# Effect of Heat Treatment and Sn Content on Superelasticity in Biocompatible TiNbSn Alloys

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Martensitic transformation and tensile properties of 4 to 5 mol%Sn-doped Ti-16 mol%Nb alloys consisting of biocompatible elements were investigated to provide superelasticity for biomedical applications as a function of heat treatment and Sn content. Martensitic transformation (bcc to orthorhombic structure) is accelerated at such quenching conditions that the bcc parent phase is slightly decomposed. Martensitic transformation temperature decreases rapidly with increasing Sn content. *In-situ* optical microscopic observation on cooling and heating indicates that the martensite is thermoelastic, corresponding to small temperature hysteresis between the martensitic and the reverse transformations, which is determined by differential scanning calorimetry. By controlling the heat treatment condition and Sn content, large superelastic strain is obtained at room temperature.

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## 1. Introduction

TiNi alloys (nitinol) are now widely used and are still being developed as biomaterials as well as industrial materials because of excellent shape memory and superelasticity. As far as biomedical applications are concerned, the surface modification becomes indispensable for the enhancement of corrosion resistance through the formation of a Ni-free TiO<sub>2</sub> layer,<sup>1)</sup> since Ni is allergenic and carcinogenic to the human body.<sup>2,3)</sup> However, this surface oxide layer is not guaranteed to be stable and work well when TiNi medical devices remain in the human body for many years.

Quite recently, the present authors have developed Ni-free Ti-Nb-Sn alloys to overcome the above drawback of TiNi alloys,<sup>4)</sup> based on references<sup>5–7)</sup> indicating good biocompatibility of Ti, Zr, Nb, Ta and Sn, according to cytotoxicity of pure metals and corrosion resistance-tissue reaction. The newly developed alloys exhibited shape memory behavior at around room temperature, dependent on alloy composition, while no appreciable superelasticity was observed. Superelasticity may be more valuable than shape memory effect in biomedical applications of currently available shape memory TiNi alloys, such as life-saving devices of distal protection filters, stents and guidewires for blood vessels.<sup>8)</sup> It is generally known that shape memory alloy systems show superelasticity as well as shape memory effect when alloy composition, heat treatment and deformation condition are properly controlled.<sup>9)</sup> Nevertheless, to the best of our knowledge no large superelasticity has been reported in titanium alloys other than TiNi alloys, although they were found to show considerable shape memory effect.<sup>10-13</sup>) The objective of this work is to investigate the superelasticity of biocompatible Ti-Nb-Sn alloys as a function of heat treatment and Sn content for biomedical applications.

#### 2. Experimental Procedure

4 to 5 mol%Sn-doped Ti-16 mol%Nb alloys were arcmelted in an Ar atmosphere using pure Ti (99.99 mass%), pure Nb (99.99 mass%) and pure Sn (99.99 mass%). Since weight changes before and after arc-melting were negligibly small, alloy compositions will be expressed in nominal compositions by mol% and abbreviated as 16Nb4Sn instead of Ti-16 mol%Nb-4 mol%Sn. The arc-melted buttons were homogenized in vacuum at 1373 K for 12 h and furnace-cooled. Then, the buttons were cold rolled to 1 mm in thickness. Samples for microscopic observations, X-ray diffraction (XRD) and tensile test were prepared by electro-discharge machining from the rolled plates, encapsuled in an evacuated quartz tube, solution-treated at 1223 K for 30 min and quenched in iced water by breaking the tube. Some sample capsules were moved outside the furnace after the solution-treatment, air cooled for various seconds and quenched in iced water. In addition, other sample capsules were put in a furnace kept at 673, 773 or 873 K immediately after the solution-treatment, held for 5 min and quenched in iced water. Tensile testing was carried out at an initial strain rate of  $0.2 \times 10^{-4}$  s<sup>-1</sup> using tensile specimens with a gage section of  $0.8 \text{ mm} \times 2 \text{ mm} \times 10 \text{ mm}$ . Superelasticity was evaluated from stress-strain curves which were directly recorded from a tensile testing machine or produced using strains measured by a strain gage method. Transformation temperature was measured by differential scanning calorimetry (DSC) at a heating or cooling rate of 10 K/min. Microstructures were observed by optical microscopy (OM) equipped with systems for Nomarski interference contrast and in-situ observation at low temperatures.

