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Shape Memory Property and Superelasticity of Biomedical Ti-Mo-Sn Alloys

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Shape memory property and superelasticity of Ti-Mo-Sn alloys consisting of biocompatible elements were investigated. The alloys with appropriate combination of Mo and Sn showed nearly perfect shape memory effect in convenient bending and heating tests. Microstructure observations and X-ray diffraction measurements before and after tensile test revealed that the stress induced β to α" martensitic transformation was origin of the shape memory effect. By controlling Sn content and the aging condition, large superelastic strain was obtained at room temperature.

Keywords: titanium-molybdenum-tin alloy, biomedical application, β-titanium alloy, α" martensite, martensitic transformation

1. INTRODUCTION

Biomedical applications of Ti-Ni shape memory and superelastic alloys such as orthodontic wire, teeth-root prosthesis, stent in blood vessels have been continuously increasing all over the world. Although only Ti-Ni alloys have been practically used for biomedical applications because of their superior shape memory property and superelasticity, it has been suspected that Ni is allergenic and carcinogenic to the human body [1]. Therefore, in order to reduce the risk of toxicity of Ni, the development of Ni-free shape memory alloys has been urgently required [2-4]. Our group has systematically investigated Ti-Mo based shape memory and superelastic alloys, several Ni-free β-Ti-Mo based shape memory alloys such as Ti-Mo-Ag, Ti-Mo-Sn, Ti-Mo-Sc alloys have been developed [5-7]. The purpose of this study is to investigate shape memory property and superelasticity of developed Ti-Mo-Sn alloys with respect to the alloy composition and heat treatment condition.

2. EXPERIMENTAL PROCEDURES

The nominal compositions of alloys investigated in the present study were listed in Table 1. These alloys were arc melted in an Ar atmosphere using pure Ti (99.7mass%), pure Mo (99.95mass%) and pure Sn (99.9mass%). Weight changes after arc melting were negligible small in the all alloys. The ingots were homogenized at 1373K for 86.4ks in vacuum and then hot and cold rolled into plated of 0.3 to 0.5mm in thickness. Specimens with prescribed shapes were prepared by spark machining from the rolled plates. They were encapsulated in an evacuated quartz tube, solution-treated at 1273K for 1.8ks and quenched into iced water with breaking tube.

Shape memory properties were evaluated with convenient bending test and cyclic tensile test. The bending test was carried out as follows. The specimens of 0.3mm in thickness were deformed in a round shape at room temperature. They were heated to about 550K and then immediately quenched into iced water after the complement of shape recovery. The cyclic tensile and heating test were performed in Instron-type machine with the initial strain rate of $4.16\times10^{-4}s^{-1}$. Phase constitution was identified by X-ray diffraction (XRD) at room temperature. The microstructures before and after tensile test were observed by optical microscopy.

Table 1 List of nominal compositions of alloys prepared in the present study. O mark showing occurrence of shape memory effect with heating after convenient bending test.

Ti-Mo (mol%)	Ti-Mo-Sn (mol%)
Ti-5.0Mo O	Ti-5.0Mo-1.0Sn O
Ti-6.0Mo O	Ti-5.0Mo-2.0Sn O
	Ti-5.0Mo-3.0Sn O
	Ti-5.0Mo-4.0Sn O
	Ti-5.0Mo-5.0Sn O
	Ti-6.0Mo-1.0Sn O
	Ti-6.0Mo-2.0Sn O
	Ti-6.0Mo-3.0Sn O
	Ti-6.0Mo-4.0Sn
	Ti-6.0Mo-5.0Sn

3. RESULTS AND DISCUSSIONS

The alloys prepared in the present study are listed in Table 1. In that table, the alloys marked 'o' exhibit shape memory effect upon heating after the convenient bending test at room temperature. The incomplete shape memory effect is obtained even in the two binary alloys, i. e., Ti-5Mo and Ti-6Mo alloys. However, brittle fracture occurred in the binary alloys after two to three cycles of bending and recovery tests. There are two types of ω phase, athermal and isothermal ones, in β-titanium alloys. Generally, the former appears during cooling and the latter appears during aging. It is difficult to distinguish whether the athermal or the isothermal ω phase from during the bending and recovery test, because the test includes both aging and cooling processes as described above. However, since it is well known that the former has little influence on the mechanical properties and the latter causes the embrittlement, the brittle fracture in the binary alloys is mainly due to the isothermal ω phase formation during the bending and recovery tests. On the other hand, there is no brittle fracture in ternary Ti-Mo-Sn alloys after five cycles. The shape memory performance in Ti-5Mo based alloys was relatively superior to that in Ti-6Mo based alloys regardless of Sn addition. Therefore, we will describe the results of Ti-5Mo based alloys hereinafter. Shape memory properties in various Ti-5Mo-Sn alloys estimated from the bending test are summarized in Fig. 1. Recovery ratio R_{sme} with shape memory effect is defined as follows;

