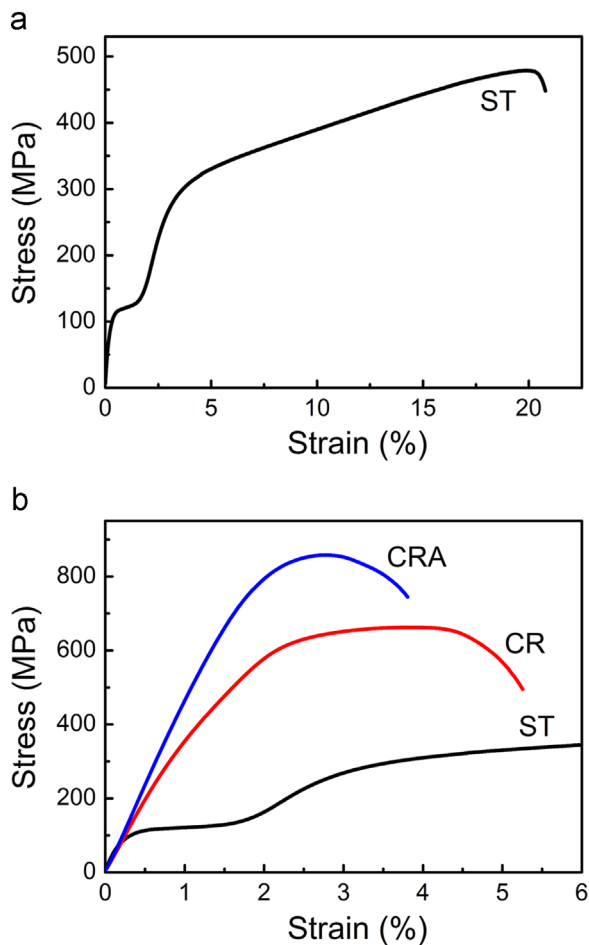


Fig. 3. Tensile stress–strain curves of specimens (a) after solution treatment, (b) after cold rolling and after cold rolling plus annealing. The stress–strain curve from 0% to 6% of the solution treated specimen is also shown in (b) for reference.

specimen is mainly attributed to the low intrinsic modulus value of β phase.

In order to clarify the origin of low modulus in β phase, the compositional partitioning between α precipitates and β matrix on the CRA specimen was determined using EDS analysis. Fig. 4 shows the compositional maps for Ti, Nb and Zr elements across a square of $200 \times 200 \text{ nm}^2$ consisting of β and α phases (shown in the bright field micrograph in the same figure). In the EDS profile (Fig. 4(b), (c) and (d)), no detectable compositional change is observed across the square area shown in Fig. 4(a), which means that the partitioning of alloying elements between the two phases is subtle. It has been proposed that in the early stages of nucleation and growth, α precipitates exhibit a composition far from equilibrium, nearly identical to that of the parent β matrix [39,40]. Clearly, the similar situation occurred in the short-time annealed Ti–36Nb–5Zr alloy. It is concluded that the diffusion of β -stabilizing elements is limited due to the short annealing time and relatively low annealing temperature.

It is widely accepted that Young's modulus of β phase increases monotonically with increasing content of β -stabilizing

element in β -type Ti alloy [11]. During conventional annealing treatment, large amount of α phase precipitates and thus causes the enrichment of β -stabilizers in the residual β matrix. As a result, Young's modulus of the annealed alloy increases due to both the improvement of the intrinsic modulus of β phase caused by chemical stabilization and the precipitation of α phase with high Young's modulus. By contrast, upon the present thermo-mechanical treatment the β phase still possesses low content of β -stabilizers, giving rise to low intrinsic elastic modulus of β matrix. In addition, the volume fraction of α precipitates formed in short time annealing was much lower than that formed in conventional annealing due to the limitation on the annealing temperature and time. Accordingly, both the low intrinsic modulus of β matrix and the small volume fraction of α precipitates lead to the low elastic modulus, $\sim 48 \text{ GPa}$, of short-time annealed Ti–36Nb–5Zr alloy. Meanwhile, the nanosized α phase as well as the high density of dislocations plays a key role in strengthening the annealed alloy. As a result, the CRA Ti–36Nb–5Zr alloy can exhibit an excellent combination of high strength and low Young's modulus.

