Shape Memory and Mechanical Properties of Biomedical Ti-Sc-Mo Alloys

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Ni-free Ti-Sc-Mo shape memory alloys are designed as a substitute for Ti-Ni alloys in the biomedical field. From results of bending and recovery test with heating, Ti-Sc-Mo alloys were found to have superior shape memory effect. The optimum composition for the shape memory effect was Ti-4.0 to 6.0Sc-6.0Mo alloys. The maximum shape recovery strain in the Ti-5.0Sc-6.0Mo alloy was 5.3% measured through cyclic tensile deformation. Vickers hardness and 0.2% proof stress were remarkably decreased and elongation was increased with Sc content. The marked grain refining was also achieved. The relationship between microstructure and mechanical properties was briefly discussed. Microstructure observations and XRD measurements before and after tensile deformation showed that the shape memory effect was associated with the stress induced β to α′ transformation.

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1. Introduction

Since Ti-Ni alloys exhibit superior shape memory properties and superelasticity, they are favorable choice for smart biomaterials such as orthodontic wire, stent in blood vessels and teeth-root prosthesis.¹ However, Ni is strongly concerned about allergenic and carcinogenic to the human body. Thus, Ni-free shape memory and superelastic alloys should be developed in order to secure absolute safety. One of the candidate materials is metastable β-titanium alloys which are designed with appropriate combination of α and β stabilizing elements.²⁻⁴ Recently, the present authors have developed Ti-Ag-Mo and Ti-Sn-Mo alloys along the above conception, which appears in this issue. Reliable shape recovery strain in both the alloys is about 3%. In order to obtain the high shape memory properties comparable with Ti-Ni alloys, a new alloy system should be developed. The present authors pay attention to Sc as α stabilizing element of β peritectoid type,⁵ since the Sc-Ti binary system is extremely unique with the continuous β solid solution at high temperature. Although it should be examined whether Sc is biocompatible or not, there is no report on the negative influence of Sc on human body so far. In the present study we demonstrate the shape memory and mechanical properties of newly developed Ti-Sc-Mo alloys.

2. Experimental Procedure

The nominal compositions of alloys investigated were listed in Table 1 together with their phase constitution at room temperature discussed later. Mo content was fixed to be 6.0 mol% from the preliminary investigation. These alloys were prepared by arc melting in an Ar atmosphere. Weight changes before and after arc melting were negligibly small in all the alloys. The ingots were homogenized at 1373 K for 1273 K for 1.8 ks followed by quenching into ice water by breaking tube. Shape memory properties were evaluated with convenient bending test. The bending test was carried out at room temperature where the specimen was deformed into a round shape and heated up about 550 K. Mechanical properties were evaluated with Vickers hardness measurement and tensile test. Vickers hardness was measured by using applied load of 1.98 N and loading time of 10 s. HV values employed were averaged at least 5 points excluding the lowest and highest values. Tensile tests were performed at room temperature under the initial strain rate of 4.16 × 10⁻⁴ s⁻¹. Cyclic tensile and heating tests were also performed to determine the shape recovery strain quantitatively. The constitutional phases of before and after tensile deformation were determined by the X-ray diffraction (XRD) and optical microscopy.

3. Results and Discussion

Phase constitution of the alloys prepared in the present study after solution treatment is listed in Table 1, which is determined from XRD measurements and optical microscopy observations at room temperature. Only β phase was detected in Ti-6.0Mo and Ti-3.0 to 7.0Sc-6.0Mo alloys. In Ti-1.0Sc-

Table 1 Nominal composition and phase constitution after solution treatment.

