

Crystal Structure, Transformation Strain, and Superelastic Property of Ti–Nb–Zr and Ti–Nb–Ta Alloys

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Abstract The composition dependences of transformation strain and shape memory, and superelastic properties were extensively investigated in Ti–Nb–Zr and Ti–Nb–Ta alloys in order to establish the guidelines for alloy design of biomedical superelastic alloys. The effects of composition on the crystal structure of the parent (β) phase and the martensite (α'') phase were also investigated. Results showed that not only transformation temperature but also transformation strain is tunable by alloy design, i.e., adjusting contents of Nb, Zr, and Ta. The lattice constant of the β phase increased linearly with increasing Zr content, while it was insensitive to Nb and Ta contents. On the other hand, the lattice constants of the α'' phase are mainly affected by Nb and Ta contents. The increase of Zr content exhibited a weaker impact on the transformation strain compared with Nb and Ta. The addition of Zr as a substitute of Nb with keeping superelasticity at room temperature significantly increased the transformation strain. On the other hand, the addition of Ta decreased the transformation strain at the compositions showing superelasticity. This study confirmed that the crystallography of

martensitic transformation can be the main principal to guide the alloy design of biomedical superelastic alloys.

Keywords Mechanical behavior · Superelasticity · Stress-induced martensitic transformation

Introduction

Over the past decade, Ti–Nb-base alloys have been extensively studied as promising candidates for Ni-free biomedical shape memory alloys, and many alloys have been reported to exhibit superelasticity at room temperature [1–14]. For the binary Ti–Nb alloys, superelastic recovery was observed when the Nb content is 26–27 at.% [4]; however, the recovery strain was as small as about 3 % even including elastic strain, which is quite smaller than those of practical Ti–Ni superelastic alloys [15]. The small recovery strain in the Ti–(26–27)Nb alloys is due to the small lattice distortion strain upon stress-induced martensitic transformation from the parent (β) phase to the martensite (α'') phase as well as the low critical stress for slip [4]. Extensive research has shown that the superelastic properties can be improved through microstructure control such as low temperature annealing and aging [4, 16–18].

Alloying is another effective way for improving superelastic properties. Among many alloying elements, Zr and Ta have attracted considerable attention due to their superior biocompatibility [19]. Many kinds of ternary and multinary alloys including Zr and/or Ta have been developed up to date, e.g., Ti–Nb–Ta [20–25], Ti–Nb–Zr [16, 18, 22, 24, 26–31], Ti–Nb–Ta–Zr [17, 32, 33], Ti–Nb–Zr–Sn [34–38], Ti–Nb–Zr–Al [39], and Ti–Nb–Zr–Mo–Sn [40]. Although substantial advances have been made in developing biomedical superelastic alloys, the understanding on the

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martensitic transformation behavior of Ti–Nb–base alloys is not sufficient yet. Particularly there is limited information regarding the effect of alloying element on the crystal structures of the β and α'' phases although they determine the transformation strain.

In this study, the effects of composition on the shape memory and superelastic properties of the Ti–Nb–Zr and Ti–Nb–Ta ternary alloys were extensively investigated. The composition dependence of lattice constants of the β and α'' phases were also investigated for Ti–Nb–Zr and Ti–Nb–Ta ternary alloys in order to clarify the effects of Zr and Ta on the transformation strain and to establish the design strategy for biomedical superelastic alloys.

Experimental Procedure

Various compositions of Ti–Nb–Zr alloys and Ti–Nb–Ta alloys were prepared using the Ar-arc melting method. The ingots were melted at least six times and flipped over after each melting in order to maximize the homogeneity. The weight change during melting was less than 0.04 %. The ingots were sealed into quartz tubes under vacuum and homogenized at 1273 K for 7.2 ks, and then cold rolled with a final reduction ratio of about 98.5 %. Specimens for tensile tests and X-ray diffraction (XRD) measurements were cut using an electro-discharge machine. The slightly oxidized surface was removed using a solution containing H₂O, HNO₃, and HF (5:4:1) at room temperature. Then the specimens were encapsulated into quartz tubes in an Ar atmosphere and solution treated at 1173 K for 1.8 ks, and then quenched into water. Shape memory and superelastic properties were characterized by a tensile testing machine. Tensile tests were carried out at a nominal strain rate of 0.005 mm/s at room temperature. The dimensions of the tensile specimens were 40 mm in length and 1.5 mm in width. Both ends of test samples were gripped through chucks so that gage length was 20 mm. Phase constitutions and their lattice constants were determined by XRD with Cu K α radiation at room temperature. It is noted that the superelastic properties and lattice constants of the β phase and α'' phase of Ti–Nb–base alloys do not change noticeably in the temperature range 293–310 K [17, 26, 41], and this allows the modeling of superelastic properties at body temperature using room temperature testing condition.

Results and Discussion

Shape Memory Effect and Superelasticity in Ti–Nb–Zr and Ti–Nb–Ta Alloys

The shape memory effect and superelasticity of Ti–Nb–Zr and Ti–Nb–Ta alloys were investigated by loading–

unloading tensile tests at room temperature. The results for selected alloys, i.e., Ti–(24–28)Nb, Ti–(15–19)Nb–12Zr, Ti–(12–16)Nb–18Zr, and Ti–(9–13)Nb–24Zr, are shown in Fig. 1. The tensile stress was applied until the strain reached about 2.5 %, and then the stress was removed. After unloading, specimens were heated up to about 500 K to investigate the shape memory effect. For the binary alloys, the shape memory effect was observed in Ti–24Nb and Ti–25 Nb alloys, while superelasticity was observed in Ti–26Nb and Ti–27Nb alloys, which is consistent with previous reports [2]. The remained strain after unloading in the Ti–26Nb and Ti–27Nb alloys was recovered by heating. For the Ti–Nb–12Zr alloys, the shape memory effect was observed when the Nb content is 15 and 16 at.% and superelasticity was observed when Nb content is 17 and 18 at.%. The properties of Ti–Nb–18Zr and Ti–Nb–24Zr alloys exhibited a similar Nb dependence to Ti–Nb and Ti–Nb–12Zr alloys: the alloys with a lower Nb content exhibited shape memory effect and the increase of Nb content caused the alloys to exhibit superelasticity. It should be mentioned that the Nb content showing superelasticity decreased with increasing Zr content, implying that the addition of Zr decreased martensitic transformation temperatures. The results of tensile tests for Ti–Nb–Zr ternary alloys with various Nb and Zr contents are summarized in Fig. 2. The compositions showing superelasticity and shape memory effect are marked by a solid circle and an open circle, respectively. Neither superelasticity nor shape memory effect was observed at room temperature in the compositions marked by up and down triangles. It is very clear that the superelasticity can be achieved over a wide composition range of Ti–Nb–Zr ternary alloys by adjustment of Nb and Zr contents.

