Mechanical Properties of a Ti-Nb-Al Shape Memory Alloy

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Ni-free Ti-base shape memory alloys (SMAs) have been systematically developed by our group for biomedical applications in order to replace Ti-Ni SMAs which possess the possibility of Ni-hypersensitivity. In this study, superelastic behavior of solution-treated Ti-24 mol%Nb-3 mol%Al alloy was investigated by means of tensile tests at room temperature (RT) as well as microstructural observation. The alloy was fabricated by Ar arc-melting followed by a homogenization at 1273 K and then cold-rolled with the reduction of 99% in thickness without intermediate annealing. The cold-rolled sheets were solution treated at 1273 K for 1.8 ks in vacuum. Then, cyclic loading-unloading tensile tests were performed at RT. In the tensile tests, the tensile direction was systematically changed from rolling direction (RD) to transverse direction (TD) in the plane of the cold-rolled sheets. It was found by the tensile tests that the superelastic behavior strongly depends on the tensile direction and the number of deformation cycles. The solution-treated alloy after 99% cold rolling exhibits the best superelasticity when loaded along RD. The nature of the anisotropy in the superelastic behavior is discussed related with the texture developed during the fabrication process. It is concluded that the thermo-mechanical treatment performed in this study is quite useful as a superelastic treatment for the Ti-base SMAs, and that this alloy should be used industrially by taking into account such anisotropy of superelasticity.

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1. Introduction

Shape memory alloys (SMAs) have been introduced to biomedical fields and widely applied to the practical use due to the unique functions of shape memory effect (SME), superelasticity (SE) and high damping capacity. The only practical SMA is Ti-Ni at present in biomedical use because of its excellence in mechanical stability, corrosion resistance, biofunctionability and biocompatibility.1) From the viewpoint of toxicity for the human body, however, the possibility of Ni-hypersensitivity due to the constituent Ni atoms has been pointed out. In order to reduce the possibility of Ni-hypersensitivity, reduction of Ni content or rather Ni-free SMAs are strongly required. On the other hand, for biomedical materials, Ti-base alloys such as CP-Ti and Ti-6Al-7Nb have been widely used as implant materials for hard tissue because of their high biocompatibility, good mechanical properties and high biocorrosion resistance.2–4) Therefore, from the viewpoint of shape memory alloys and biomaterials, SMAs composed of Ti and other nontoxic elements should be useful for biomedical applications. In previous works by other researchers, Ti-Nb-Sn and Ti-Mo-Al compositions have been investigated as Ni-free Ti-base SMAs.5–7) We have been systematically investigating other new “Ni-free” Ti-base SMAs composed of nontoxic elements.8–17)

It has been known that these Ti-base SMAs have the austenite phase (β) of a bcc crystal structure and the martensite phase (α′) of a c-centered orthorhombic lattice.10) Besides, these alloys exhibit moderate mechanical properties such as ultimate tensile strength of 500–1000 MPa, fracture strain of 10–40% and Young’s modulus of 30–60 GPa, and moderate SME.5–10) However, in comparison with Ti-Ni SMA, the transformation strain generated from β to α′ in martensitic transformation is essentially small due to their crystallographic relationship. Then, the development of texture should be effective to increase the apparent transformation strain available practically. In our previous work, we have investigated microstructures and mechanical properties of Ti-24 mol%Nb-3 mol%Al (abbreviated as TiNbAl) SMA which was severely cold-rolled up to 95% reduction in thickness and solution-treated at 1273 K.15,16) In the subsequent researches, it was found that an increase in the rate of reduction in thickness from 95% to 99% improves superelastic properties of TiNbAl.19) Especially, our recent work revealed that (110)β(112)β recrystallization texture is well developed when 99% cold-rolling followed by the solution treatment at 1273 K is carried out,20) where the subscripts β indicates the β-austenite phase. Based on such background, superelastic behavior of the 99% cold-rolled and solution-treated TiNbAl was investigated by means of microstructure observation and mechanical tests, especially in order to clarify the effect of tensile direction and the number of cyclic deformation on superelastic behavior. The quantitative evaluation for the relationship between the superelastic behavior and the crystallographic of the transformation is presented elsewhere.20)