<table>
<thead>
<tr>
<th>composition (mol%)</th>
<th>phase constitution</th>
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<tbody>
<tr>
<td>Ti-6.0Mo</td>
<td>β</td>
</tr>
<tr>
<td>Ti-1.0Sc-6.0Mo</td>
<td>α′, β, Sc₂O₃</td>
</tr>
<tr>
<td>Ti-2.0Sc-6.0Mo</td>
<td>α′, β, Sc₂O₃</td>
</tr>
<tr>
<td>Ti-3.0Sc-6.0Mo</td>
<td>β, Sc₂O₃</td>
</tr>
<tr>
<td>Ti-4.0Sc-6.0Mo</td>
<td>β, Sc₂O₃</td>
</tr>
<tr>
<td>Ti-5.0Sc-6.0Mo</td>
<td>β, Sc₂O₃</td>
</tr>
<tr>
<td>Ti-6.0Sc-6.0Mo</td>
<td>β, Sc₂O₃</td>
</tr>
<tr>
<td>Ti-7.0Sc-6.0Mo</td>
<td>β, Sc₂O₃</td>
</tr>
</tbody>
</table>
6.0Mo and Ti-2.0Sc-6.0Mo alloys, $\beta + \alpha'$ phases were identified. In addition to these two phases, Sc oxide was detected in all the ternary alloys. Since the relative intensity of Sc oxide in XRD was not changed with Sc content and there are no unidentified peaks other than three phases mentioned above, the rest of Sc were probably solved into titanium. It is expected that both $\beta$ and martensitic transformation temperatures are increased by addition of Sc, because Sc is $\alpha$ stabilizing element as mentioned above. Contrary to the expectation, the experimental results show opposite tendency as increasing Sc contents. These results might be explained by mutual balance between the decrease of athermal $\omega$ phase formation and solid solution strengthening by Sc as well as Al in Ti-Mo-Al and Ti-V-Al alloys.\(^6,7\) In those alloys, the $M_s$ temperature increases with decreasing the athermal $\omega$ phase formation in low Al alloys and decreases with increasing the solid solution strengthening of Al in high Al alloys. It is likely that similar phenomena take place in the Ti-Sc-Mo alloys.

Figure 1 shows results of convenient bending test of Ti-6.0Mo and Ti-6.0Sc-6.0Mo alloys. Shape memory effect was observed by heating after deformation in both the alloys. It is clearly seen that the shape memory effect in Ti-6.0Sc-6.0Mo alloy is superior to that in Ti-6.0Mo alloy. Sc content dependence of shape memory behavior in Ti-Sc-Mo alloy is summarized in Fig. 2. Recovery ratio $R_{\text{sme}}$ with shape memory effect is defined as follows;

$$R_{\text{sme}} = \left(\frac{\epsilon_s - \epsilon_r}{\epsilon_s}\right) \times 100$$  \hspace{1cm} (1)

where $\epsilon_s$: surface strain after bending deformation and $\epsilon_r$: residual surface strain after heating as presented in Figs. 1(b) and (c), respectively. In addition to the $R_{\text{sme}}$, recovery ratio $R_{\text{sb}}$ with spring back after bending deformation is also evaluated, since the $R_{\text{sb}}$ gives a kind of potentiality that the specimen exhibits superelasticity, as described below. The $R_{\text{sb}}$ is given as follows;

$$R_{\text{sb}} = \left(\frac{\epsilon_d - \epsilon_s}{\epsilon_d}\right) \times 100$$  \hspace{1cm} (2)

where $\epsilon_d$: applied surface strain with bending deformation as presented in Fig. 1. The $R_{\text{sme}}$ increases with increasing Sc content up to 3 mol% and keeps constant about 95% in 4.0 to 7.0 mol%Sc. The $R_{\text{sb}}$ keeps constant about 25% up to 6.0 mol%Sc and then increases about 35% in 7.0 mol%Sc. From these results, optimum composition for the shape memory effect is determined to be Ti-4.0 to 6.0Sc-6.0Mo alloys. The stress-strain curve of these alloys showed shape memory behavior as typically seen in that of Ti-5.0Sc-6.0Mo alloy later presented in Fig. 3, i.e., there is no superelastic like reversion upon unloading. On the other hand, superelastic like reservation was partially recognized upon unloading in the stress-strain curve of Ti-7.0Sc-6.0Mo alloy. Therefore, it is considered that the increase of $R_{\text{sb}}$ relates to the appearance of superelasticity due to the instability of stress induced martensite resulting from the lowering of transformation temperature by addition of 7.0 mol%Sc. This suggests that Ti-7.0Sc-6.0Mo alloy might exhibit superelastic property at room temperature with appropriate structure control through the aging, thermomechanical treatment and so on. In fact, we have succeeded to obtain the nearly perfect superelastic recovery of 2.0% tensile strain in the aged Ti-7.0Sc-6.0Mo
alloy at room temperature, which will be reported soon.

