タイトル：Development and characterization of biomedical Ti-Zr-Nb based metastable alloys

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1. Introduction

Ti-based alloys are considered to be the most attractive metallic materials for biomedical applications due to their excellent mechanical properties, high corrosion resistance, good biocompatibility, low weight, etc. According to the demands put on them by the applications, Ti-based alloys can be roughly divided into two groups: alloys used as medical devices in which superelasticity is taken advantage of and alloys used as implants in which a combination of high strength and low Young's modulus that is comparable to human bones is desired. In this research, new Ti-Zr-Nb based alloy systems were developed in both groups exhibiting excellent mechanical properties.

Ti-Ni shape memory alloys have been widely used as biomedical devices such as orthodontic arc wires, guide wires and stents because of their excellent superelastic properties and outstanding mechanical properties. However, there has been a concern about the release of Ni which is well-known as an allergic and toxic element. In recent years, β-type Ti-Nb based alloys only consisting of non- or low toxic elements have attracted great attention aiming to develop more biocompatible shape memory and superelastic alloys. To date, many Ti-Nb based alloys have been reported to show superelastic properties at room temperature. Some examples are Ti-(26, 27)Nb, Ti-Nb-Sn, Ti-Nb-Al, Ti-Nb-Ta, Ti-Nb-Mo, Ti-Nb-Zr and Ti-Nb-Zr-Sn. However, most of the alloys reported to date have a small recovery strain (<4%) when compared with that of commercial Ti-Ni alloys. For example, the superelastic recovery strain of the binary Ti-27at.%Nb alloy was less than 3% even though including elastic recovery strain. This is because of a small lattice distortion associated with martensitic transformation from body-centered cubic parent phase (β) to orthorhombic martensite phase (α″): the calculated maximum transformation strain of the Ti-27Nb single crystal is only 2.5%. The addition of Zr as a substitute of Nb is effective in increasing the transformation strain while keeping transformation temperature in a similar level so as to maintain its superelasticity at room temperature. It has also been reported that the texture control is essential to achieve a larger superelastic recovery since the transformation strain from the β phase to the α″ phase is strongly anisotropic. In this study, new Ti-18Zr-Nb-Sn alloys were designed attempting to develop superelastic alloys with a larger superelastic recovery strain comparable to Ti-Ni alloys. The effects of Nb and Sn contents on crystal structure and shape memory and superelastic properties were investigated. It was found that Ti-18Zr-(9.5-12.5)Nb-(2-4)Sn alloys exhibited a large recovery strain of 6.0% which is more than two times larger than that of the Ti-27Nb superelastic alloy. The effects of Sn addition on recrystallization texture were investigated in order to clarify the reason for the larger recovery strain.

In the case of implants replacing failed human bones, a seemingly impossible mechanical property of a good combination of high strength and low Young's modulus is required. The Young's moduli of implant devices should be comparable to that of cortical bone, because the mismatch between Young's modulus of implant device and human bone results in bone absorption and progressive loosening of the device. Although the Young's moduli of commercial pure Ti (~110GPa) and Ti-6Al-4V (~114GPa) are much lower than traditional stainless steel (~200GPa), they are still much higher compared to that of cortical bone (<30GPa). Up to now, among the developed Ti alloys in these decades the lowest value of Young's modulus is still more...
than 40 GPa. It is necessary to further lower Young's moduli of Ti alloys to the level of cortical bone while keeping a high strength. It has been known that Young's modulus of a single β phase crystal shows a strong anisotropy. The <001> fauna crystallographic direction exhibits the lowest value of Young's modulus. However, alloys with a desirable {hkI} = <001> fauna texture have not been reported till now. It is also known that metastable β-type Ti alloys exhibit lower Young's moduli compared with α-type and α + β types. The Young's modulus of a metastable β-type Ti alloy depends on the phase stability. With decreasing the content of β phase stabilizer, the Young's modulus decreases monotonously and reaches the lowest value in the least stable β phase. However, the least stable β phase favors martensitic transformation by loading, resulting in a critical problem in application. Therefore, the addition of alloying elements to keep low β phase stability while suppressing martensitic transformation should be carefully designed. In this study, new metastable β-type Ti-Zr-Nb base alloys were proposed. By careful element modification through varying N and Sn content, an alloy with an excellent combination of high strength and low Young's modulus near that of human bones was successfully designed. Investigations were focused on the effects of N, Sn addition on mechanical properties, recrystallization texture, phase stability, non-linear elastic deformation behaviors, etc.