$$R_{sme}=(\varepsilon_s-\varepsilon_r)/\varepsilon_d\times100 \qquad (1)$$

Recovery ratio R_{sb} with spring back after bending deformation is also evaluated, since the R_{sb} gives a kind of potentially that the specimen exhibits superelasticity. The R_{sb} is given as follows;

$$R_{sb}=(\varepsilon_d-\varepsilon_s)/\varepsilon_d\times100 \qquad (2)$$

where ε_d: applied surface strain with bending deformation, ε_s: surface strain after bending deformation and ε_r: residual surface strain after heating.

The R_{sme} increases with increasing Sn content up to 3% and then decreases gradually. It is supposed that optimum composition for the shape memory effect is determined to be Ti-5Mo-3Sn alloy. The R_{sb} remarkably increases about 81 and 83% in Ti-5Mo-4Sn and Ti-5Mo-5Sn alloys, respectively. From the results, the addition of Sn improves the shape memory effect and suppresses the isothermal ω phase in Ti-Mo alloy.

The quantitative measurement of shape recovery strain is performed in Ti-5Mo-3Sn alloy by cyclic tensile and heating test as shown in Fig. 2. Broken lines with arrows indicate the shape recovery with heating. After heating, the specimen was immediately quenched into ice water to avoid the formation of isothermal ω phase. The maximum shape recovery strain in the Ti-5Mo-3Sn alloy is 3.5% after the first cycle. Young's modulus of Ti-5Mo-3Sn is 79GPa. This young's modulus value is lower than that of Ti which is 106GPa [8]. It is suitable for the biomedical material.

Microstructure and XRD profiles changes in Ti-5Mo-3Sn alloy before and after tensile deformation are shown in Fig.3. There are β phase before the deformation as shown in Figs. 3 (a) and (b). After the bending deformation with 4% strain banded surface relief of α" martensitic phase appears as shown in Fig. 3 (c). This is supported by XRD profiles in Fig. 3 (d) in which the intensity of β phase decreases and that of α" phase increases remarkably. It is clear that the stress induced β to α" martensitic transformation associates with the shape memory effect in this alloy.

Although shape memory effect is obtained in the

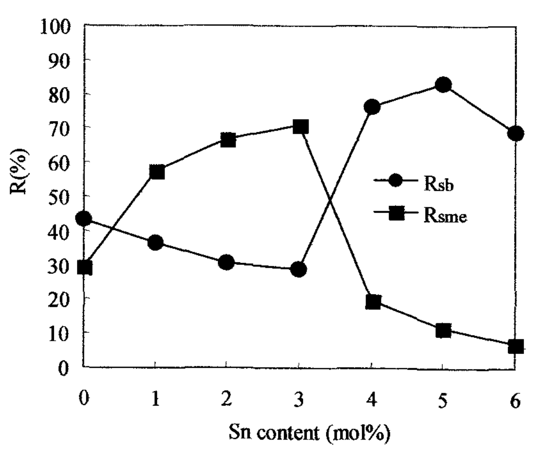

Fig. 1 Shape recovery properties estimated from convenient bending test in Ti-5Mo-XSn (X=0 – 6mol%) alloys.

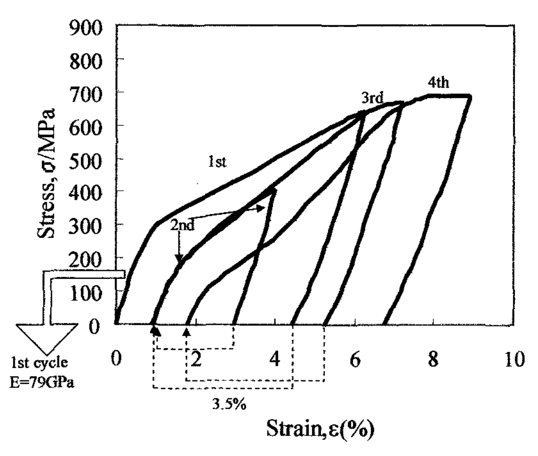

Fig. 2 Stress-strain curves obtained from cyclic tensile test in Ti-5Mo-3Sn alloy at room temperature. Broken lines indicated shape recovery with heating.