#### 3. Results and Discussion

Figure 1 shows the DSC curve of 16Nb4Sn solution-treated and directly quenched in iced water. The quenched sample was first cooled to 220 K to complete martensitic transformation and then the DSC curve was measured to identify the reverse (austenitic) transformation on heating and martensitic

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transformation on cooling. A clear peak on the reverse transformation is seen on heating, while only a very weak transformation peak appears on subsequent cooling. Correspondingly, the as-quenched sample consists of a fully martensitic microstructure as shown in Fig. 2(a), while the sample after the DSC measurement consists of a partially martensitic microstructure as shown in Fig. 2(b), where martensite thin plates are formed only along the grain boundaries. In agreement with the above OM observation, XRD analysis revealed that the XRD pattern of the as-quenched sample is composed of a single orthorhombic phase, while weak orthorhombic diffraction peaks from the martensite phase are detected along with very strong bcc peaks in the sample after the DSC measurement. Preferential formation of martensite at the grain boundaries was observed by Duerig et al. in a commercial  $\beta$  phase alloy Ti-10V-2Fe-3Al (by mass%).<sup>11)</sup> They claimed that such microstructures are associated with quenching strains, which decrease with decreasing specimen thickness, and mechanical polishing strains. If the homogeneous microstructure in Fig. 2(a) is concerned with the quenching strains leading to accelerated martensite formation, the inhomogeneous martensitic microstructure in Fig. 2(b) would be caused by small quenching strains (cooled from 423 K after the reverse transformation). A similar inhomoge-



Fig. 1 DSC curve of Ti-16Nb-4Sn quenched in iced water after solution treatment.

neous martensite microstructure was observed in the same alloy by Ohmori *et al.*<sup>14)</sup> They found that short time holding at low temperature around 573 K and at high temperature around 873 K prior to the final quench in iced water can accelerate the martensitic transformation and homogenize the microstructure. The acceleration of the martensitic transformation was attributed to an increase of nucleation sites at  $\omega/\beta$  interfaces for low temperature holding, and to a preceding phenomenon prior to transformation such as a lattice softening on high temperature holding. If this scenario is applicable to the present alloy, the inhomogeneous martensite microstructure in Fig. 2(b) will be related to low nucleation sites at the interior of grains for martensitic transformation.

Figures 1 and 2 as well as the observations by Duerig *et al.*<sup>11)</sup> and Ohmori *et al.*<sup>14)</sup> reveal that the martensite nucleation in  $\beta$  Ti alloys is very sensitive to quenching strain and/or heat treatment. To investigate the effect of quenching rate or quenching strain on martensitic transformation, DSC curves of oil quenched and air cooled 16Nb4Sn, which are measured in the same manner as Fig. 1, are compared with that of iced water quenching, as seen in Fig. 3. Transformation temperatures related to martensitic and reverse transformations appear clearly in oil quenching and air cooling. The quenching rate in this experiment is highest in the iced water quench, thus leading probably to maximum quenching strains. However, the air cooled 16Nb4Sn having the lowest quenching rate also consisted of completely martensitic microstructure like 16Nb4Sn quenched in iced water. DSC curves of 16Nb4Sn quenched in iced water after solution treating followed by air cooling for various seconds are shown in Fig. 4. Evidently, air cooling for a short time results in clear transformation peaks of the reverse and martensitic transformations. Although the quenching temperature of a specimen in a capsule after air cooling could not be measured, the specimen air cooled for the longest time of 30 s would reach the lowest temperature among the various holding times and hence yield the lowest quenching strains. Nevertheless, fully martensitic microstructure was observed in the specimen quenched after air cooling for 30 s. It should be noted, therefore, that the quenching strains are not responsible for the acceleration of martensitic transformation in quenched 16Nb4Sn. As can be seen in Fig. 4, the DSC peaks in the reverse and martensitic



Fig. 2 OM micrographs of Ti–16Nb–4Sn quenched in iced water after solution treatment. (a) as quenched. (b) cooled after reverse transformation on heating.