Similar tensile tests were carried out for Ti–Nb–Ta alloys. Figure 3 shows the stress–strain curves of Ti–(14–20)Nb–10Ta, Ti–(8–14)Nb–20Ta, and Ti–(1–6)Nb–30Ta alloys. In case of the alloys containing 10 at.% Ta, superelasticity was observed in Ti–(19–20)Nb–10Ta. In case of the alloys containing 20 at.% Ta, partial superelastic recovery was observed in Ti–(12,13)Nb–20Ta alloys. It is noticed that the superelasticity was rarely observed in the alloys containing 30 at.% Ta although shape memory effect was observed. The results of tensile tests for Ti–Nb–Ta ternary alloys with various Nb and Ta contents are summarized in Fig. 4. From Fig. 4, it is evident that Ta has a weaker impact in decreasing the martensitic transformation temperature when compared with Nb. In the binary Ti–Nb alloys, it has been reported that the martensitic transformation temperature decreases by about 40 K with 1 at.% increase of Nb content [2]. By considering the effect of Nb on the martensitic transformation temperature of the Ti–Nb binary alloys, the reduction of the martensitic transformation temperature by the addition of 1 at.% Ta is

Fig. 1 Loading–unloading tensile test results of Ti–Nb–Zr alloys

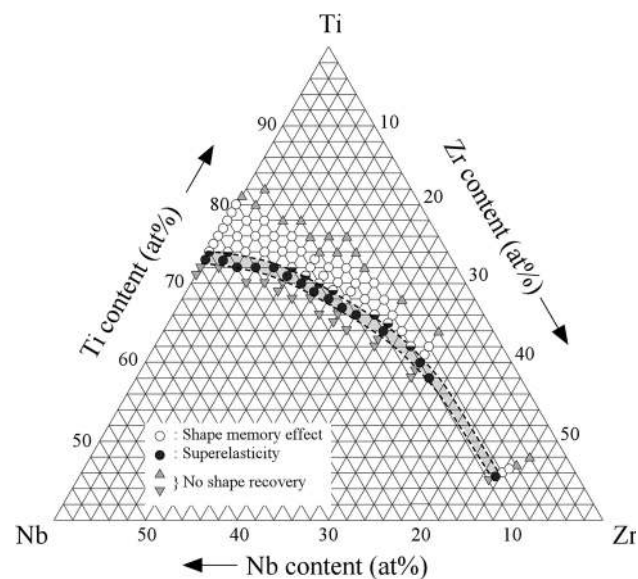
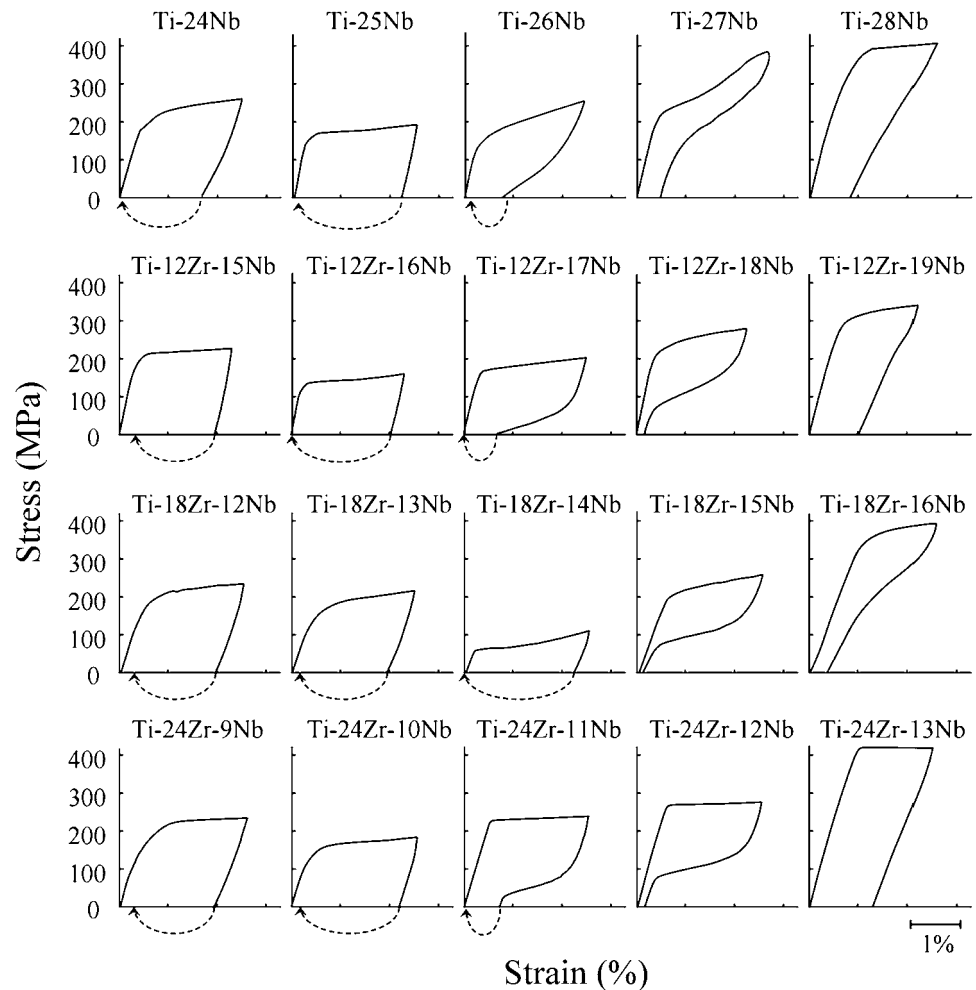


Fig. 2 Composition dependence of shape memory effect and superelasticity for Ti–Nb–Zr alloys

estimated to be 30 K [20]. It is also noted that the composition range showing superelasticity is narrower than that in the Ti–Nb–Zr alloys: the alloys with a higher Ta content exhibited only partial superelastic recovery.