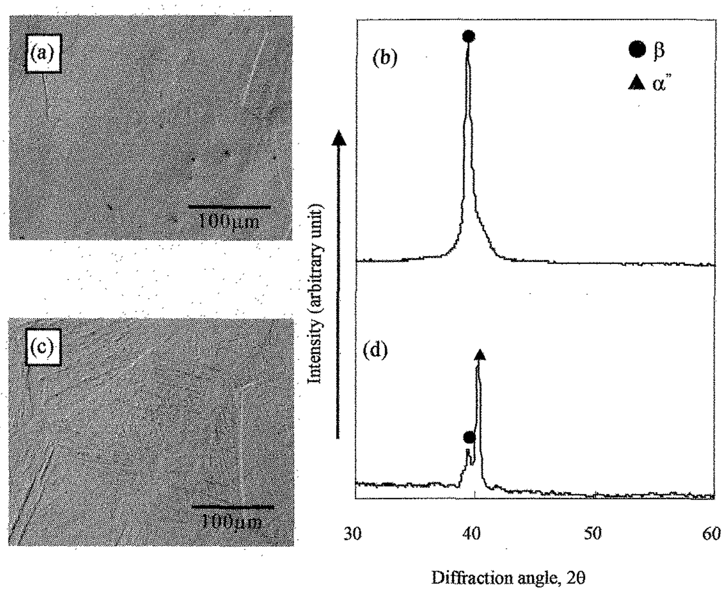

Fig. 3 Optical micrographs and X-ray diffraction profiles in Ti-5Mo-3Sn alloy, (a) and (b) before, and (c) and (d) after tensile deformation with 4% strain.

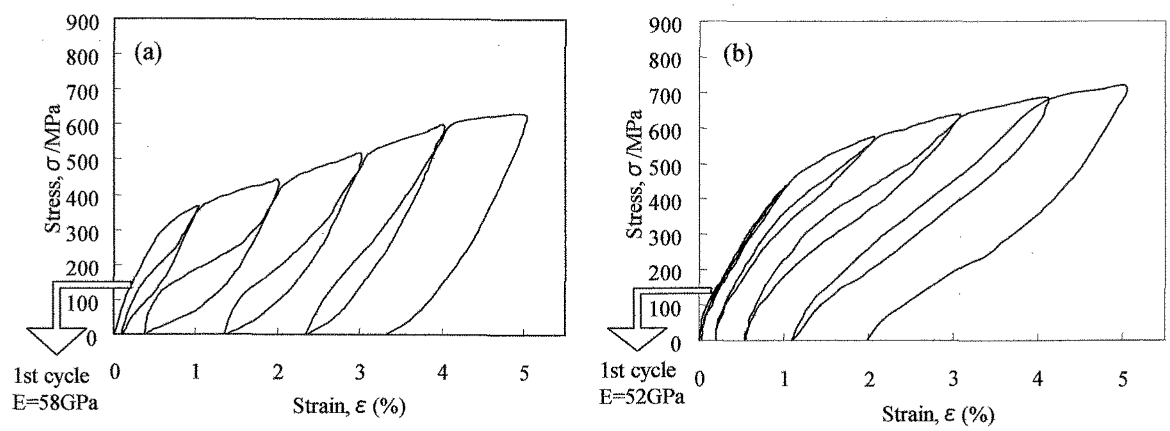

Fig. 4 Stress-strain curves obtained from cyclic tensile test in Ti-5Mo-4Sn (a) and Ti-5Mo-5Sn (b) at room temperature.

Ti-Mo-Sn alloys, a practical importance is to obtain superelasticity around body temperature. In order to obtain superelasticity at body temperature, the reverse martensitic transformation finish temperature should be below body temperature. From the results of convenient bending test in Fig. 1, the martensitic transformation temperature decreased with increasing Sn content and that of Ti-5Mo-4 and 5Sn is probably close to body temperature. Figs. 4 (a) and (b) show stress-strain curves of measured through cyclic tensile deformation of Ti-5Mo-4Sn and Ti-5Mo-5Sn alloys, respectively. In the curves of both alloys, the incomplete superelastic like reversion is clearly recognized upon unloading, but no large superelasticity has been obtained even in the both alloys. Young's modulus of Ti-5Mo-4Sn is 58GPa and that of Ti-5Mo-5Sn is 52GPa. These young's modulus values are lower than that of Ti-5Mo-3Sn.