2. Experimental Procedures

The ingots were prepared by arc-melting in an Ar atmosphere, and were homogenized at 1273K for 7.2ks in vacuum, followed by cold-rolling into plates of approximately 0.15 mm in thickness. For Ti-18Zr-(9-16)Nb-(0-4)Sn(at.%) alloy, the final reduction ratio was 98.5%. Due to the degraded cold workability by N addition, the N added alloys were subjected to lower reduction ratios of 92.5% and 96.3%, respectively. Specimens for tensile tests were cut along the rolling direction with a rectangular shape of 40 mm×1.5 mm using an electro-discharge machine. Specimens for A solution containing H2O, HNO3 and HF (5:4:1) was used to remove the oxidized surface layer of the samples at room temperature. Then the samples were encapsulated in quartz tubes in an Ar atmosphere and solution treated at 1173 K for 1.8 ks, and then quenched into water without breaking the quartz tubes to avoid oxidation.

Tensile tests were carried out at a strain rate of 0.3 mm per minute at room temperature. The gage length of the samples was 20 mm. In order to measure Young's moduli accurately, strain gauges were used to record stress-strain curves using specimens with a width of 3 mm. Phase constitutions of samples were investigated by X-ray diffraction (XRD) with Cu Kα radiation (40 kV, 40 mA) at room temperature. Lattice constants of the β phase and the α’’ phase were also measured by XRD using Si powder as a reference material at room temperature. Three incomplete pole figures of {110}β, {200}β and {211}β planes were measured using a conventional back-reflection method. Orientation distribution function (ODF) was derived based on the three pole figures. Specimens for TEM observation were prepared by twin-jet polishing technique at 233 K, using a solution of hydrofluoric acid, sulfuric acid and methanol (2:5:93). TEM observations were carried out using a JEOL 2010F instrument operating at 200kV.

3. Results and discussion

3.1 Ti-18Zr-Nb-Sn superelastic alloys with large recovery strains

3.1.1 Superelastic properties of Ti-18Zr-xNb-ySn alloys

In order to investigate the effect of Nb and Sn contents on shape memory and superelastic properties of Ti-18Zr-(9-16)Nb-(0-4)Sn alloys, loading-unloading tensile tests were. The specimens were elongated up to 2.5% strain and unloaded. After unloading, specimens which did not present complete superelastic recovery were heated up to approximately 500 K. It was found that mechanical properties were strongly influenced by both Nb and Sn contents. For example, in alloys with 1 at.% Sn, shape memory effect was observed in Ti-18Zr-12.5Nb-1Sn and Ti-18Zr-13Nb-1Sn alloys, whereas superelastic recovery were observed in Ti-18Zr-13.5Nb-1Sn and Ti-18Zr-14Nb-1Sn alloys, indicating that Nb decreases martensitic transformation.
temperature. When Nb content was kept at 13%, the 1 at. % Sn alloy (Ti-18Zr-13Nb-1Sn) exhibited shape memory effect while the 2 at. % Sn alloy (Ti-18Zr-13Nb-2Sn) was confirmed to show superelasticity, implying that Sn also decreases martensitic transformation temperature.

In order to evaluate superelastic properties of Ti-18Zr-xNb-ySn alloys, cyclic tensile tests were conducted for the alloys showing superelasticity. The applied strain of the first cycle was 2.5%, and then the strain was increased by 0.5% at each following cycle. The maximum recovery strain ($\varepsilon_r$) increased remarkably by the addition of Sn: Ti-18Zr-13.5Nb-1Sn, Ti-18Zr-12.5Nb-2Sn, Ti-18Zr-11Nb-3Sn and Ti-18Zr-9.5Nb-4Sn exhibited a larger maximum $\varepsilon_r$ of 5.2%, 6.0%, 6.0% and 6.0%, respectively. It should be noted that the maximum recovery strain of 6.0% is the largest one reported in Ti based superelastic alloys until now and is also comparable to those of Ti-Ni based superelastic alloys.