Effect of Composition on Lattice Constants

In order to explore the effect of composition on the transformation strain of the β – α' phase transformation, the lattice constants were evaluated using XRD measurements for Ti–Nb–Zr and Ti–Nb–Ta ternary alloys. Typical examples of the XRD profile are shown in Fig. 5 where the peaks corresponding to Si were obtained from standard sample powders. Figure 6a shows the Nb dependence of the lattice constant a_0 of the β phase for Ti–Nb, Ti–Nb–6Zr, Ti–Nb–12Zr, Ti–Nb–18Zr, Ti–Nb–24Zr, and Ti–Nb–30Zr alloys. The plot shows that the Zr concentration strongly affects the lattice constant a_0 of the β phase, while the effect of Nb content on a_0 is very small. The Zr content dependence of a_0 of the β phase is plotted with respect to

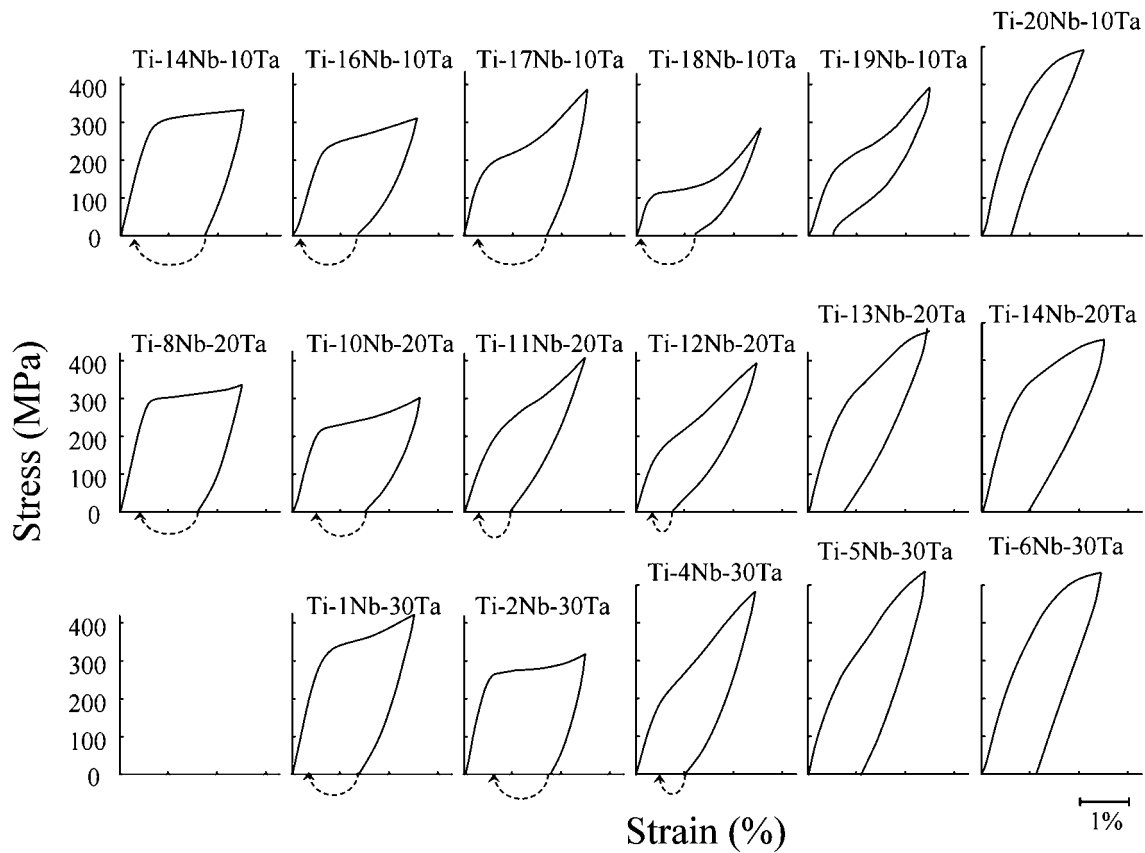


Fig. 3 Loading–unloading tensile test results of Ti–Nb–Ta alloys

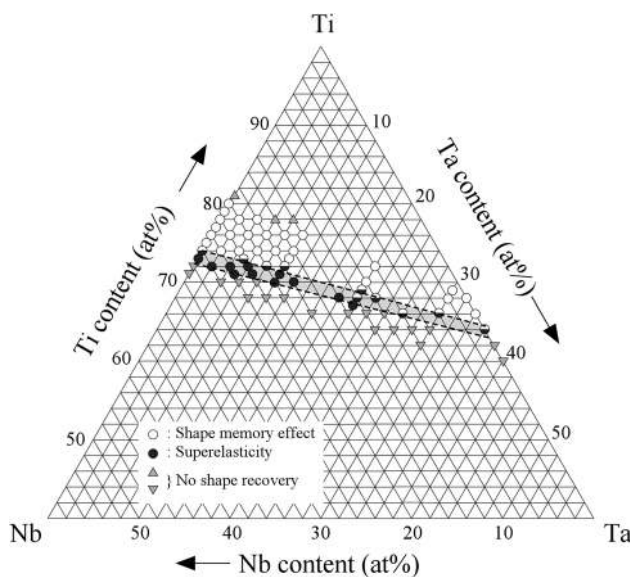


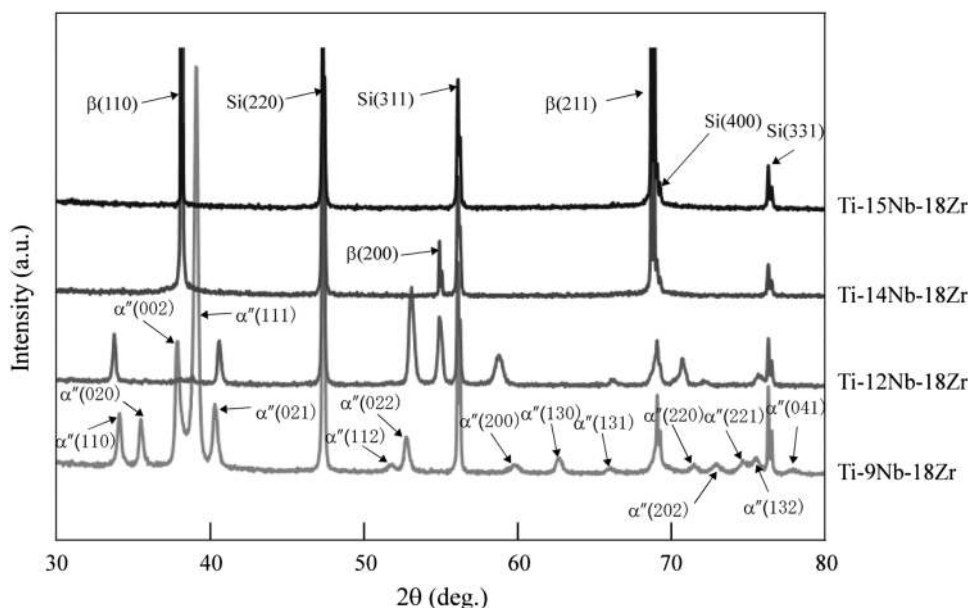
Fig. 4 Composition dependence of shape memory effect and superelasticity for Ti–Nb–Ta alloys

Zr content for Ti–Nb–Zr alloys in Fig. 6b. It is clearly seen that a_0 of the β phase increases linearly with increasing Zr content of the alloys. This is reasonable considering the

fact that the atomic sizes of Ti and Nb atoms are similar to each other and the atomic size of Zr is larger than those of Ti and Nb [42]. Contrary to the lattice constant of the β phase, the lattice constants a' , b' , and c' of the α'' orthorhombic martensite phase are mainly affected by the Nb content of the alloys as shown in Fig. 6c. Note that the scale of the vertical axis in Fig. 6c is 10 times larger than those in Fig. 6a and b. It is seen that a' increases but b' decreases with increasing Nb content. The change of c' is relatively small when compared with those of a' and b' .

The lattice constants were also measured for Ti–Nb–Ta alloys with various compositions and the results are shown in Fig. 7. Figure 7 shows the Nb dependence of the lattice constant a_0 of the β phase and the lattice constants a' , b' , and c' of the α'' phase for Ti–Nb, Ti–Nb–10Ta, Ti–Nb–20Ta, and Ti–Nb–30Ta alloys. It is seen from Fig. 7a that the lattice constant a_0 of the β phase is insensitive to not only Nb content but also to Ta content, which is due to the fact that the atomic size of Ta is very close to those of Ti and Nb [42]. On the other hand, the lattice constants of the α'' phase show a relatively strong Nb content dependence: a' increases but b' decreases with increasing Nb content with a similar slope for the Ti–Nb, Ti–Nb–10Ta, Ti–Nb–20Ta, and Ti–Nb–30Ta alloys as shown in Fig. 7(b). It is

