Effect of Cu Addition on Shape Memory Behavior of Ti-18 mol% Nb Alloys

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Shape memory characteristics of Ti-18 mol%Nb alloys containing 3, 4, 5 and 6 mol% Cu (termed Ti18Nb3Cu, Ti18Nb4Cu, Ti18Nb5Cu, and Ti18Nb6Cu, respectively) were investigated and effects of Cu addition on shape memory behavior was clarified. The alloys fabricated by Ar arc-melting method were cold-rolled with 98% reduction thickness and solution-treated at 1273 K for 1.8 ks followed by quenching into water. It was found by θ-2θ X-ray diffraction analysis (XRD) at room temperature (RT) that Ti18Nb3Cu is composed of α′ (c-centered tetragonal) martensite phase and β (bcc) phase. The other alloys with higher Cu contents are β single phase. These results indicate that 6 mol% Cu is completely dissolved in Ti-18 mol% Nb alloys. Besides, the lattice parameter of α′ phase is decreased by Cu addition with a rate of 0.2 × 10⁻³ nm/mol% Cu, and then, the atomic radius of Cu in Ti-18 mol%Nb alloys is estimated to be 0.130 nm. By tensile test it was found that (1) shape recovery strain of Ti18Nb3Cu reaches 3% by heating after deformation, (2) Ti18Nb4Cu exhibits superelasticity at RT, and (3) either shape memory effect or superelasticity does not appear at RT for Ti18Nb5Cu and Ti18Nb6Cu. Besides, the stress for slip deformation is increased by Cu addition with a rate of 50 MPa/mol% Cu. By tensile tests at cryogenic temperatures, the martensitic transformation start temperature (Ms) of Ti18Nb5Cu is determined to be 75 K, and the Cu addition to Ti-18 mol% Nb alloys decreases Ms with a rate of 100 K/mol% Cu. Moreover, more than 5% in transformation strain is observed for Ti18Nb5Cu at 173 K. It was concluded that Cu is an effective additional element in order to improve shape memory and superelastic properties of Ti-Nb alloys.

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Keywords: TiNb alloys, copper addition, biomedical, α′ martensite, shape memory effect, superelasticity

1. Introduction

Extensive studies on mechanical properties and shape memory effect (SME) of β-Ti alloys have been done after when SME of a Ti-35 mass%Nb binary alloy was reported by Baker in 1971. It is known at present that the shape memory effect of such Ti-base alloys comes from a thermoelastic martensitic transformation from β phase (bcc) to α′ phase (c-centered orthorhombic). Superelasticity is also possible to appear in some β-Ti alloys by controlling the martensitic transformation temperatures (Ms). Superelasticity stands for a shape recovery due to stress induced martensitic transformation by loading and its reverse martensitic transformation by unloading even after the deformation beyond the elastic limit. Superelasticity becomes widely applied for various industrial and biomedical fields. Ti-Ni alloy is de facto the only one practical superelastic alloy. However, a possibility of the onset of the Ni-hypersensitivity is alerted and some reports suggest a poor biocompatibility of Ti-Ni for orthodontic applications. As implant materials, Ti alloys such as CP-Ti and Ti-6Al-4V have been widely used due to high corrosion resistance, good mechanical properties and superior biocompatibility. According to the above backgrounds, we have systematically designed several ternary, quaternary Ti-Nb and Ti-Mo base alloys composed of nontoxic elements only, and have succeeded to obtain superelasticity at room temperature (RT). Besides, it has been also reported that the superelasticity can be improved by doping with B and Si. The martensitic transformation behavior of the Ti alloys is affected by alloying with additional elements. As for the non-thermoelastic martensitic transformation from β to α′ (hcp), the effects of binary alloying elements on the martensitic transformation temperature (Ms) were already clarified. For example, the addition of transition metals belonging to 8-, 9- and 10-groups in the Periodic Table reduces Ms much significantly in comparison with those belonging to 5-group. It was also reported that the phase transformation in β-Ti alloys is affected by the density of d-electrons. Thus, the addition of 3d-transition metals should change the phase stability of bcc and martensite phases due to the change in the d-electron density. From this point of view, the effects of 3d-transition-metal elements (V, Cr, Mn, Fe, Co and Ni) addition on the phase constitution and on the β to α′ martensitic transformation behavior were studied. In this work, the effects of Cu addition on the phase constitution and mechanical properties of a Ti-Nb alloy are systematically investigated.