Fig. 3 DSC curves of Ti–16Nb–4Sn. After solution treatment, (a) iced water quenched, (b) oil quenched (c) air cooled.



Fig. 4 DSC curves of Ti–16Nb–4Sn. After solution treatment, air cooled for 0, 10, 20 and 30 s and then quenched in iced water.



Fig. 5 OM micrographs of Ti-16Nb-4Sn. (a) quenched in iced water after air cooling for 20 s and (b) after DSC measurement.

transformations appear most pronounced after air cooling for 20 s. Then, using this sample the effect of air cooling prior to quenching in iced water on microstructure was investigated. Figures 5(a) and (b) show OM microstructures of 16Nb4Sn quenched in iced water after air cooling for 20 s and cooled in the DSC after heating to 423 K for the reverse transformation, respectively. In contrast to Fig. 2(b), martensitic transformation is totally completed, which is also confirmed by XRD analysis. Using the specimen in Fig. 5, heating and cooling cycles are repeated four times in the DSC as shown in Fig. 6, indicating that the curves are superimposed with almost no deviation in each cycle. This result suggests that thermoelastic martensite disappear on heating and appear on cooling in the same manner for each cycle.

The formation sequence of martensite was investigated in OM equipped with a cooling stage using 16Nb4.9Sn whose martensitic transformation temperature was determined to be 240 K by DSC. Figure 7 shows the sequential OM micrographs on cooling and heating. Obviously, single phase bcc at 298 K changes to partial martensitic microstructure at 240 K. On further cooling to 213 K fully martensitic microstructure is generated and the martensite disappears on heating to 298 K. These sequential changes of microstructures are in good correspondence to a DSC curve for 16Nb4.9Sn subjected to the



Fig. 6 DSC curves of Ti-16Nb-4Sn quenched in iced water after solution treatment followed by air cooling for 20 s. DSC measurements are repeated four times.

same heat treatment, *i.e.*, quenching in iced water after air cooling for 20 s. Thus, the obtained results confirm that the martensite is thermoelastic. It is well known that a small temperature hysteresis is observed in the thermoelastic martensite when it is evaluated by a temperature difference between



cooling and heating of Ti–16Nb–4.9Sn quenched in iced water after solution treatment followed by air cooling for 20 s.



Fig. 8 Sn content dependence of  $M_s$  and  $A_f$  for Ti–16Nb–xSn (x = 4 to 5 mol%Sn) quenched in iced water after solution treatment followed by air cooling for 20 s.

 $A_{\rm s}$  and  $M_{\rm s}$ .<sup>9)</sup> Since most thermoelastic martensite alloys have been found to show a hysteresis of about 15 K or less, the observed hysteresis of TiNbSn alloys of less than 25 K, dependent on alloy composition and heat treatment, is comparable to other alloy systems.

Sn content dependence of  $A_f$  and  $M_s$  temperatures is shown in Fig. 8, where all the alloys are quenched in iced water after air cooling for 20 s. It is evident that both transformation temperatures decrease rapidly with increasing Sn content. That is, 1 mol% increase in Sn content from 4 to 5 mol% leads to a decrease in  $A_f$  or  $M_s$  of about 150 K. It is noted in Fig. 8 that the difference between  $A_f$  and  $M_s$  has a tendency to decrease with increasing Sn content. According to Nitta *et al.*, lattice strains needed to form the orthorhombic structure from bcc in  $\beta$  Ti alloys decrease with increasing Nb or Sn content.<sup>4)</sup> Therefore, the decrease in the hysteresis at high Sn contents, which is estimated from Fig. 8, would be ascribed to the decrease of lattice strains in the transformation. If this speculation is correct, significant superelasticity will be generated at high Sn contents.