Fig. 5 XRD profiles of Ti–Nb–18Zr alloys obtained at room temperature



also seen that the increase in Ta content causes the similar effect on the lattice constants as that in Nb: *a'* increases but *b'* decreases with increasing Ta content in the alloys with same Nb content. The lattice constants of the α' phase are plotted with respect to total amount of Nb and Ta in Fig. 7c. It is seen that the lattice constants change almost linearly with increasing total amount of Nb and Ta. From the results of Figs. 6 and 7, it is concluded that the lattice constants of the α' martensite phase for both Ti–Nb–Ta and Ti–Nb–Zr alloys are mainly governed by the total amount of β stabilizing elements of the alloy, whereas the lattice constant of the β phase is strongly affected by the amount of Zr but not by the amount of Nb and Ta.

Effect of Composition on Transformation Strain

As shown in Fig. 8, the lattice correspondence between the β(bcc) and α'(orthorhombic) phases are expressed as follows:

$$[100]_{\alpha'} - [100]_{\beta}, \quad [010]_{\alpha'} - [011]_{\beta}, \quad [001]_{\alpha'} - [0\bar{1}1]_{\beta}.$$

Therefore, the lattice deformation strains along the three principal axes of the orthorhombic crystal can be calculated using the lattice constants of the β parent and α' martensite phases as follows:

$$\eta_1 = \frac{a' - a_0}{a_0}, \quad \eta_2 = \frac{b' - \sqrt{2}a_0}{\sqrt{2}a_0}, \quad \eta_3 = \frac{c' - \sqrt{2}a_0}{\sqrt{2}a_0}$$

Figure 9a and b shows the Nb dependence of η₁, η₂ and η₃ for Ti–Nb–Zr and Ti–Nb–Ta alloys, respectively. It is seen from Fig. 9a that η₁ and η₂ are of similar magnitudes

but opposite signs, and their absolute values decrease as the Nb content increases for the Ti–Nb–Zr alloys irrespective of Zr content. The change of η₃ is very small but slightly decreases with increasing Nb content (ranging from 0.008 to –0.003) for all Ti–Nb–Zr alloys investigated. A small amount of η₃ implies that lattice invariant shear (LIS) associated with the β to α' martensitic transformation is not required. For Ti–Nb binary alloys, η₃ is zero when Nb content is 20 at.% [4] and it has been confirmed that non-twinned martensites are formed in the Ti–20 at.% Nb alloy. As shown in Fig. 9b, the Nb content dependence of the lattice deformation strain looks similar for the Ti–Nb–Ta alloys with a fixed Ta content. It is also clear that the increase in Ta content caused similar changes in the lattice deformation strains but the effect of Zr on the lattice strains is substantially smaller than that of Nb or Ta since the lattice constants of the α' phase is less sensitive to the Zr content of the alloys as shown in Fig. 6c.