2. Experimental Procedure

The alloys selected were based on Ti-18 mol%Nb, and 3, 4, 5 and 6 mol% of Cu were added. The alloys are termed Ti18Nb3Cu, Ti18Nb4Cu, Ti18Nb5Cu and Ti18Nb6Cu, respectively, hereafter. The ingots were fabricated by a conventional Ar arc-melting method in Ar-1%H₂ atmosphere using a non-consumable W electrode. High purity starting elements of Ti (99.99%), Nb (99.9%) and Cu (99.99%) were used. Each ingot was about 5 g and no chemical analysis was made because the weight change was smaller than 0.15 mass% during alloying. The ingots were homogenized at 1273 K for 3.6 ks in vacuum by encapsulating quartz tubes followed by quenching into water by breaking the tubes. After the homogenization, the surface was mechanically polished, and a part of each ingot was cold-rolled with a final reduction in thickness of 98% (≈ 0.15 mm). The cold-rolled
materials were solution-treated at 1273 K for 1.8 ks in vacuum followed by quenching into water.

In order to determination of phase constitution and precise lattice parameters by θ-2θ X-ray diffraction analysis, another part of each ingot was cold-rolled with a final reduction in thickness of 30% due to the avoidance of texture formation. Then, these materials were also solution-treated at 1273 K for 0.6 ks in vacuum followed by quenching into water. The surface of the specimens for XRD analysis was electro-polished using a solution of perchloric acid : butanol : methanol = 1 : 6 : 10 in volume at 220 K. The XRD measurement was carried out at RT with Cu-Kα radiation using a Philips X’pert-Pro Galaxy system. Si powder was used as an external standard material. The lattice parameters were precisely determined by CellCalc, a lattice parameter refinement program based on the least-square method using the reciprocal lattice parameters. The lattice parameters of orthorhombic α′ phase were represented by \( a_{α′}, \ b_{α′}, \ c_{α′} \) and defined as \( b_{α′} > c_{α′} > a_{α′} \).

The specimens for scanning electron microscopy (SEM) were chemically etched in a solution of hydrofluoric acid : nitric acid : distilled water = 8 : 15 : 77 in volume at RT after the electropolishing. SEM observation was made using a Hitachi S-4300SE equipped with field-emission-gun at a working distance of 15 mm and accelerating voltage of 20 kV.

Mechanical properties were evaluated using a Shimadzu AG500NI Autograph, an Instron-type machine, equipped with a temperature-controlled furnace. Four kinds of tensile tests were made: (1) First one is a usual tensile test at RT. (2) Second one is a cyclic loading-unloading tensile test with a constant strain increment of 1% per cycle. The test temperature was RT but the specimens were heated up to about 523 K after unloading per cycle in order to evaluate shape memory effect. After heating, the specimens were sufficiently cooled down to RT, and next cyclic deformation was done. Such cyclic deformation was repeated up to 10% in the maximum strain. (3) Third one is similar but isothermal cyclic loading–unloading tensile tests where the test temperatures were always kept to be RT, not heated after deformation. (4) Forth is similar isothermal cyclic tensile tests but the test temperatures were selected to be 173 K, 193 K, 233 K and 213 K. This test was applied for Ti18Nb5-Cu only. In all the tests, the strain rate was a constant of \( 5.0 \times 10^{-4} \text{s}^{-1} \). The gauge length, width and thickness of the specimens were 10 mm, 2 mm and 0.15 mm, respectively. The longitudinal axis (tensile axis) was set to be parallel to RD. Figure 1 is a schematic isothermal stress-strain curve showing a loading-unloading cycle for a superelastic alloy. The critical stress for inducing martensite (\( σ_{σθα′} \)) is defined to be the stress at the first yielding point in the stress-strain curve. The transformation strain (\( ε_{σθα′} \)) per cycle is also evaluated which is calculated to be the total shape recovery by unloading minus the elastic strain.