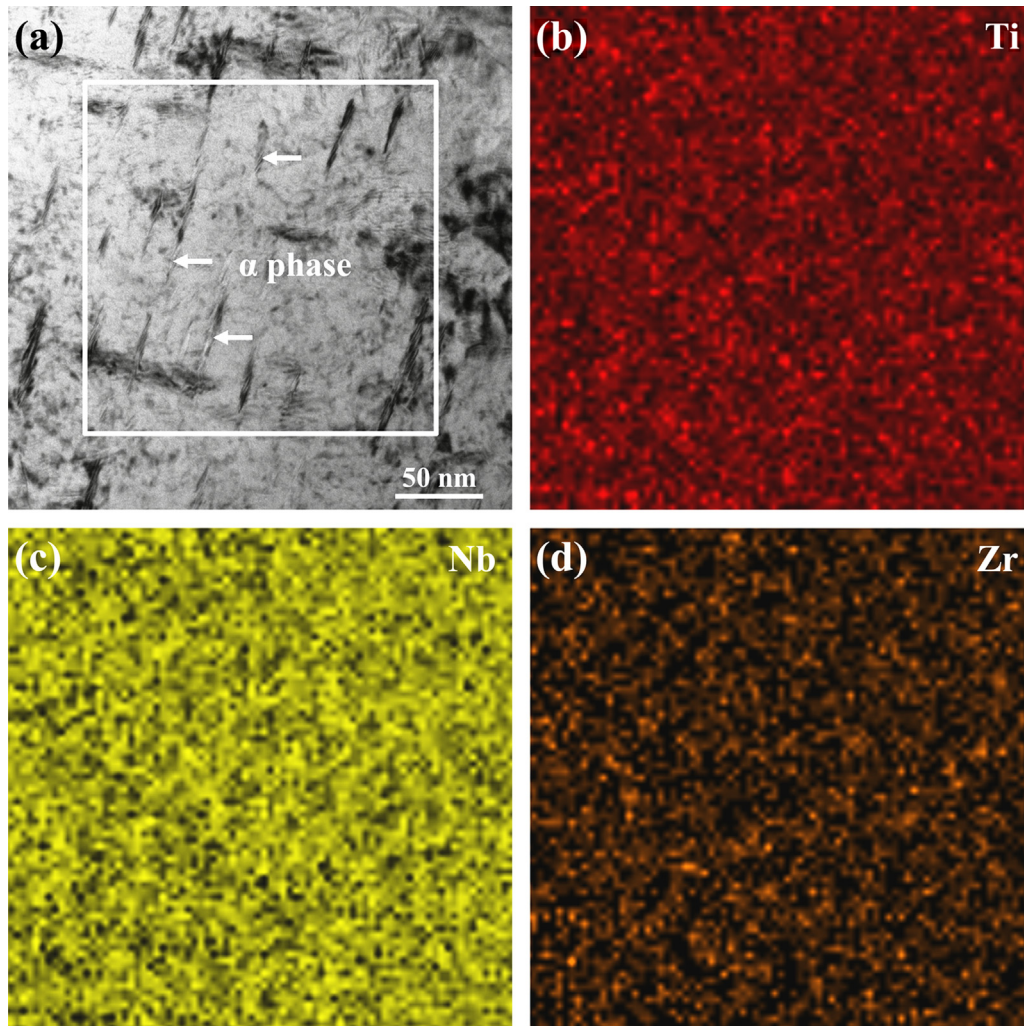


Fig. 4. Bright-field micrograph of the cold rolled plus annealed specimen (a) and the corresponding compositional maps for Ti (b), Nb (c) and Zr (d) elements across a square of $200 \times 200 \text{ nm}^2$ shown in (a).

4. Conclusions

A β -type Ti–36Nb–5Zr (wt%) alloy with low Young's modulus and high strength was developed for biomedical applications and the microstructure evolution and its influence on mechanical properties were investigated after cold rolling and subsequent annealing treatment. The results can be summarized as follows.