2. Experimental Procedure

The nominal composition of the material was Ti-24 mol%Nb-3 mol%Al, and the alloy is termed TiNbAl, hereafter. The alloy was prepared by Ar arc-melting method using high purity elemental Ti (99.99%), Nb (99.99%) and Al (99.99%) with non-consumable W electrode. The ingot was homogenized at 1273 K for 7.2 ks in vacuum and then quenched into water. The homogenized ingot was cold-rolled to be 99% reduction in thickness, and the final thickness of 0.1 mm. After the cold rolling, the sheets were solution-treated at 1273 K for 1.8 ks in vacuum followed by quenching into water. It should be noted that this alloy exhibits good workability: more than 99% reduction in thickness can be
performed without intermediate annealing. The recrystallization texture formed in the solution-treated material is a well-developed $\langle 110 \rangle_{\beta} \langle 112 \rangle_{\beta}$-type, and the details of texture appeared in the solution-treated sheets are described elsewhere.\textsuperscript{20}

Thin foils for transmission electron microscopy (TEM) observation were prepared using a twin-jet polishing technique in a solution of hydrofluoric acid: sulfuric acid: methanol = 2:5:93 in volume at 243 K. TEM observation was conducted using Philips CM 200 operated at 200 kV.

The transformation temperature of the alloy was determined by dynamic mechanical analysis (DMA). DMA was performed using Netzsch DMA 242C in a temperature range between 123 K and 423 K with heating/cooling rate of 0.083 K/s (5 K/min). The gage size of DMA specimen was 10 mm in gage length, 1 mm in width and 0.1 mm in thickness. The loading direction for DMA was RD. The deformation mode was the tension under the static force of 2, 4, 6 and 8 N. These applied forces correspond to 15, 31, 46 and 62 MPa. The ratio between static force and dynamic force was kept a constant ratio of 4:3. The frequency of dynamic force was 2 Hz.

Superalastic properties were evaluated through cyclic loading-unloading tensile tests performed at RT under a stain rate of $5 \times 10^{-4}$/s and a constant strain increment of 1% per a loading-unloading cycle using Shimadzu Autograph 500NI. The specimens with a gauge length of 10 mm were made by mechanical cutting and damaged surface layer was removed by mechanical polishing. The longitudinal direction of the specimens (i.e., tensile direction) was systematically changed from RD to TD in the plane of the sheets (ND-plane). These relationships are shown in Fig. 1. The angle between RD and the tensile direction is defined as $\phi$ and selected $\phi$ are 0°, 30°, 45°, 60° and 90°. From the results obtained by cyclic loading-unloading tensile tests, superelastic strain ($\varepsilon_{SE}$) was evaluated by subtracting ‘pure’ elastic strain from applied strain \textit{i.e.} $\varepsilon_{SE}$ is recovery stain by unloading, and stress for inducing martensite ($\sigma_{SMT}$) was also evaluated by being 0.2% flow stress.

3. Results and Discussion

3.1 TEM observation

Figures 2(a) and (b) shows a TEM bright field (BF) and a dark field (DF) images of TiNbAl, respectively. It was confirmed that the matrix is $\beta$ phase, and no martensite phase was seen under this condition. Besides, few dislocations were observed in these images. This suggests that this alloy is fully

![Fig. 1](image1.png)

Fig. 1 A schematic illustration of the directions of the tensile specimens. Hatched rectangles depict the tensile specimens prepared. Note that the direction shown by 0 degree is the rolling direction (RD) and that by 90 degrees is the transverse direction (TD). The ND-plane is the plane of the paper.