3. Results and Discussion

3.1 Phase constitution and lattice parameter of β phase

Figure 2 shows XRD profiles of the solution treated alloys with cold rolling of 30%, where the diffraction angles are selected from 36 to 42 degrees for the clear understanding of phase constitution. It should be mentioned that the phase constitution of the solution treated alloys is not influenced by the difference in cold rolling reduction. Then, the phase constitution appeared in the 30% cold rolled alloys is in nature same as that appeared in the 98% cold rolled alloys used for the mechanical tests. Subscript \( α′ \) and \( β \) in Fig. 2 indicate \( α′ \) martensite and \( β \) parent phase, respectively. The diffraction pattern of Ti18Nb3Cu shows that this alloy is composed of \( α′ \) and \( β \) phases. On the other hand, the diffraction patterns of the other alloys with higher Cu contents exhibit \( β \) phase only. In all the cases, no other phase other than \( α′ \) or \( β \) was found. Probably, athermal omega (\( α_{ωθ} \)) phase may be also formed in all the alloys, but it is not identified by XRD. The results indicate that \( α′ \) martensite disappears with increasing Cu content, and that added Cu is completely dissolved in Ti-18 mol% Nb, at least within 6 mol% Cu. The disappearance of \( α′ \) by increasing Cu addition must be caused by decrease in \( M_s \) by Cu addition.
The lattice parameters of the alloys are precisely evaluated and summarized in Table 1. It should be noted that the lattice parameter of C12 phase in Ti18Nb3Cu could not precisely determined due to insufficient number of clear C12 peaks. The lattice parameter of C12 phase in Ti18Nb4Cu, Ti18Nb5Cu and Ti18Nb6Cu are also plotted as a function of Cu concentration as Fig. 3, and the data for the binary Ti-18 mol%Nb in the literature is also plotted. It should be noted that Ti-18 mol%Nb binary alloy is C11 martensite phase at RT, then, the lattice parameters of C12 phase of the Ti-18 mol%Nb binary alloy (plotted at 0Cu in the figure) are the estimated values. The estimation was done based on the assumption that there is no volume change taken place during the C12–C11 martensitic transformation. This assumption is an acceptable approximation for the thermoelastic martensitic transformation in general. Then, the lattice parameter of C12 phase, aC12, can be calculated using the lattice parameters of C11 phase, aC11, bC11 and cC11, as eq. (1).

\[ a_{\beta} = \sqrt{\frac{a_{\alpha'} b_{\alpha'} c_{\alpha'}}{2}} \]  

It is seen that the lattice parameter linearly decreases with increasing Cu concentration with a rate of \(-0.2 \times 10^{-3} \text{ nm/mol}\%\text{Cu}\). The lattice parameter decrease by Cu addition is quite acceptable from the viewpoint of Goldschmidt radii (0.147 nm for Ti and Nb, and 0.128 nm for Cu). By extrapolation of the relationship in Fig. 3, the atomic radius of Cu atom in Ti-18 mol%Nb alloys is estimated to be 0.130 nm. This is comparable to the Goldschmidt radius of Cu. Based on the smaller atomic size of Cu, Cu addition must cause the solid solution strengthening, and then, the tensile properties must be changed by Cu addition.

### Table 1 Lattice parameters of α′ and β phases of TiNbCu alloys at RT.

<table>
<thead>
<tr>
<th></th>
<th>Ti18Nb3Cu</th>
<th>Ti18Nb4Cu</th>
<th>Ti18Nb5Cu</th>
<th>Ti18Nb6Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a_{\alpha'})/nm</td>
<td>—</td>
<td>0.3268</td>
<td>0.3265</td>
<td>0.3263</td>
</tr>
<tr>
<td>(a_\beta)/nm</td>
<td>0.312</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>(b_{\alpha'})/nm</td>
<td>0.483</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>(c_\beta)/nm</td>
<td>0.465</td>
<td>—</td>
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<td>—</td>
</tr>
</tbody>
</table>