The quantitative measurement of shape recovery strain is performed in Ti-5.0Sc-6.0Mo alloy by cyclic tensile and heating test as shown in Fig. 3. Broken arrows in the bottom of figure indicate the shape recovery with heating. After heating, the specimen was immediately quenched into ice water to avoid the formation of isothermal α phase. The residual strain of specimen is about 5.2% after the first cycle. Then the shape recovery strain was 4.8%. The residual strain of 3.4% after the second cycle is recovered perfectly. The residual strain after the third cycle is about 5.3% as indicated by the bold broken arrow. The constant recovery strain about 5% was obtained after several tensile cycles. These results demonstrate that the developed Ti-5.0Sc-6.0Mo alloy possesses excellent shape memory effect. Young’s modulus of Ti-5.0Sc-6.0Mo alloy is determined to be 61 GPa by the strain gage method. This young modulus value is lower than that of Ti which is 106 GPa. It is suitable for the biomedical application. It is deduced that the improvement of shape memory effect is achieved by grain refining as indicated later. The positive effects of grain refining on the shape memory properties have been reported in many of Cu base shape memory alloys. However, since the origin of shape memory effect is derived from thermoelastic nature of martensitic transformation and mobility of martensite/parent and parent/martensite interfaces, influences of Sc on the martensitic transformation behavior, morphology and crystallography of stress induced martensite should be investigated in detail. This is now under study and will be reported in due course.

Figures 4(a) and (b) show Vickers hardness, 0.2% proof stress and elongation changes with Sc content in the alloys, respectively. The HV value decreases drastically with addition of only 1.0 mol% Sc and further decreases slightly in Ti-2.0Sc-6.0Mo alloy. Subsequently, the HV value slightly increases in Ti-3.0Sc-6.0Mo alloy and decreases up to 5.0 mol%Sc. Consequently, the HV value gradually increases up to 7.0 mol%Sc. Correspondingly, 0.2% proof stress decreases gradually with increasing Sc content up to 5.0 mol% and then increases with increasing Sc content up to 7.0 mol%. Both minimum values are obtained in Ti-5.0Sc-6.0Mo alloy. Tensile elongation remarkably increases about 35 to 38% with increasing Sc content from 3.0 to 6.0 mol% and then decreases about 26% in Ti-7.0Sc-6.0Mo alloy. The origin of mechanical property changes with Sc content is discussed later.