The transformation strain was calculated as a function of crystal orientation for the Ti–Nb–Ta alloys and Ti–Nb–Zr alloys using the lattice correspondence between β and α' phases and their lattice constants mentioned above. For example, the calculated results for Ti–10Nb, Ti–10Nb–20Ta, and Ti–10Nb–20Zr alloys are shown in Fig. 10 to compare the effects of Zr and Ta on the transformation strain. A detailed description of the calculation method for the transformation strain has been reported in previous papers [4, 22]. The orientation dependence of transformation strain is expressed by contour lines in a [001] – [011] – [1̄11] standard stereographic triangle. In all three alloys, although the amount of transformation strain is different, the dependence of the transformation strain on

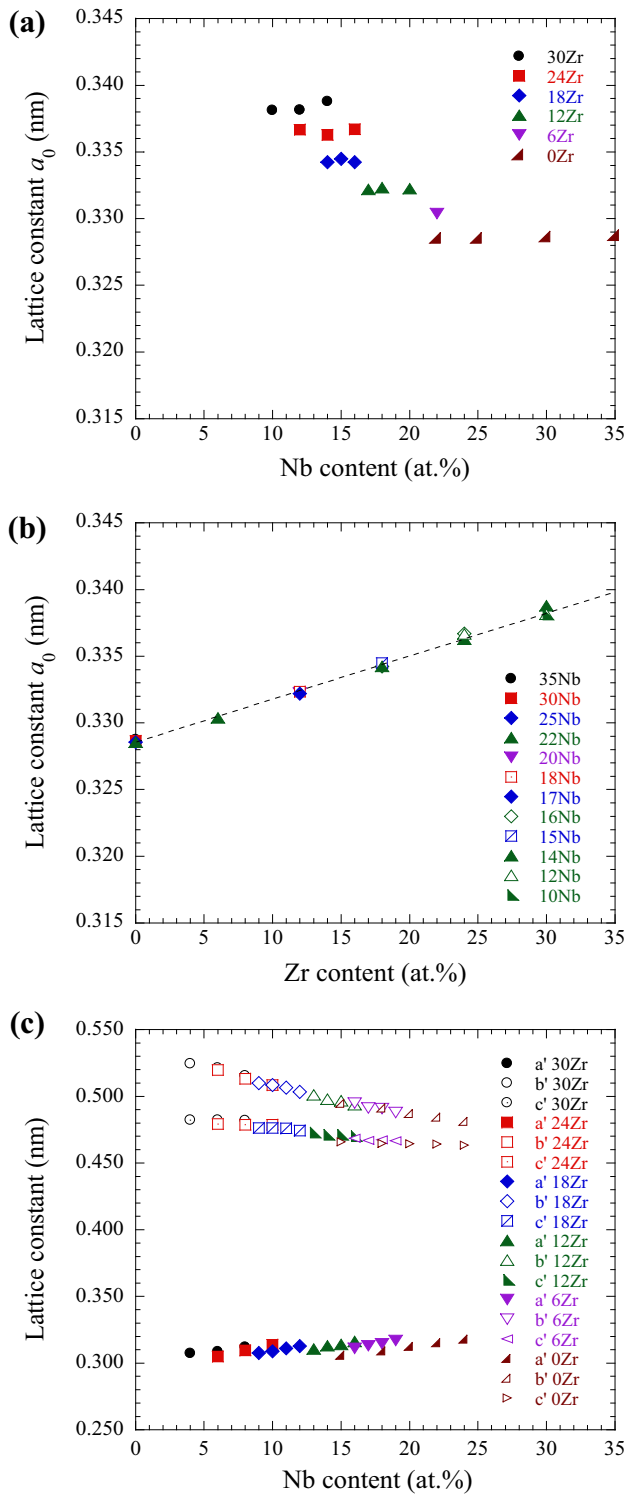


Fig. 6 Composition dependence of the lattice parameters of the β phase and α'' martensite phase of Ti-Nb-Zr alloys. **a** Nb dependence of a_0 of the β phase, **b** Zr content dependence of a_0 of the β phase, and **c** Nb dependence of a' , b' , and c' of the α'' phase

crystal direction is essentially the same: the maximum transformation strain is obtained along the [011] direction, which corresponds to the $[010]_{\alpha''}$ direction, and the