The lattice parameters of the alloys are precisely evaluated and summarized in Table 1. It should be noted that the lattice parameter of β phase in Ti18Nb3Cu could not precisely determined due to insufficient number of clear β peaks. The lattice parameter of β phase in Ti18Nb4Cu, Ti18Nb5Cu and Ti18Nb6Cu are also plotted as a function of Cu concentration as Fig. 3, and the data for the binary Ti-18 mol%Nb in the literature is also plotted. It should be noted that Ti-18 mol%Nb binary alloy is α′ martensite phase at RT, then, the lattice parameters of β phase of the Ti-18 mol%Nb binary alloy (plotted at 0Cu in the figure) are the estimated values. The estimation was done based on the assumption that there is no volume change taken place during the β–α′ martensitic transformation. This assumption is an acceptable approximation for the thermoelastic martensitic transformation in general. Then, the lattice parameter of β phase, \(a_\beta\), can be calculated using the lattice parameters of α′ phase, \(a_{\alpha'}\), \(b_{\alpha'}\) and \(c_{\alpha'}\), as eq. (1).

\[ a_{\beta} = \sqrt{\frac{a_{\alpha'} b_{\alpha'} c_{\alpha'}}{2}} \]  

It is seen that the lattice parameter linearly decreases with increasing Cu concentration with a rate of \(-0.2 \times 10^{-3} \text{ nm/mol}\%\text{Cu}\). The lattice parameter decrease by Cu addition is quite acceptable from the viewpoint of Goldschmidt radii (0.147 nm for Ti and Nb, and 0.128 nm for Cu). By extrapolation of the relationship in Fig. 3, the atomic radius of Cu atom in Ti-18 mol%Nb alloys is estimated to be 0.130 nm. This is comparable to the Goldschmidt radius of Cu. Based on the smaller atomic size of Cu, Cu addition must cause the solid solution strengthening, and then, the tensile properties must be changed by Cu addition.

### 3.2 Microstructure

Scanning electron micrographs of solution treated Ti18Nb3Cu, Ti18Nb4Cu and Ti18Nb6Cu are shown in Fig. 4(a), (b) and (c), respectively. The black dots in the figures were etch pits. In Fig. 4(a) the martensite plates and the prior β grain boundary are seen in Ti18Nb3Cu which is \(\alpha' + \beta\) two phase by the XRD analysis. On the other hand, equiaxed grains are observed in the alloys with higher Cu contents, which are β single phase. In all the alloys,
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3.3 Tensile behavior

3.3.1 Tensile tests

Figure 5 shows the stress-strain curves obtained by the tensile tests for (a) Ti18Nb3Cu, (b) Ti18Nb4Cu, (c) Ti18Nb5Cu, and (d) Ti18Nb6Cu at RT. Two-stage yield behavior, which is usually seen in general shape memory and superelastic alloys, was seen in the stress-strain curves of (a) Ti18Nb3Cu and (b) Ti18Nb4Cu. The first yield stress in Ti18Nb3Cu is considered to be the stress for reorientation of martensite variants ($\sigma_{RO}$) and/or the stress for inducing martensite ($\sigma_{SM}$), since Ti18Nb3Cu is two phase of TiNbAl and TiB phases at RT. The second yield point is considered to be the yield point for plastic deformation by slip. For the Ti18Nb4Cu, the first yield stress of is considered to be $\sigma_{SM}$, since Ti18Nb4Cu is B phase at RT. On the other hand, Ti18Nb5Cu and Ti18Nb6Cu do not exhibit similar two yield behavior but usual monotonous work hardening behavior. Then, slip deformation occurs prior to martensitic transformation in both Ti18Nb5Cu and Ti18Nb6Cu due to higher $\sigma_{SM}$ than the stress for plastic deformation.

The ultimate tensile strength (UTS) and the elongation to fracture ($\varepsilon_F$) are 520 MPa and 10.4% for Ti18Nb3Cu, 555 MPa and 16.7% for Ti18Nb4Cu, 550 MPa and 6.1% for Ti18Nb5Cu and 525 MPa and 8% for Ti18Nb6Cu, respectively. The UTS of the alloys are almost similar each other, but $\varepsilon_F$ is larger in the alloys which exhibit second yield behavior than the others. The elongation seems to increase by the deformation related with stress induced martensite and/or reorientation of martensite variants.