3.1.2 Transformation strain of Ti-18Zr-Nb-Sn alloys
The transformation strain is associated with the lattice distortion upon martensitic transformation, which is determined by lattice correspondence between martensite and parent phases and their lattice constants. The transformation strain due to the stress induced martensitic transformation from the $\beta$ to $\alpha''$ phase along different crystallographic orientations was calculated using the lattice constants of both phases and lattice correspondence. In order to compare the transformation strain of the alloys showing superelasticity, i.e. Ti-18Zr-15Nb and Ti-18Zr-11Nb-3Sn, the lattice constants of the $\alpha''$ phase were determined by extrapolation from those of lower Nb content alloys consisting of $\alpha''$ phase. The orientation dependences of the calculated transformation strain are very similar in both alloys although the strains of the Ti-18Zr-11Nb-3Sn alloy are slightly larger than those of the Ti-18Zr-15Nb alloy. For the Ti-18Zr-15Nb alloy, the transformation strains along [001], [011] and [-111] directions are 2.6%, 5.1% and 1.9%, respectively, while those are 2.9%, 5.3% and 1.8% in the Ti-18Zr-11Nb-3Sn alloy. These results indicate that the transformation strain is not a primary reason for the larger superelastic recovery in Sn-added alloys. Also it should be mentioned that the transformation strains in both alloys are more than two times larger than those of a Ti-27Nb superelastic alloy.

3.1.3 Recrystallization texture of Ti-18Zr-xNb-ySn alloys
The ODFs showed that the Ti-18Zr-15Nb alloy exhibited a weak texture with a major component of $\{112\}_\beta$<0-21>$_\beta$, whereas the Sn-added alloys revealed a very strong $\{100\}_\beta$<011>$_\beta$ recrystallization texture, indicating that <011>$_\beta$ direction of crystals aligns parallel to rolling direction preferentially. The transformation strain along <011>$_\beta$ is the largest along all crystallographic directions and becomes small as the crystal direction changes from <011>$_\beta$. It is evident that a large recovery strain of the Sn-added alloys is due to the combination effect of a large transformation strain and a desirable recrystallization texture.

3.2 Ti-Zr-Nb base alloys with an excellent combination of high strength and extremely low Young's moduli
3.2.1 Phase constituents of the alloys
In this study N with different concentrations was added to a metastable Ti-Zr-Nb base alloy. All the alloys with a 92.5% reduction ratio solution treated at 1173 K for 0.3 ks consist of single $\beta$ phase with a well-developed equiaxed structure. The average grain size of the alloys is about 60 $\mu$m, indicating that the addition of N has no effect on the grain size.

3.2.2 Results of tensile tests
The yielding stress increases with increasing N content, indicating the suppression effect of N addition on martensitic transformation. The elongation of the alloys decreases nearly monotonically with the addition of N content due to two reasons: one is the solid solution strengthening effect of N, and the other one is the
suppression of stress induced martensitic transformation. The solid solution strengthening effect can be clearly confirmed by the fact that N added alloys have much higher strength than the alloy without N addition.

3.2.3 Young's modulus and deformation behavior

The deformation behaviors were strongly affected by N content for the alloys. The 0N alloy exhibited shape memory effect at room temperature. By increasing N content, superelasticity was revealed in 0.6N, 0.9N, 1.2N and 1.5N alloys. The hysteresis loop in the stress-strain curves became narrow by increasing N content. With increasing N content, the yielding point became obscure in 0.9N, 1.2N and 1.5N alloys that exhibited peculiar nonlinear elastic deformation.

The incipient Young's moduli of the alloys were determined as the slope between 0 and 50MPa which was elastic region in stress-strain curves. The Young's moduli of the alloys as a whole exhibited relatively low values less than 60 GPa. The 0N alloy exhibited the lowest value less than 40 GPa. This is due to the fact that β phase is extremely unstable because the martensitic transformation temperature is near room temperature. By increasing N content, the Young's modulus increased in the 0.6N alloy. However with further increasing N content, Young's modulus decreased and reached the lowest value in the 1.2N alloy. In general opinions, Young's modulus will increase by adding N content considering the strong Ti-N bonding force. The peculiar Young's modulus dependence on N content indicates there are other mechanisms influencing the Young's moduli of the alloys.