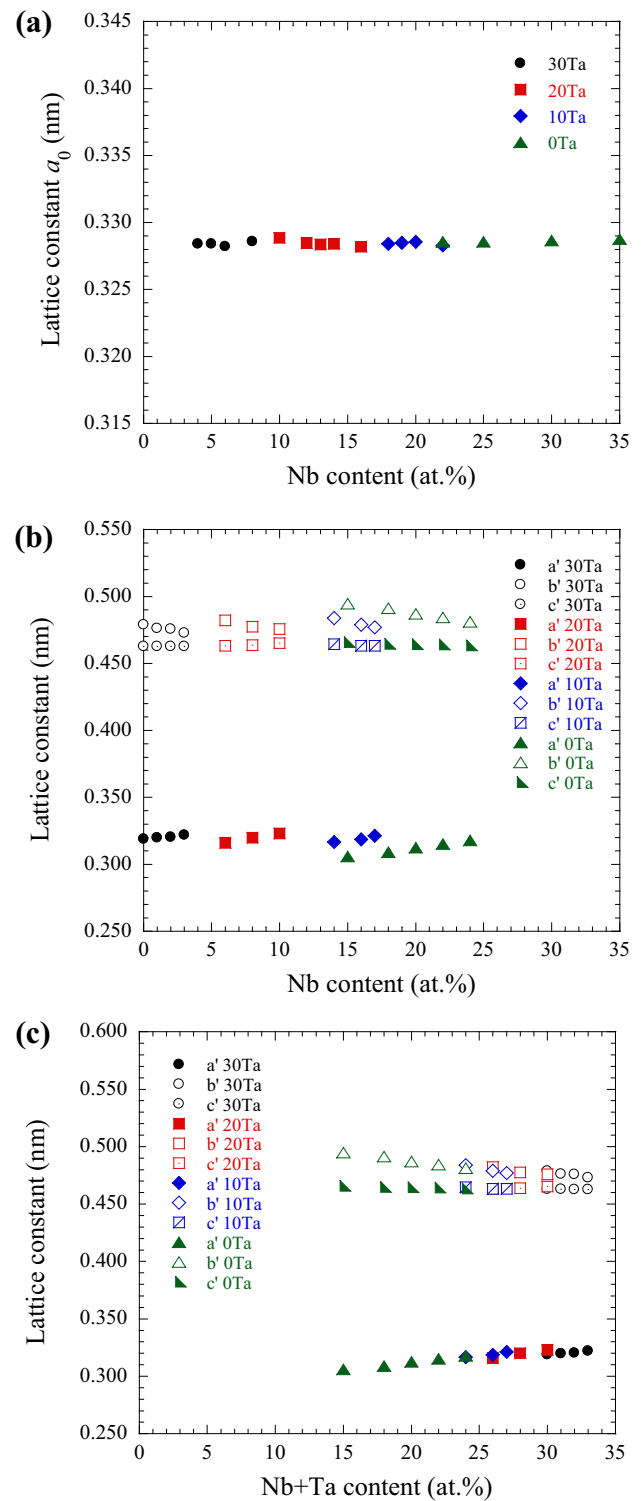


Fig. 7 Composition dependence of the lattice parameters of the β phase and α'' martensite phase in Ti-Nb-Ta alloys. **a** Nb dependence of a_0 of the β phase, **b** Nb dependence of a' , b' , and c' of the α'' phase and **c** Nb + Ta dependence of a' , b' , and c' of the α'' phase

transformation strain decreases with changing direction from [011] toward the directions of [001] and $[\bar{1}11]$, respectively. The transformation strains along [011], [001],

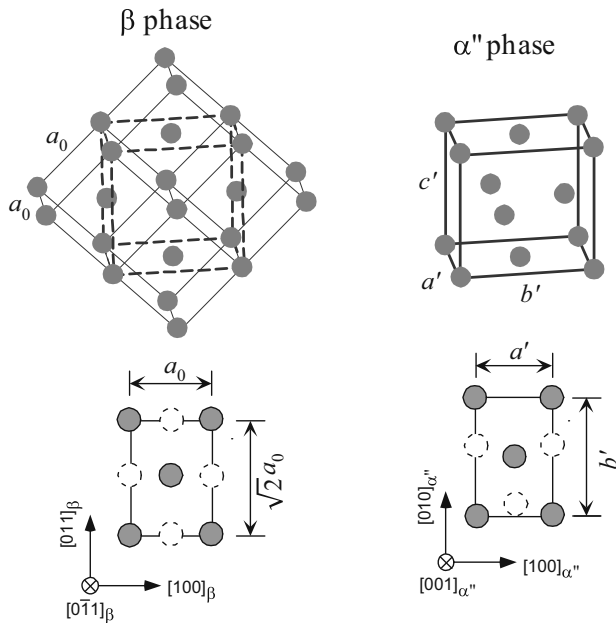


Fig. 8 Lattice correspondence between the β (bcc) and α'' (orthorhombic) phases

and $[\bar{1}11]$ of the Ti–10Nb alloy were calculated to be 8.3, 4.5, and 2.9 %, respectively. The addition of 20 at.% Zr slightly decreases the transformation strains; the transformation strains along $[011]$, $[0\bar{1}1]$, and $[\bar{1}11]$ of the Ti–10Nb–20Zr alloy are 7.5, 4.0, and 2.8 %, respectively. On the other hand, the addition of Ta significantly reduces the transformation strain; the transformation strains along those directions of the Ti–10Nb–20Ta alloy are 2.5, 1.3, and 1.1 %, respectively. Note that each of the transformation strain of the Ti–10Nb–20Zr alloy is as much as about three times greater than that of the Ti–10Nb–20Ta alloy.

The composition dependences of the transformation strain along the $[011]$ direction, which corresponds to the maximum transformation strain, of the Ti–Nb–Zr and Ti–Nb–Ta ternary alloys are plotted by means of contour lines in the composition map in Fig. 11. The results of tensile tests of the Ti–Nb–Zr (Fig. 2) and Ti–Nb–Ta (Fig. 4) are also superimposed in Fig. 11a and b, respectively. Figure 11a shows that the increase in Zr content in the Ti–Nb–Zr alloys exhibited a weaker effect as compared to that of Nb on the transformation strain. It is noted that the decreasing effect of Zr on the transformation strain becomes less pronounced than that of Nb in the Ti–Nb–Zr alloys. The most interesting feature of Fig. 11a is that the addition of Zr as a substitute of Nb with keeping superelasticity at room temperature increases the transformation strain. For example, the transformation strain along the $[011]$ direction of the Ti–27Nb alloy is only 2.6 % but it

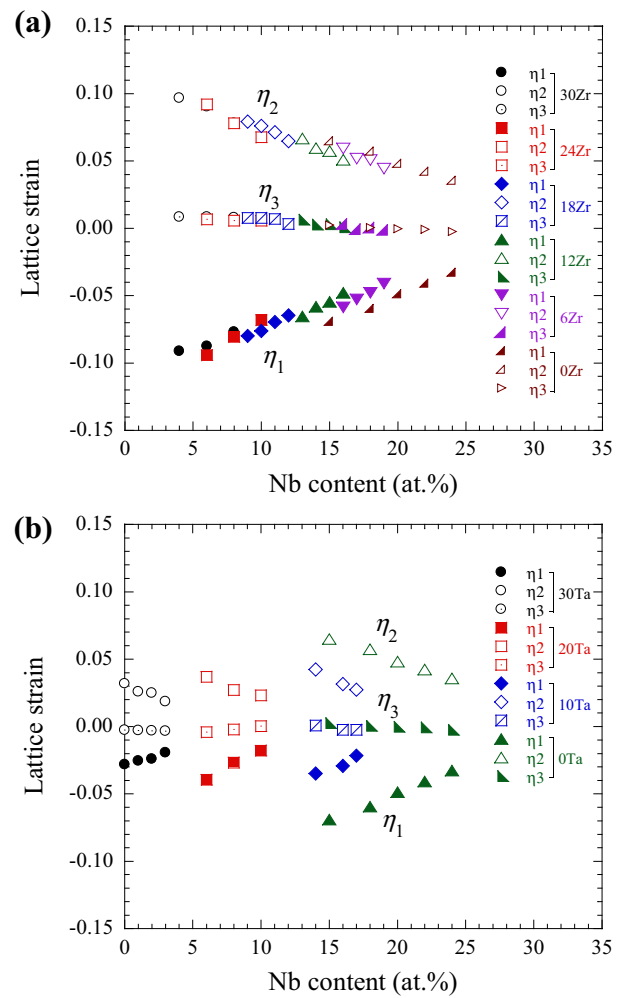


Fig. 9 Composition dependence of the principal lattice deformation strains of **a** Ti–Nb–Zr and **b** Ti–Nb–Ta alloys

increases to 4.1 % and 5.1 % for the Ti–18Nb–12Zr and Ti–15Nb–18Zr alloys, respectively. Furthermore, a large transformation strain more than 7 % is expected in the Ti–Nb–Zr alloys with Zr content higher than 30 at.%.