It was already suggested in the above that solid solution hardening by Cu addition is expected in the alloys. In order to evaluate the solid solution hardening, the stress for plastic deformation ($\sigma_P$) was evaluated as shown in Fig. 5, and plotted as a function of Cu concentration as shown in Fig. 6. $\sigma_P$ corresponds to the second yield point for Ti18Nb3Cu and Ti18Nb4Cu, and to the general yield point for Ti18Nb5Cu and Ti18Nb6Cu. It is seen in Fig. 5 that $\sigma_P$ seems to increase linearly with increasing Cu content. This increase is due to the solid solution strengthening by Cu addition, and the increase in strength by 1 mol% Cu addition is experimentally estimated to be 50 MPa/mol%Cu by judging from the slope in the figure. It should be mentioned that (1) $\sigma_P$ is the slip stress for $\alpha''$ phase for Ti18Nb3Cu and Ti18Nb4Cu instead of $\beta$ phase for Ti18Nb5Cu and Ti18Nb6Cu, and that (2) $\sigma_F$ for Ti18Nb3Cu and Ti18Nb4Cu contains work hardening introduced during stress inducing martensite formation. Thus, the accurate evaluation of solid solution hardening by Cu addition cannot be done based on Fig. 6. However, we believe that the tendency that $\sigma_P$ increases with increasing Cu addition is correct, and that Cu is an effective strengthener of Ti-Nb base alloys.

3.3.2 Cyclic loading-unloading tensile tests with heating after unloading

Figure 7 shows the cyclic loading-unloading stress-strain curves up to 5th cycle of (a) Ti18Nb3Cu, (b) Ti18Nb4Cu and (c) Ti18Nb5Cu. After each cyclic deformation, each specimen was heated and shape recovery by heating was measured. The shape recovery strain ($\varepsilon_{REC}$) by heating is shown by the arrows below the vertical axis in the figure.

It was found in Fig. 7(a) that shape recovery was clearly recognized by heating for Ti18Nb3Cu. Since Ti18Nb3Cu is $\alpha'' + \beta$ two phase and exhibited two stage yield behavior by the tensile test, the shape recovery by heating is due to the reverse martensitic transformation by heating.

It was confirmed in Fig. 7(b) that Ti18Nb4Cu exhibited nonlinear but large shape recovery appeared just by unload-
4.2% strain was recovered by unloading at the 5th cycle. Small residual strain was introduced after each cyclic deformation, but the residual strain was also shape recovered by heating. The shape recovery by unloading only is considered to be superelasticity caused by stress-inducing martensite and its reverse transformation. Small amount of formed martensite must be retained after the deformation, and the retained martensite was reverse-transformed into β phase by heating. In Fig. 7(c), Ti18Nb5Cu exhibited no shape recovery observed by heating. Thus, this alloy does not exhibit shape memory effect as expected from the phase constitution of β phase at RT. Besides, this alloy did not exhibit clear superelasticity like Ti18Nb4Cu, but slight nonlinear shape recovery by unloading seen as loops in the stress-strain curve. This alloy was judged to be mostly deformed by slip, because a large amount of unrecoverable permanent strain was introduced by the cyclic deformation. However, the slight shape recovery seen as the loops may be superelasticity due to stress-induced martensitic transformation activated by cyclic deformation. Ti18Nb6Cu exhibited similar cyclic loading-unloading stress-strain curves to (c).

The shape recovery strain per cycle by heating (εREC) of each alloy is plotted as a function of the number of cycles in Fig. 8. It is seen that the maximum εREC was 3% in Ti18Nb3Cu at 6th cycle. On the other hand, the maximum shape recovery by heating was approximately 0.6% for Ti18Nb4Cu. Due to the incomplete reverse martensitic transformation by unloading, Aβ of deformed Ti18Nb4Cu is thought to be slightly higher than RT. The recovery strain of Ti18Nb5Cu and Ti18Nb6Cu was not recognized. This is because Ti18Nb5Cu and Ti18Nb6Cu do not transform into martensite by loading, or at least, induced martensite is not retained after unloading due to lower Aβ than RT.