- (1) The solution treated specimen is composed of β and α'' phases, which means that the Ms is above room temperature. After cold rolling and subsequent annealing treatment, α'' martensites completely transformed to β phase and a small amount of α phase precipitated. The decrease of Ms is due to the microstructure changes rather than the chemical stabilization of the residual β matrix.
- (2) The cold rolled specimen exhibits peculiar nonlinear elasticity originating from the induction of martensite and/or the rearrangement of martensite variants upon loading. However, it changes to normal linear elastic deformation behavior after annealing treatment due to the strengthening of the β phase.
- (3) High density of dislocations and nanosized α precipitates were introduced by the cold rolling plus annealing treatment and this results in high yield strength and ultimate tensile strength of the alloy. Meanwhile, the solute partitioning was neglectable and the low chemical stability of β phase retained after annealing treatment, guaranteeing low elastic modulus of the short-time annealed specimen.
- (4) The present Ti–Nb–Zr alloy consisting only of nontoxic elements and exhibiting an excellent combination of high strength (860 MPa) and low Young's modulus (48 GPa) is expected to be a desirable candidate material for biomedical applications.

Prime novelty statement

- A novel β -type Ti–36Nb–5Zr (wt%) alloy with an excellent combination of low elastic modulus (48 GPa) and high ultimate tensile strength (860 MPa) was fabricated through alloying and thermo-mechanical treatment.
- The high density of dislocations and nanosized α precipitates were introduced by the cold rolling plus annealing treatment and this resulted in high yield strength and ultimate tensile strength of the alloy.
- In spite of the formation of α precipitates, the β -stabilizers are not enriched in the parent β matrix due to the short duration and low temperature of the thermal treatment, leading to the low chemical stability of β phase.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant no. 51271010 and 51221163) and the National Basic Research Program of China (Grant no. 2012CB619403).