Microstructure and XRD profile in Ti-6.0Mo alloy are shown in Figs. 5(a) and (b), respectively. Those in Ti-5.0Sc-6.0Mo alloy before tensile deformation are shown in Figs. 5(c) and (d), respectively. Grain size of Ti-6.0Mo alloy is about 270 μm and that of Ti-5.0Sc-6.0Mo alloy is about 25 μm as clearly recognized from (a) and (c). XRD results in (b) and (d) suggest that both the alloys consist of β phase. In Ti-5.0Sc-6.0Mo, Sc oxide is also detected, which may correspond to dispersed small particles in (c). The marked grain refining is probably achieved by grain boundary
pinning effect of Sc oxide. After the deformation with 4% strain, banded surface relief of stress induced \( \alpha'' \) martensitic phase appears as shown in Fig. 5(e). This is confirmed by XRD profiles in Fig. 5(f) in which the intensity of \( \beta \) phase and Sc oxide decreases and that of \( \alpha'' \) phase increases. The disappearance of Sc oxide peak might be due to the increase of the background intensity with the change of surface roughness, i.e., surface relief of \( \alpha'' \) martensite. It is apparent that the shape memory effect in Ti-Sc-Mo alloy is associated with the stress induced \( \beta \) to \( \alpha'' \) martensitic transformation. From these results, the origin of mechanical property changes with Sc content is deduced as follows. The drastic decrease of hardness in Ti-1.0Sc-6.0Mo alloy might be attributable to the decrease of solution strengthening with oxygen due to the formation of Sc oxide, which is a kind of scavenging effect. It is likely that the scavenging effect is completed by addition of 1.0 mol% Sc, since HV values are roughly constant up to 4.0 mol% Sc. It is also likely that the softening with scavenging effect is more dominant than the strengthening with grain refining in all the ternary alloys. The slight decrease of hardness in Ti-2.0Sc-6.0Mo alloy is due to the formation of \( \alpha' \) martensite. The decrease and increase of hardness with increasing the content of \( \alpha \) stabilizing element has been reported in several \( \beta \)-titanium alloys where no martensitic phase forms.\(^6\) The origin of hardness change in those alloys is well explained by the mutual effect of volume fraction change in athermal \( \omega \) phase and solid solution strengthening of \( \alpha \) stabilizing element. Similarly, the hardness change between Ti-3.0Sc-6.0Mo and Ti-7.0Sc-6.0Mo alloys might be explained by the mutual effect of athermal \( \omega \) phase and solid solution strengthening of Sc. The origin of 0.2% proof stress change with Sc content might be explained essentially by the above concept, since both minimum values of hardness and 0.2% proof stress are obtained in Ti-5.0Sc-6.0Mo alloy as already mentioned. To confirm these explanations, TEM observations of athermal phase are required. The remarkable increment of elongation in Ti-3.0 to 6.0Sc-6.0Mo alloys is attributable to the grain refining, since coarse grains about 200 \( \mu \)m in diameter were occasionally observed in Ti-1.0Sc-6.0Mo and Ti-2.0Sc-6.0Mo alloys. However, the origin of elongation decrease in Ti-7.0Sc-6.0Mo alloy with fine grains of 25 \( \mu \)m in average diameter cannot be clarified. In the Ti-Sc-Mo system, optimum compositions for the biomedical shape memory alloy are Ti-4.0Sc-6.0Mo, Ti-5.0Sc-6.0Mo and Ti-6.0Sc-6.0Mo alloys which have excellent shape recovery about 5% of tensile strain and desirable mechanical properties such as low Young’s modulus and high ductility.
4. Conclusion

In order to develop the biomedical Ni-free \( \beta \)-titanium shape memory alloys substituting for Ti-Ni alloys, shape memory and mechanical properties of Ti-Sc-Mo alloys were investigated. The obtained results are summarized as follows.

(1) Ti-3.0 to 7.0Sc-6.0Mo alloys exhibited superior shape recovery ratio more than 90% in convenient bending and heating test. The recovery strain about 5% was constantly obtained in Ti-5.0Sc-6.0Mo alloy with tensile deformation and heating cycles.

(2) Vickers hardness and 0.2% proof stress are remarkably decreased and elongation is increased with Sc content up to 6.0 mol% Sc. The former is attributable to the decrease of solution strengthening in Ti matrix with decrease of oxygen due to the formation of Sc oxide. The latter is derived from the grain refining due to the grain boundary pinning effect of Sc oxide.

(3) Microstructure observation before and after tensile deformation showed that the shape memory effect in Ti-Sc-Mo alloys is associated with stress induced \( \beta \rightarrow \alpha'' \) martensitic transformation.

According to these results, Ti-Sc-Mo alloys are promising for new biomedical shape memory alloy with desirable mechanical properties.

REFERENCES