Figure 11b reveals that the increase in the content of Nb or Ta reduces the transformation strain in the Ti–Nb–Ta alloys, but the impact of Nb is more significant than that of Ta. For instance, the transformation strain decreases by 0.35 % with 1 at.% increase of Nb content in Ti–Nb–20Ta alloys, while it decreases by 0.28 % with 1 at.% increase of Ta content in Ti–20Nb–Ta alloys. When comparing different composition alloys which reveal superelastic recovery at room temperature, it is clear that the increase of Ta content in Ti–Nb–Ta alloys decreases the transformation strain. For example, the transformation strain along the $[011]$ direction is only 1.7 % in Ti–19Nb–10Ta and 1.2 % in Ti–13Nb–20Ta.

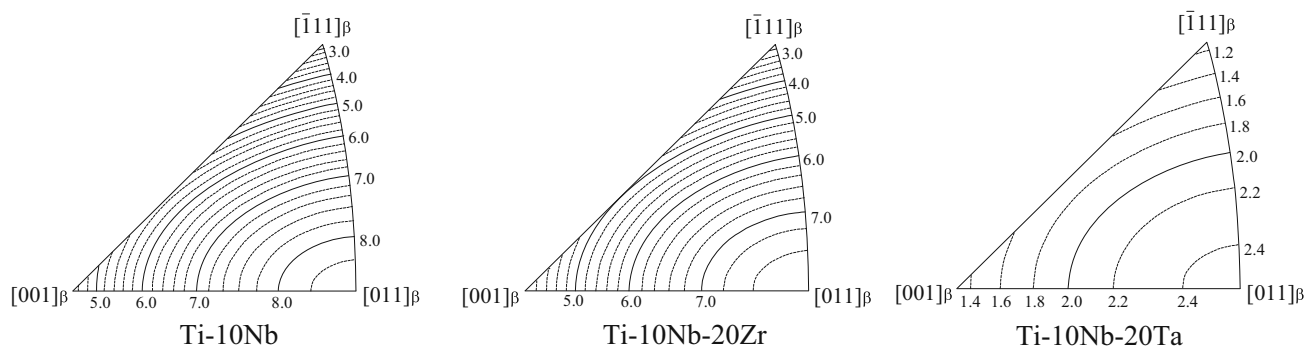


Fig. 10 Orientation dependence of the calculated transformation strain of Ti-10Nb, Ti-10Nb-20Ta, and Ti-10Nb-20Zr alloys