In the recent result of Ti-Nb-Sn alloys, it has been reported that a short time aging at 873K, where ω phase never precipitated and the α laths were ready nucleate, accelerated the α" martensite formation. This phenomenon may be common in β-Ti alloys. Large superelasticity is obtained in the specimen aged at 873K, whose reverse martensitic transformation finish temperature is close to body temperature [2, 9]. Therefore, recovery ratio in Ti-5Mo-4Sn and Ti-5Mo-5Sn were evaluated with convenient bending test in various aging time at 873K as shown in Fig. 5. R_{sb} decreases with increasing aging time, although R_{sme} increases in Ti-5Mo-4Sn alloy as shown in Fig. 5 (a). The aging promotes not superelasticity but shape memory property in Ti-5Mo-4Sn alloy. In Fig. 5 (b), R_{sb} gradually increases with increasing aging time up to 300s and decreases in Ti-5Mo-5Sn alloy. Thus, the optimum aging condition to

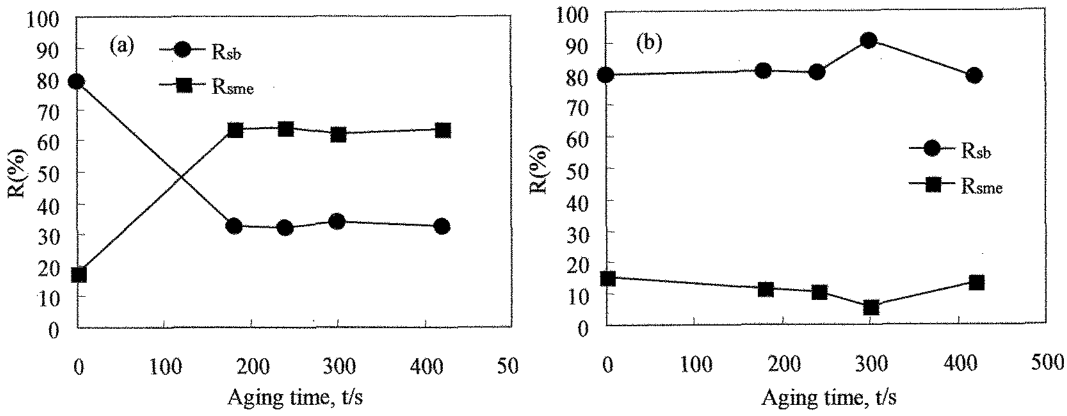

Fig. 5 Effect of aging time on shape recovery properties estimated from convenient bending test of Ti-5Mo-4Sn (a) and Ti-5Mo-5Sn (b).

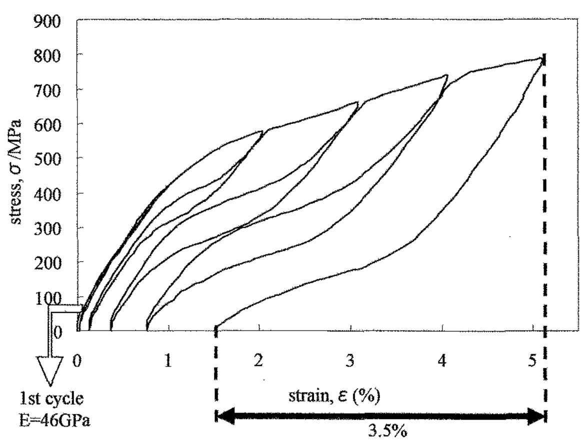

Fig. 6 Stress-strain curves obtained from cyclic tensile test at room temperature in Ti-5Mo-5Sn alloy aged at 873K for 300s after solution treated.

obtain superelasticity is at 873K for 300s in Ti-5Mo-5Sn alloy. The quantitative measurement of superelastic strain is performed in Ti-5Mo-5Sn alloy aging at 873K for 300s by cyclic tensile test as shown in Fig. 6. In the stress-strain curves, the superelastic like reversion is clearly recognized upon unloading. The recovery strain increases with increasing of applied strain. The maximum superelastic strain in the Ti-5Mo-5Sn alloy is 3.5%, where the applied strain in 5%, as shown in Fig. 6. Young's modulus of aged Ti-5Mo-5Sn is 46GPa. This value is lower than that of as solution-treated Ti-5Mo-5Sn alloy. It is concluded that Ti-Mo-Sn alloys are promising as a new biomedical shape memory and superelastic materials

4. CONCLUSIONS

Ti-Mo-Sn alloys for biomedical applications were developed and their shape memory property and superelasticity were investigated. The results are summarized as follows.

(1) The shape memory effect is obtained in most of the prepared alloys and Ti-5Mo-3Sn alloy exhibits the best performance.

(2) Martensitic transformation temperatures decrease with increasing Sn content. Martensitic transformation behavior is strongly influenced by aging. Large superelastic strain is obtained in Ti-5Mo-5Sn alloy aged at 873K for 300s.

(3) Microstructure and XRD profiles changes before and after tensile test revealed that the shape memory effect and superelastic behavior in Ti-Mo-Sn alloys is associated with stress induced β to α" martensitic transformation.

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