3.3.3 Isothermal cyclic loading-unloading tensile tests at RT

Figure 9 shows the stress-strain curves obtained by the cyclic loading-unloading tensile test at RT of (a) Ti18Nb3Cu, (b) Ti18Nb4Cu, (c) Ti18Nb5Cu and (d) Ti18Nb6Cu. In Fig. 9(a), nonlinear shape recovery was observed by unloading for Ti18Nb3Cu. By taking into account the XRD profile and stress-strain curves described, the nonlinear shape recovery is pseudoelasticity due to rearrangement of martensite variants. In Fig. 9(b), Ti18Nb4Cu exhibited superelasticity similar to Fig. 7(b). The maximum transformation strain obtained was 1.8% in this case. This value is less than the maximum shape recovery of 3% in Fig. 8 for Ti18Nb3Cu. This is probably because the amount of retained martensite in Ti18Nb4Cu is increased by cyclic deformation. The martensitic transformation temperature becomes higher by the accumulation of dislocations as the Clausius-Clapeyron equation. The increase in martensitic transformation temperature is judged from the decrease in σSIM per cycle with increasing the number of cycles. In Fig. 9(c) and (d), no shape recovery by unloading was observed in Ti18Nb5Cu and Ti18Nb6Cu, similar to Fig. 7. Small pseudoelasticity was seen in Ti18Nb5Cu and only elastic deformation was observed in Ti18Nb6Cu. The pseudoelasticity observed in Ti18Nb5Cu may be related with the stress induced martensitic transformation as mentioned above. No martensitic transformation is expected for the deformation in Ti18Nb6Cu.

3.3.4 Cyclic loading-unloading tensile tests of Ti18Nb5-Cu at cryogenic temperatures

By summarizing the results obtained for Ti18Nb5Cu, the disappearance of superelasticity and shape memory effect at RT is considered to be lower martensitic transformation than required. Then, it is expected that the superelasticity may appear by cooling down to near martensitic transformation temperature. Figure 10 shows the similar stress-strain curves of Ti18Nb5Cu obtained at (a) 233 K, (b) 213 K, (c) 193 K and (d) 173 K. It is clear that the superelasticity appears at all the test temperatures. It is also seen that the flow stress level is decreased with decreasing test temperature. This is because lower stress is required for inducing martensite at nearer Ms.

The σSIM and δTR obtained in Fig. 10 are plotted as a function of the number of cycles as shown in Fig. 11. In Fig. 11(a) for σSIM that σSIM decreases with increasing the number of cycles regardless of the Cu concentration. This is due to the accumulation of dislocations introduced during deformation. An internal stress field assisting the martensitic transformation is formed by the accumulation of dislocations during the cyclic loading. The reduction rate of σSIM by increasing the number of cycles, ΔσSIM, is estimated to be 20 MPa/cycle at 253 K and 5 MPa/cycle at 193 K as shown in Fig. 11(a). The reduction rate of ΔσSIM seems to decrease...
Fig. 9 Stress-strain curves of (a) Ti18Nb3Cu, (b) Ti18Nb4Cu, (c) Ti18Nb5Cu and (d) Ti18Nb6Cu obtained by the cyclic loading-unloading tensile tests at RT.

Fig. 10 Stress-strain curves of Ti18Nb5Cu at (a) 233 K, (b) 213 K, (c) 193 K and (d) 173 K obtained by the cyclic loading-unloading tensile tests.
with decreasing the test temperature. This must be due to increase in slip stress by decreasing test temperature. Figure 11(b) shows transformation strain as a function of the number of cycles. $\varepsilon_{TR}$ increases with increasing the number of cycles regardless of test temperature, and reaches maximum values at around 8th or 9th cycle. The largest $\varepsilon_{TR}$ obtained is 5.4% at 9th cycle at the test temperature of 173 K. Then, it can be said that Ti18Nb5Cu exhibits good super-elasticity at cryogenic temperature around 173 K. Besides, it can be seen that the maximum $\varepsilon_{TR}$ increases with decreasing test temperature: 3.5% at 233 K and 213 K, 4.6% at 213 K and 5.4% at 173 K. The increase in $\varepsilon_{TR}$ by decreasing test temperature must be resultant of suppression of dislocation accumulation due to increase in slip stress as similar manner to $\Delta \sigma_{SIM}$.