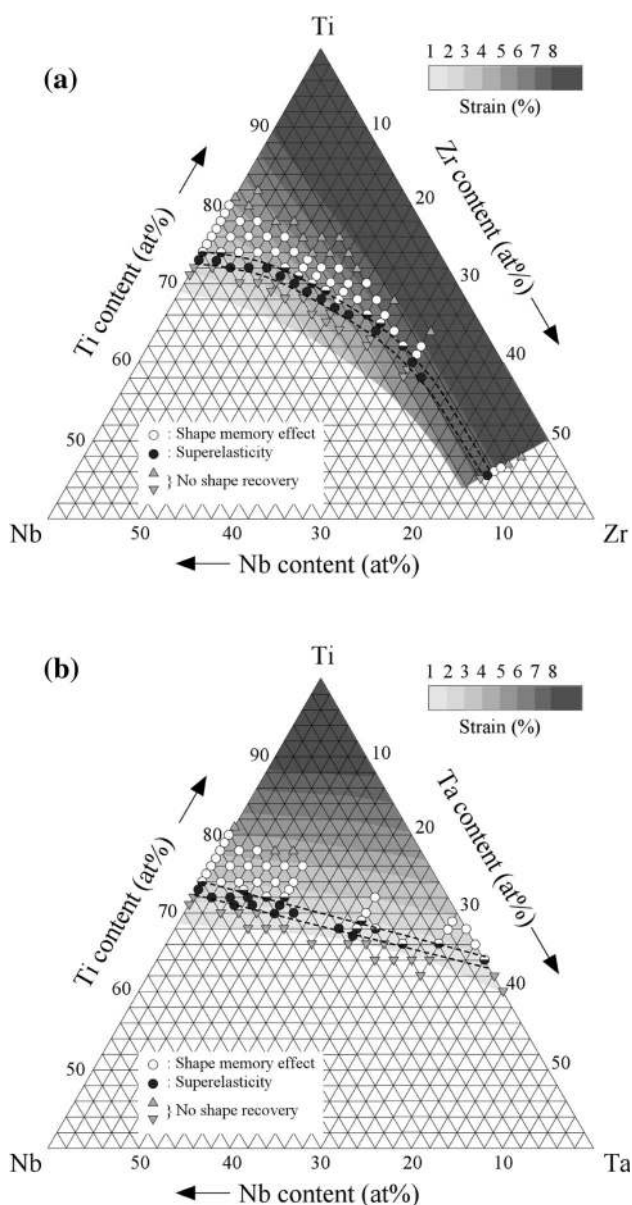


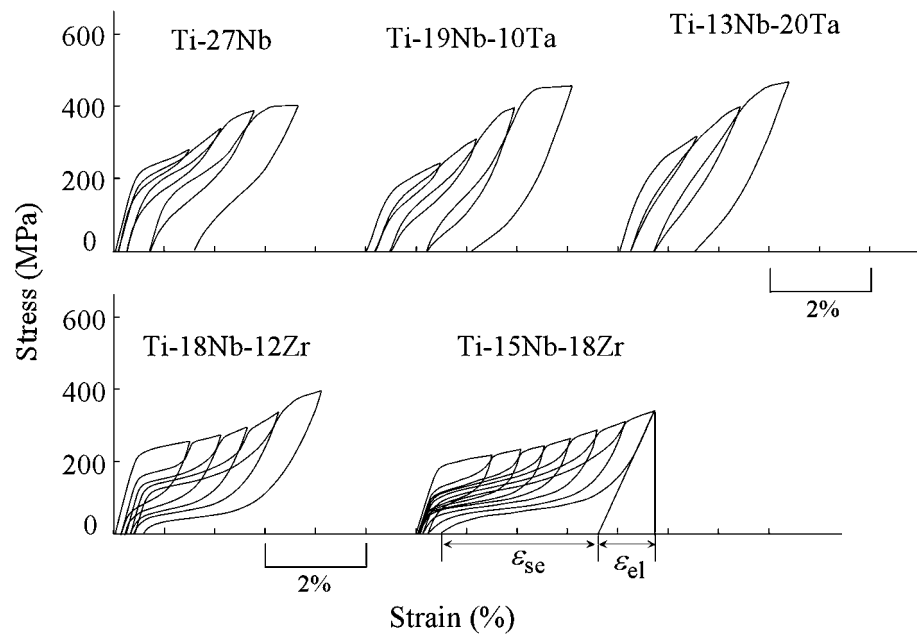
Fig. 11 Composition dependences of the transformation strain along the [011] direction in **a** Ti-Nb-Zr and **b** Ti-Nb-Ta alloys

Superelastic Properties of Ti-Nb-Zr and Ti-Nb-Ta Alloys

As shown in Fig. 11, shape memory effect and superelasticity were observed in a wide composition range of Ti-Nb-Zr and Ti-Nb-Ta alloys; however, the properties were strongly dependent on the composition because not only transformation temperature but also transformation strain is changed by the addition of Zr or Ta in Ti-Nb alloys. Superelasticity is more applicable for biomedical applications than shape memory effect since most of medical applications of Ti-Ni alloys, e.g., orthodontic arch wires, self-expanding stents, and guide wires, use the superelasticity rather than shape memory effect. It is concluded that the addition of Zr is better than Ta in terms of superelastic properties owing to the increase in the transformation strain at the composition showing superelastic recovery at room temperature. This is due to the fact that Zr has a weak impact on the lattice constants of the α'' martensite phase, while it decreases the martensitic transformation temperature so as that the superelasticity occurs at compositions at lower Nb content. To verify the effect of Zr and Ta contents on superelastic recovery strain, loading-unloading cyclic tensile tests were carried out for various Ti-Nb-Zr and Ti-Nb-Ta alloys.

Figure 12 shows the results of cyclic tensile tests for the Ti-27Nb, Ti-12Zr-18Nb, Ti-18Zr-15Nb, Ti-19Nb-10Ta, and Ti-13Nb-20Ta alloys. Similar to our previous reports, at the first cycle, tensile stress was applied until the strain reached about 1.5 %, then the stress was removed. The test was repeated by increasing the maximum strain by 0.5 % upon loading for each following cycle using the same specimen. As expected, the results in Fig. 12 show a strong composition dependence of superelastic properties, although all specimens exhibited superelasticity. It is seen that the strain was almost recovered upon unloading up to the second cycle for the Ti-27Nb alloy, and the superelastic recovery became incomplete with increasing applied strain, i.e., the remained plastic strain increased with

Fig. 12 Comparison of superelastic properties for the Ti–27Nb, Ti–12Zr–18Nb, Ti–18Zr–15Nb, Ti–19Nb–10Ta, and Ti–13Nb–20Ta alloys



increasing number of cycles. The maximum superelastic strain ε_{se}^{\max} of 1.0 % and maximum recovery strain ε_r^{\max} of 2.0 % were obtained in the Ti–27Nb alloy. It is clearly seen that ε_r^{\max} increases with increasing Zr content: the values of ε_r^{\max} were measured to be 3.5 and 4.1 % for the Ti–18Nb–12Zr and Ti–15Nb–18Zr alloys, respectively. The increase in ε_r^{\max} is due to the increase in ε_{se}^{\max} which is directly related to the transformation strain as mentioned above; 2.4 % for the Ti–18Nb–12Zr alloy and 3.0 % for the Ti–15Nb–18Zr alloy. Figure 12 also shows that ε_{se}^{\max} decreases with increasing Ta content in the alloys; 0.8 % for the Ti–19Nb–10Ta alloy and 0.6 % for the Ti–13Nb–20Ta alloy. These results are well consistent with the calculated results shown in Fig. 11 and verify that the alloy design based on the composition dependence of the transformation strain is very useful. It is also suggested that the texture control is essential because the transformation strain is very sensitive to the crystal direction. The increase in the critical stress for inducing plastic deformation through thermomechanical treatment or alloying is another important issue for improving superelastic properties. Further systematic research on these issues is required to draw the full potential of the Ti–Nb–Zr alloys.

Conclusion

In this study, the effects of composition on the shape memory and superelastic properties, and the lattice constants of the β and α'' phases in the Ti–Nb–Zr and Ti–Nb–Ta ternary alloys were extensively investigated. The results of the present study can be summarized as follows:

- (1) The shape memory effect and superelasticity were observed over a wide composition range in Ti–Nb–Zr and Ti–Nb–Ta ternary alloys.
- (2) The lattice constant of the β phase increased linearly with increasing Zr content, whereas the lattice constants of the α'' orthorhombic martensite phase are mainly affected by the Nb content in the Ti–Nb–Zr alloys.
- (3) The lattice constant of the β phase was insensitive to not only Nb content but also to Ta content in the Ti–Nb–Ta alloys. On the other hand, the lattice constants of the α'' orthorhombic martensite phase were mainly governed by the total amount of Nb and Ta in the Ti–Nb–Ta alloys.
- (4) Zr exhibited a weaker impact on the transformation strain compared with Nb and Ta. The addition of Zr as a substitute of Nb with keeping superelasticity at room temperature increased the transformation strain.
- (5) The superelastic recovery strain increased with increasing Zr content, while it decreased with increasing Ta content in both Ti–Nb–Zr and Ti–Nb–Ta alloys.

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