References

- [1] M. Long, H.J. Rack, *Biomaterials* 19 (1998) 1621–1639.
- [2] M. Geetha, A.K. Singh, R. Asokamani, A.K. Gogia, *Prog. Mater. Sci.* 54 (2009) 397–425.
- [3] J.-Y. Rho, T.Y. Tsui, G.M. Pharr, *Biomaterials* 18 (1997) 1325–1330.
- [4] M. Niinomi, *Mater. Sci. Eng. A* 243 (1998) 231–236.
- [5] H.J. Rack, J.I. Qazi, *Mater. Sci. Eng. C* 26 (2006) 1269–1277.
- [6] M. Niinomi, M. Nakai, J. Hieda, *Acta Biomater.* 8 (2012) 3888–3903.
- [7] Y.L. Hao, R. Yang, M. Niinomi, D. Kuroda, Y.L. Zhou, K. Fukunaga, A. Suzuki, *Metall. Mater. Trans. A* 34 (2003) 1007–1012.
- [8] D. Kuroda, M. Niinomi, M. Morinaga, Y. Kato, T. Yashiro, *Mater. Sci. Eng. A* 243 (1998) 244–249.
- [9] T. Saito, T. Furuta, J.-H. Hwang, S. Kuramoto, K. Nishino, N. Suzuki, R. Chen, A. Yamada, K. Ito, Y. Seno, T. Nonaka, H. Ikehata, N. Nagasako, C. Iwamoto, Y. Ikuhara, T. Sakuma, *Science* 300 (2003) 464–467.
- [10] Y.L. Hao, S.J. Li, S.Y. Sun, C.Y. Zheng, Q.M. Hu, R. Yang, *Appl. Phys. Lett.* 87 (2005) 091906-1–091906-3.
- [11] M. Abdel-Hady, K. Hinoshita, M. Morinaga, *Scr. Mater.* 55 (2006) 477–480.
- [12] M. Tane, S. Akita, T. Nakano, K. Hagihara, Y. Umakoshi, M. Niinomi, H. Nakajima, *Acta Mater.* 56 (2008) 2856–2863.
- [13] P. Laheurte, F. Prima, A. Eberhardt, T. Gloriant, M. Wary, E. Patoor, *J. Mech. Behav. Biomed. Mater.* 3 (2010) 565–573.
- [14] T.-K. Jung, S. Semboshi, N. Masahashi, S. Hanada, *Mater. Sci. Eng. C* 33 (2013) 1629–1635.
- [15] Y.L. Hao, S.J. Li, S.Y. Sun, R. Yang, *Mater. Sci. Eng. A* 441 (2006) 112–118.
- [16] D.C. Zhang, S. Yang, M. Wei, Y.F. Mao, C.G. Tan, J.G. Lin, *J. Mech. Behav. Biomed. Mater.* 13 (2012) 156–165.
- [17] Y.L. Hao, R. Yang, M. Niinomi, D. Kuroda, Y.L. Zhou, K. Fukunaga, A. Suzuki, *Metall. Mater. Trans. A* 33 (2002) 3137–3144.
- [18] H. Matsumoto, S. Watanabe, S. Hanada, *Mater. Trans.* 46 (2005) 1070–1078.
- [19] M.-H. Cai, C.-Y. Lee, Y.-K. Lee, *Scr. Mater.* 66 (2012) 606–609.
- [20] M. Abdel-Hady Gepreel, M. Niinomi, *J. Mech. Behav. Biomed. Mater.* 20 (2013) 407–415.
- [21] M. Niinomi, *Biomaterials* 24 (2003) 2673–2683.
- [22] H.Y. Kim, Y. Ikehara, J.I. Kim, H. Hosoda, S. Miyazaki, *Acta Mater.* 54 (2006) 2419–2429.
- [23] Y.L. Hao, S.J. Li, S.Y. Sun, C.Y. Zheng, R. Yang, *Acta Biomater.* 3 (2007) 277–286.
- [24] S.L. Raghunathan, A.M. Stapleton, R.J. Dashwood, M. Jackson, D. Dye, *Acta Mater.* 55 (2007) 6861–6872.
- [25] J.I. Kim, H.Y. Kim, T. Inamura, H. Hosoda, S. Miyazaki, *Mater. Sci. Eng. A* 403 (2005) 334–339.
- [26] L. You, X. Song, *Scr. Mater.* 67 (2012) 57–60.
- [27] F. Sun, S. Nowak, T. Gloriant, P. Laheurte, A. Eberhardt, F. Prima, *Scr. Mater.* 63 (2010) 1053–1056.
- [28] J. Zhang, F. Sun, Y. Hao, N. Gozdecki, E. Lebrun, P. Vermaut, R. Portier, T. Gloriant, P. Laheurte, F. Prima, *Mater. Sci. Eng. A* 563 (2013) 78–85.
- [29] Q. Li, M. Niinomi, M. Nakai, Z. Cui, S. Zhu, X. Yang, *Mater. Sci. Eng. A* 536 (2012) 197–206.
- [30] W. Xu, K.B. Kim, J. Das, M. Calin, B. Rellinghaus, J. Eckert, *Appl. Phys. Lett.* 89 (2006) 031906-1–031906-3.
- [31] W. Xu, X. Wu, M. Calin, M. Stoica, J. Eckert, K. Xia, *Scr. Mater.* 60 (2009) 1012–1015.
- [32] M.-H. Cai, C.-Y. Lee, S. Kang, Y.-K. Lee, *Scr. Mater.* 64 (2011) 1098–1101.
- [33] S. Guo, Q. Meng, L. Hu, G. Liao, X. Zhao, H. Xu, *J. Alloys Compd.* 550 (2013) 35–38.
- [34] S. Guo, Z. Bao, Q. Meng, L. Hu, X. Zhao, *Metall. Mater. Trans. A* 43 (2012) 3447–3451.
- [35] H. Matsumoto, S. Watanabe, S. Hanada, *J. Alloys Compd.* 439 (2007) 146–155.
- [36] J. Llorca, M. Elices, Y. Termonia, *Acta Mater.* 48 (2000) 4589–4597.
- [37] Z. Fan, *Scr. Metall. Mater.* 29 (1993) 1427–1432.
- [38] A.W. Bowen, *Scr. Met.* 5 (1971) 709–715.
- [39] O.M. Ivasishin, P.E. Markovsky, S.L. Semiatin, C.H. Ward, *Mater. Sci. Eng. A* 405 (2005) 296–305.
- [40] S. Nag, R. Banerjee, R. Srinivasan, J.Y. Hwang, M. Harper, H.L. Fraser, *Acta Mater.* 57 (2009) 2136–2147.