![Fig. 2](image2.png)

Fig. 2 TEM micrographs of TiNbAl (a) bright field image and (b) dark field image using a $\omega$-spot shown in the diffraction patterns. The inset is a corresponding selected area diffraction (SAD) pattern. Few dislocations and fine $\omega$-particles are seen entirely.
recrystallized by the solution treatment. In DF image of (b), fine \( \omega \)-particles were observed where encircled \( \omega \)-reflection (indicated in SAD pattern) was used. These \( \omega \)-particles appeared must be ‘athermal \( \omega \)’ which is commonly exists in the Ti-Nb binary alloys. The existence of \( \omega \)-particles must not influence the ductility in TiNbAl since it was reported that the ‘athermal \( \omega \)’ formed during the quenching in the Ti-Nb alloys does not degrade ductility.\(^{21}\)

3.2 Transformation behavior

Figure 3 shows a strain-temperature (S-T) relationship of the material measured by DMA during thermal cycles. The strain-temperature curves in Fig. 3 were not measured under constant stresses. However, these S-T curves are believed to be essentially similar to the S-T curves under constant stresses being equal to static stress. It is clear that large shape changes starts corresponding to \( M_s \) and that the shape change finishes corresponding to \( M_f \) on cooling. On the other hand, the shape recovery starts at \( A_f \) and finishes at \( A_s \) for the heating process. These transformation temperatures depend on the magnitude of the applied stress due to the Clausius-Clapeyron relationship. Then, the relationships between transformation temperatures and applied stress are plotted in Fig. 4 as a representative of each transformation temperature. A liner relationship is seen in this figure. Thus, the transformation temperatures of this alloy were found to be influenced by applied stress in a general manner. By extrapolating these transformation temperatures into the vertical axis corresponding to the “stress-free” condition, transformation temperatures under zero stress can be evaluated and these transformation temperatures are listed in Table 1. All these temperatures are lower than RT, therefore, this alloy has a potential to exhibit superelasticity in nature. The transformation temperature hysteresis between \( M_f \) and \( A_s \) is 13 K. These results are in good agreement with the results of phase analysis by TEM.

3.3 Superelastic properties of TiNbAl alloy

Figure 5 shows stress-strain curves obtained by the cyclic loading-unloading tensile tests with \( \phi = 0 \) (RD), 30, 45, 60,
and 90 (TD) degrees. In these experiments, the specimens were firstly deformed up to 1% and unloaded. Then, the specimens were again loaded up to 2% (previous strain of 1% plus additional strain of 1% constant) strain and unloaded. And the specimens were loaded again up to 3% (= 2% +1%) and unloaded. This procedure of cyclic loading-unloading deformation was repeated up to 8% of tensile strain. It was found that the shape recovery appears by unloading without heating. By taking the transformation temperatures in Table 1 into account, the shape recovery by unloading is deduced to be superelasticity. It was also found that the superelasticity occurs regardless of the tensile direction. However, the superelastic behavior depends on the tensile direction. It was found that the alloy exhibits the excellent superelasticity when the tensile direction is selected to be RD as seen in Fig. 5. The superelastic strain exceeds 4% in this case. It should be noted that the term ‘superelastic strain’ is defined to indicate the total recoverable strain appeared by unloading. Then, the superelastic strain contains both the transformation strain and the elastic strain, in this study. It was also found that the superelastic strain increases with increasing φ. Superelasticity was not clearly recognized when φ = 90 degree (i.e., the tensile direction is parallel to TD). From these results, it is concluded that this alloy exhibits a large anisotropy in superelasticity.

3.4 Effect of cyclic deformation on superelasticity

In order to clarify the effect of cyclic deformation, the stress for inducing martensite ($\sigma_{\text{SIMT}}$) and the superelastic strain ($\varepsilon_{\text{SE}}$) are plotted in Fig. 6 as a function of the number of loading-unloading cyclic deformation ($N$): (a) $\sigma_{\text{SIMT}}$ and (b) $\varepsilon_{\text{SE}}$. It is clear in Fig. 6(a) that $\sigma_{\text{SIMT}}$ monotonically decreases with increasing the number of cyclic deformation, regardless of the tensile direction. This behavior was considered to be due to the training effect. An internal stress field assisting the martensitic transformation is formed by the accumulation of dislocations introduced during the cyclic loading. Thus $\sigma_{\text{SIMT}}$ decreases with increasing the number of cycles of loading, according to the Clausius-Clapeyron relationship. It is also clear in Fig. 6(b) that $\varepsilon_{\text{SE}}$ increases with increasing the number of cyclic deformation regardless of the tensile direction. This is caused by work hardening caused by the cyclic deformation: stress-induced martensite transformation is stabilized by suppression of the dislocation slip, in general. It should be noted that the lowest value of $\sigma_{\text{SIMT}}$ and the largest value of $\varepsilon_{\text{SE}}$ appeared along RD.