3.2.4 Recrystallization texture

The 0N alloy exhibited a weak component of \( \{100\}_{\beta}\langle011\rangle_{\beta} \) recrystallization texture. With increasing N content, \( \{110\}_{\beta}\langle001\rangle_{\beta} \) recrystallization texture formed in the 0.6N alloy and became the dominating component in the 0.9N and 1.2N alloys. However with further increasing N content, \( \{100\}_{\beta}\langle011\rangle_{\beta} \) component dominated again. As is known, texture is an important factor influencing the Young's moduli in Ti alloys. This explains partly the lower Young's modulus of the 1.2N alloy although it includes a high N content.

3.2.5 The effects of N addition on internal microstructure of the alloys

Although X ray results revealed only a single β phase in these alloys, SAD patterns obtained using TEM exhibited extra diffuse streaks in addition to the fundamental spots of β phase. The corresponding dark field (DF) images obtained from the diffuse streaks featured domain-like morphology (referred to as nanodomains) with a size of several nanometers were confirmed and distributed homogeneously in β phase matrix. The similar phenomena were also reported in Ti-Ni alloys and later in Ti-Nb alloys with oxygen addition. Nanodomains are considered to be a lattice modulation of β phase with interstitial element added. In Ti-Nb-O metastable alloys consisting of a single β phase, the interstitial oxygen atoms were considered to locate in the octahedral sites of bcc lattices randomly and result in elastic distortion. It was proposed that the \( \{1-10\}\langle110\rangle \) shear mode which is similar to the shuffling mode of martensitic transformation could release the strain field caused by oxygen atoms. The shuffling mode will help to release the strong local strain fields caused by addition of N to some extent. The shear mode is reasonable considering the fact that the elastic constant \( c' \) corresponding to the resistance to \( \{1-10\}\langle110\rangle \) shear mode is low when the martensitic transformation temperature is near room temperature in metastable Ti-Nb based alloys. Similar to martensitic transformation, there are six variants of nanodomains depending on different octahedral sites where interstitial element is. It can be seen that the intensity of the diffuse streaks increases with increasing N content.

3.2.6 The effects of nanodomains on the mechanical properties of β phase

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The formation of nanodomains due to N addition is believed to affect the deformation behaviors of β phase. The peculiar deformation behaviors can be interpreted using nanodomain as follows. Without external stress, nanodomains of six different orientations distribute homogenously in β phase matrix. By applying external stress, nanodomain variants that are suitable to release the stress grow preferentially, contributing to the tensile strain. Further growth of preferential nanodomains requires higher external stress due to the surrounding stress fields caused by other nanodomain variants. Undoubtedly a high concentration of nitrogen atoms causes a high density of nanodomains, leading to strong local strain fields. Hence preferential nanodomains can not grow into long-range order martensite even by further increasing tensile stress. This process is considered to be second-order phase transition. By unloading nanodomains return to their original state. This process explains the superelasticity and non-linear deformation behaviors in N added alloys.

4. Conclusions
(1) The maximum recovery strain increased by the addition of Sn to Ti-18Zr-Nb alloys. Particularly, Ti-18Zr-12.5Nb-2Sn, Ti-18Zr-11Nb-3Sn, Ti-18Zr-9.5Nb-4Sn alloys exhibited a larger recovery strain of 6.0%. By calculating the transformation strain, the Ti-18Zr-15Nb and Sn-added alloys exhibited larger transformation strains more than two times larger than that of a binary Ti-27Nb superelastic alloy. The addition of Sn is effective in developing \{001\}_β<110>β recrystallization texture which is desirable for a large transformation. A combination effect of a large transformation strain and a desirable recrystallization texture made Ti-18Zr-Nb-Sn alloys show a large recovery strain.
(2) By the addition of N to Ti-Zr-Nb base alloy, the \{110\}_β<001>β type recrystallization texture which is favorable to low Young's modulus formed. N addition also resulted in the formation of nanodomains which contributed to the release the strain field caused by N addition and superelasticity and nonlinear deformation behavior of N added alloys. The N added Ti-Zr-Nb base alloys exhibited a good combination of high strength due to N and low Young's moduli due to Goss texture and low phase stability. The yielding stress was also high in high N content alloy due to the suppression of stress induced martensitic transformation and slip deformation via dislocation movement.