It is generally accepted that superelasticity appears most significantly at a temperature about 30 K higher than  $A_{\rm f}$ . Therefore, the superelasticiy of 16Nb4.9Sn was investigated at room temperature (298 K), since the alloy has  $A_{\rm f}$  of 268 K when air cooled for 20s before quenching in iced water. Figure 9 shows stress-strain curves of 16Nb4.9Sn at 298 K, which are drawn from records in a tensile testing machine, as a function of time in air cooling (0, 10, 20 and 40 s), where loading and unloading are repeated with an increase of interrupted strain. At zero of air cooling time in Fig. 9(a) no superplasticity is observed, while at 10 s in Fig. 9(b) superelasticity appears obviously with increasing interrupted strain. With increasing air cooling time the superelasticity becomes more significant as shown in Figs. 9(c) and (d). Especially, at air cooling time of 40 s the total elastic strain of about 5% is recovered after unloading, revealing that superelastic strain is strongly affected by air cooling time. This implies that a decrease of specimen temperature during air cooling causes some decomposition of the parent bcc phase, which changes the superelastic behavior. If this is the case, aging after solution treatment will also change superelastic behavior.

Figure 10 shows stress-strain curves of 16Nb4.9Sn aged at 673, 773 and 873 K for 5 min, where specimens for the aging treatment were moved in an aging furnace immediately after solution treatment, held for 5 min and then quenched in iced water. Figure 10 includes a stress-strain curve of 16Nb4.9Sn directly quenched in iced water after solution treatment for comparison. The elastic deformation behavior in Fig. 10 is remarkably changed by aging, suggesting again some decomposition of the parent bcc phase during aging. The superelasticity can be seen very clearly when aged. All the stress-strain curves in Fig. 10 are drawn using strains from a strain gage to evaluate true elastic strain. The magnitude of elastic strain recovered on unloading is of great importance in industrial applications of superelasticity. Here, we should be careful to



Fig. 9 Stress-strain curves at 298 K of Ti–16Nb–4.9Sn quenched in iced water after solution treatment followed by air cooling for (a) 0 s, (b)10 s, (c) 20 s and (d) 40 s.



Fig. 10 Stress-strain curves at 298 K of Ti–16Nb–4.9Sn quenched in iced water after solution treatment followed by holding for 5 min at 673, 773 and 873 K.

measure elastic strain, because the strains in Fig. 9, which are directly measured from records in a tensile testing machine, result from not only the gage section but also from the tensile testing machine itself, tensile jigs and joints. To measure the true elastic strain, strains were measured by a strain gage. A stress-strain curve drawn by the strains from a strain gage is shown in Fig. 11, where the specimen indicated as 873 K 5 min in Fig. 10 is used. It is evident that the maximum elastic strains are quite different from each other, although no significant difference is observed in retained strain after unloading. That is, the apparent total elastic strain measured by the records of a tensile testing machine is almost doubled, as compared with the true total elastic strain by a strain gage. Figure 12 shows stress-strain curves by the strain gage



Fig. 11 Stress-strain curves at 298 K of Ti–16Nb–4.9Sn quenched in iced water after solution treatment followed by holding for 5 min at 873 K. Strains are obtained from a strain gage (solid line) and records of a tensile testing machine (dotted line).

method when loaded and unloaded repeatedly. Evidently, a stress at the initiation of reverse transformation decreases, as the loading-unloading cycle is increased. This is common behavior in most superelastic alloys.

Shape recovery in many shape memory and superelastic alloys has been explained by considering the ordered structure and strength of a parent phase. If the parent phase is ordered, such as the B2 structure in TiNi or CuZn alloys, the shape recovery of deformed alloys occurs to avoid violating the ordered structure. However, the parent phase of the present alloys, when quenched in iced water after solution treatment, was found to be a disordered bcc structure from XRD and TEM diffraction analysis. Therefore, the strength



Fig. 12 Stress-strain curves at 298 K of Ti–16Nb–4.9Sn quenched in iced water after solution treatment followed by holding for 5 min at 873 K, where loading and unloading are repeated three times.

of the parent phase should be considered, since it has been recognized that shape memory effect appears pronouncedly in a parent phase with high strength. This is because dislocation glide accompanied by transformation strains is difficult in the parent phase with high strength. Although Baker reported shape memory effect in a binary Ti-35 mass%Nb alloy quenched or aged, he did not demonstrate superelasticity.<sup>10)</sup> In contrast, the present experiment exhibits obvious superelasticity in the specimen quenched after air cooling. The discrepancy is not understood at present. One possible explanation is that Sn addition strengthens the parent phase by solid solution hardening, since Sn is generally classified as a solid solution strengthening element in many Ti alloys. Also, the  $\omega$  or  $\alpha$  precipitation hardening behavior of Sn-doped alloy may be different from that of the binary alloy. Moreover, our preliminary experiment reveals that Sn addition lowers the elastic modulus of bcc Ti-Nb alloys. The decrease in elastic modulus will enhance superelasticity through suppression of dislocation glide accompanied by transformation strains.