In Fig. 11(a), it is also found that $\sigma_{SIM}$ at a certain cycle decreases with decreasing test temperature. At 4th cycle, $\sigma_{SIM}$ is 380 MPa at 233 K, 300 MPa at 213 K, 280 MPa at 193 K and 240 MPa at 173 K. These $\sigma_{SIM}$ at 4th cycle were plotted as a function of test temperature as shown in Fig. 12. A liner relationship between $\sigma_{SIM}$ and the test temperature is obtained. The slope of the Clausius-Clapeyron type equation, $\Delta \sigma / \Delta T$, is evaluated to be 2.0 MPa/K. Similar value was reported for a Ti-Nb base alloy. 33) Based on the relationship, $M_s$ under zero stress can be evaluated by extrapolation to be 75 K. $M_s$ of Ti-18 mol%Nb binary alloy (Ti18Nb) is estimated to be 540 K based on the $M_s$ change by Nb addition of 40 K/mol%Nb. 31,34) By using $M_s$ of 75 K for Ti18Nb5Cu and 540 K for Ti18Nb, $M_s$ is decreased by addition of 5 mol%Cu by 485 K. This reduction in $M_s$ by Cu addition can be calculated to be $-100$ K/mol%Cu. Cu is an effective additional elements to decrease $M_s$ of Ti-Nb alloys.

Kim et al. have investigated the Nb concentration dependence of the lattice deformation strain between $\alpha^\prime\prime$ phase and $\beta$ phase, and they show that the lattice deformation strain increase with decrease in Nb concentration. 31) Nb concentration can be reduced by Cu addition under the condition of constant transformation temperatures required for room temperature superelasticity. Hence, it is possible to appear larger superelastic strain at RT in TiNbCu alloys by controlling Nb and Cu contents. Cu addition is effective on improvement of shape memory/superelastic properties of Ti-Nb alloy due to the strengthening of 50 MPa/mol%Cu and larger decrease in $M_s$ of 100 K/mol%Cu than 40 K/mol%Nb.

4. Conclusions

(1) Ti18Nb3Cu is two phases of $\alpha^\prime\prime$ martensite phase and $\beta$
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parent phase at RT. On the other hand, Ti18Nb4Cu, Ti18Nb5Cu and Ti18Nb6Cu are β phase at RT.

2. The solubility limit of Cu in Ti-18 mol%Nb is higher than 6 mol% Cu.

3. The lattice parameter of β phase is decreased by Cu addition with a rate of 0.2 \times 10^{-3} \text{nm/mol}%Cu. The atomic radius of Cu in Ti-18 mol%Nb alloys is estimated to be 0.130 nm.

4. The stress for slip deformation is increased by Cu addition with 50 MPa/mol% Cu. The strengthening of 50 MPa/mol% Cu and larger increase in \( M_s \) of Cu addition is judged to be solid solution hardening by replacing Cu with smaller atomic size to Ti.

5. Ti18Nb3Cu exhibits shape memory effect at RT, and the maximum shape recovery strain reaches 3%. Ti18Nb4Cu exhibits superelasticity at RT. Either shape memory effect or superelasticity does not appear at RT for Ti18Nb5Cu and Ti18Nb6Cu at RT.

6. Ti18Nb5Cu exhibit good superelasticity at temperatures from 173 K to 233 K. The transformation strain in superelastic shape recovery of Ti18Nb5Cu exceeds 5% at 173 K.

7. \( M_s \) of Ti18Nb5Cu is evaluated to be 75 K.

8. The reduction of \( M_s \) by Cu addition in Ti-18 mol%Nb alloys is −100 K/mol% Cu.

9. Cu addition is effective on improvement of shape memory/superelastic properties of Ti-Nb alloy due to the strengthening of 50 MPa/mol% Cu and larger decrease in \( M_s \) of 100 K/mol% Cu than 40 K/mol% Nb.

Acknowledgments


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