3.5 Effect of Tensile Direction on Superelasticity

As shown in Figs. 2 and 5, the superelastic behavior strongly depends on the tensile direction. Then, in order to clarify the effect of tensile direction on superelasticity, $\sigma_{\text{SIMT}}$, $\varepsilon_{\text{SE}}$ and transformation strain due to the martensitic transformation ($\varepsilon_{\text{SIMT}}$) are summarized in Figure 7 as a function of $\phi$: (a) $\sigma_{\text{SIMT}}$ and (b) $\varepsilon_{\text{SE}}$ and $\varepsilon_{\text{SIMT}}$. These values are obtained from the measured stress-strain curves at the 5th cycle ($N = 5$) of loading. It is clearly seen that $\sigma_{\text{SIMT}}$ monotonically increases with increasing $\phi$. However, on the contrary to $\sigma_{\text{SIMT}}$, $\varepsilon_{\text{SE}}$ decreases with increasing $\phi$. It is obvious that the superelastic strain increases linearly with increasing applied stress since the part of elastic strain increases with increasing applied stress. On the other hand, the increase in elastic strain by the increase in $\sigma_{\text{SIMT}}$ is not so significant because the maximum applied stress is almost the same in each tensile direction. Therefore, the $\phi$-dependence of the superelastic strain is almost due to that of the transformation strain.

It was already found that the formation of a well developed (110)$_{\beta}$∥(112)$_{\beta}$ recrystallization texture has been confirmed in the same material and that RD and TD are parallel to (110)$_{\beta}$ and (111)$_{\beta}$ respectively. The dilatation component of
the transformation strain of the $\beta$-\(\alpha''\) transformation takes the maximum value along \(\langle 110\rangle_\beta\). Theoretically calculated transformation strain is about +2.7% when the sheet was loaded along RD and the martensitic transformation occurs entire specimen. These theoretical evaluations are good agreement with the experimental value of 2.5% found in this study. Moreover, the predicted transformation strain of +0.9% along TD is in good agreement with the experimental value of +0.6%. Thus, the nature of the anisotropy in the superelastic strain and a large amount of superelastic strain of 4.7% comes from the \(\langle 110\rangle_\beta\langle 112\rangle_\beta\) texture formed during the thermo-mechanical treatment employed in this study. It is concluded that the thermo-mechanical treatment performed in this study is quite useful to enhance the superelasticity of the Ti-base SMAs, and that this alloy should be used by taking into account such anisotropy of superelasticity.

4. Conclusions

(1) Although the dislocation was not observed, fine \(\omega\)-particles observed in TiNbAl. These \(\omega\)-particles must be athermal \(\omega\) which is commonly exists in Ti-Nb binary alloys.

(2) TiNbAl alloy exhibits superelasticity regardless of the tensile direction. Superelastic strain of 4.7% was observed when the tensile direction was parallel to RD, and only 1.3% of superelastic strain was observed when the tensile direction was parallel to TD. A large superelastic strain of 4.7% was successfully brought out.

(3) The stress for inducing martensite (\(\sigma_{\text{SIMT}}\)) becomes lower and superelastic strain (\(\varepsilon_{\text{SE}}\)) becomes larger with increasing the number of deformation cycles. This is due to the training effect.

(4) \(\sigma_{\text{SIMT}}\) becomes larger and \(\varepsilon_{\text{SE}}\) becomes smaller with increasing the angle between the tensile direction and RD, comparing at the same number of deformation cycles.

(5) According to the crystallographic analysis carried out in our latest study, the nature of a large superelastic strain along RD and the anisotropy in the superelastic behavior is due to a well developed recrystallization texture of \(\langle 110\rangle_\beta\langle 112\rangle_\beta\) in the sheet.

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Fig. 7 Effect of tensile direction on the stress inducing martensite (\(\sigma_{\text{SIMT}}\)) (a) and the superelastic strain (\(\varepsilon_{\text{SE}}\)) and transformation strain (\(\varepsilon_{\text{SIMT}}\)) at the 5th cycle of the cyclic loading (b).