Our recent studies on the corrosion of TiNbSn alloys reveal that the alloys are very stable and corrsion-resistant in 0.9% NaCl and 1.0% lactic acid solutions.<sup>15)</sup> Thus, it is concluded that a TiNbSn superelastic alloy is promising as an alternative for TiNi alloys for biomedical applications, although further studies on the decomposition of the parent phase on aging and the role of Sn alloying will be needed to understand the superelasticity.

#### 4. Conclusions

Superelasticity of ternary TiNbSn alloys consisting of biocompatible elements was investigated as a function of Sn content and heat treatment. The obtained results are summarized as follows.

(1) *In-situ* optical microscopy reveals that the martensite of TiNbSn alloys is thermoelastic.

(2) Martensitic transformation (bcc to orthorhombic structure) behavior is strongly influenced by heat treatment. Controlled quenching accelerates martensitic transformation.

(3)  $M_{\rm s}$  and  $A_{\rm f}$  temperatures decrease rapidly with increasing Sn content. 1% increase in Sn content lowers the temperatures by about 150 K.

(4) Small temperature hysteresis,  $A_f - M_s$ , of less than 25 K is observed.

(5) Large superelastic strain is obtained at high Sn content when the decomposition of bcc parent phase is occurring during quenching after solution treatment.

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## REFERENCES

- C. M. Chan, S. Trigwell and T. Duerig: Surf. Interface Ana. 15 (1990) 349–354.
- R. Köster, D. Vieluf, M. Kiehn, M. Sommerauer, J. Kähler, S. Baldus, T. Meinertz and C. W. Hamm: The Lancet 356 (2000) 1895–1897.
- International Agency for Research on Cancer, Monograph on the Evaluation of Carcinogenic Risk of Chemicals to Humans, (IARC, Lyon, 1990) pp. 257–411.
- K. Nitta, S. Watanabe, N. Masahashi, H. Hosoda and S. Hanada: Structural Biomaterials for 21st Century, ed. By M. Niinomi (TMS, Warrendale, Pennsylvania, 2001) pp. 25–34.
- S. G. Steinemann: Surface Performance of Titanium, ed. By J. K. Gregory, H. J. Rack and D. Eylon (TMS, Warrendale, Pennsylvania, 1996) pp. 33–45.
- 6) Y. Okazaki: Materia Japan 37 (1998) 838-842.
- 7) M. Niinomi: Materia Japan 37 (1998) 843-846.
- 8) T. W. Duerig: MRS Bulletin 27 (2002) 101–104.
- K. Shimizu and T. Tadaki: Shape Memory Alloys, ed. By H. Funakubo, (Gordon and Breach Science Publishers, New York, 1987) pp. 1–59.
- 10) C. Baker: Metal Sci. J. 5 (1971) 92-100.
- T. W. Duerig, J. Albrecht, D. Richter and P. Fischer: Acta Metall. 30 (1982) 2161–2172.
- H. Sasano and T. Suzuki: Proc. 6th World Conf. Titanium, ed. By P. Lacombe *et al.* (Les Ulis, Les Editions de Physique, 1988) pp. 1667– 1674.
- M. Y. Kollerov, A. A. Ilyin, D. Y. Makarenkov and M. Y. Brun: Proc. Titanium '95 Science and Technology, pp. 2571–2578.
- 14) Y. Ohmori, T. Ogo, K. Nakai and S. Kobayashi: Mater. Sci. Eng. A312 (2001) 182–188.
- A. Kawashima, S. Watanabe and S. Hanada: Proc. 15th Inter. Corrosion Congress, in press.