Effects of Sn Content and Aging Conditions on Superelasticity in Biomedical Ti–Mo–Sn Alloys*¹

Takashi Maeshima^{1,*2}, Satoshi Ushimaru^{1,*2}, Kiyoshi Yamauchi² and Minoru Nishida³

¹Graduate School of Science and Technology, Kumamoto University, Kumamoto 860-8555, Japan

²Biomedical Engineering Research Organization, Tohoku University, Sendai 980-8579, Japan

³Department of Materials Science and Engineering, Kumamoto University, Kumamoto 860-8555, Japan

The effects of Sn content and aging conditions on superelasticity in Ti–Mo–Sn alloys were investigated. Martensitic transformation temperature decreased with an increasing of Sn content. A large superelastic strain of 3.0% was obtained in a solution-treated Ti–5 mol%Mo–5 mol%Sn alloy in the tensile test. The superelasticity in the Ti–5 mol%Mo–5 mol%Sn at room temperature was improved by aging at 873 K for short periods between 180 and 420 s. A specimen aged at 873 K for 300 s exhibited superelasticity with a recovery strain of 3.5% in the tensile test. A recovery strain of 3.0% was consistently achieved in cyclic tensile deformations.

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1. Introduction

Among many shape memory alloys, only Ti–Ni alloys are now widely used and are still being developed as biomaterials such as orthodontic wire, teeth-root prosthesis, stent in blood vessels, because of their superior shape memory property and superelasticity. However, it has been suspected that pure Ni is a toxic element and causes Ni-hypersensitivity to the human body. Any suspicion should be eliminated in the biomedical applications. Although clear Ni-hypersensitivity to the human body in Ti–Ni alloys has not been reported yet, the development of absolutely safe Ni-free Ti-based shape memory alloys for biomedical applications has been required.

It is well known that quenching from β phase leads to the two martensitic transformations from the β (disordered bcc) phase to either α' martensite (hexagonal) and α'' martensite (orthorhombic) in β -type Ti-based alloys. It has been reported that the reverse transformation from the α'' phase to the β phase causes shape recovery to appear.¹⁾ Recently the ternary β -Ti alloy that exhibited the shape memory effect with this transformation was reported by many researchers.^{2–11)}

Biomedical shape memory alloys are required to have not only excellent shape memory effect but also biocompatibility¹²⁾ and superior corrosion resistance. The Ni-free ternary β -Ti alloys satisfy the above requirements. The present authors have systematically investigated the shape memory effect of Ti–Mo–X (X = Ag, Sc, Sn) and have confirmed the appearance of the superior shape memory effect.^{8–10)} However, superelasticity with the large recovery strain around human body temperature is necessary to apply the newly developed alloys to biomedical applications. We reported the possibility that superelasticity at body temperature appears at the amount of Sn contents more than 4 mol% in the Ti–5 mol%Mo–Sn alloys.⁸⁾ In the present study, in order to

develop Ni-free Ti-based biomedical superelastic alloys, the effects of Sn content and aging conditions on superelasticity in Ti–Mo–Sn alloys were investigated.

2. Experimental Procedure

Ti–5 mol%Mo–(0–6) mol%Sn ingots were arc melted in an Ar atmosphere using pure Ti (99.7 mass%), pure Mo (99.95 mass%) and pure Sn (99.9 mass%). Hereafter, Ti–5 mol%Mo–X mol%Sn is abbreviated to Ti5MoXSn. Weight changes after arc melting were negligibly small in the all alloys. The ingots were homogenized at 1373 K for 86.4 ks in vacuum, followed by hot and cold rolled into plate of about 0.4 mm in thickness with a final rolling ratio of 95%. Specimens with prescribed shapes were prepared by spark machining from the rolled plates. They were encapsulated in an evacuated quartz tube, solution-treated at 1273 K for 1.8 ks and quenched into iced water with breaking tube. Some specimens were aged in the temperature range between 623 and 873 K for various periods after the solution treatment and followed by quenched into iced water.

In order to evaluate the shape memory properties, the convenient bending test was carried out at room temperature. The specimens with a thickness of 0.3 (± 0.01) mm were deformed into a round shape ($= \phi 7$ mm) and heated up about 500 K. 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. In order to investigate the shape memory and superelastic characteristics quantitatively, cyclic tensile tests were carried out at room temperature by constant strain increment of 1% per a loading-unloading cycle under the initial strain rate of $4.16 \times 10^{-4} \text{ s}^{-1}$.

3. Results and Discussion

3.1 Effect of Sn content on superelasticity

Figure 1 shows results of the convenient bending tests in the Ti5Mo, Ti5Mo3Sn and Ti5Mo5Sn after the solution treatment at 1273 K for 1.8 ks. The incomplete shape memory

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*²Graduate Student, Kumamoto University

Fig. 1 Results of convenient bending and recovery test in Ti-5Mo, Ti-5Mo-3Sn and Ti-5Mo-5Sn alloys.

Fig. 2 Shape memory properties estimated from convenient bending test in Ti-5Mo-XSn (X = 0–6 mol%) alloys.

effect is obtained in the Ti5Mo. On the contrary, it is clearly seen that the perfect shape memory effect is obtained in the Ti5Mo3Sn. It is agreed with a former report showing that superior shape memory effect is exhibited in the Ti5Mo(2–3)Sn.⁸⁾ Large spring back is obtained after deformation in the Ti5Mo5Sn. However, little shape memory effect is exhibited after heating.

Shape recovery properties in the Ti5Mo(0–6)Sn estimated from the convenient bending tests are summarized in Fig. 2. Recovery ratio R_{sb} with spring back after deformation and R_{sme} with shape memory effect after heating are defined as follows, respectively;

$$R_{sb} = (\varepsilon_d - \varepsilon_s) / \varepsilon_d \times 100 (\%)$$

$$R_{sme} = (\varepsilon_s - \varepsilon_r) / \varepsilon_d \times 100 (\%)$$

In addition to R_{sb} and R_{sme} , the recovery ratio is defined as follows;

$$R_{tot} = R_{sb} + R_{sme} (\%)$$

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

The R_{sme} increases with increasing Sn content up to 3 mol% and then decreases with increasing Sn content up to 6 mol%. On the other hand, the R_{sb} decreases slightly with increasing Sn content up to 3 mol% and increases drastically with increasing Sn content up to 5 mol% and then decreases in 6 mol%Sn. It has been reported that martensitic transformation temperature decreases with increasing Sn content in the Ti-Mo-Sn⁸⁾ and Ti-Nb-Sn alloys.⁴⁾ These facts explain the result of the convenient bending test as follows. Shape memory effect and superelastic behavior was due to the rearrangement of martensite variants and stress induced martensitic transformation during deformation followed by the reverse transformation upon heating or unloading. The stress induced martensites were remained upon unloading, and then the shape is recovered with the $\alpha'' \rightarrow \beta$ reverse martensitic transformation by heating in the Ti5Mo(0–3)Sn. The R_{sb} increases drastically in the Ti5Mo(4–5)Sn. The reverse transformation probably happens because the start temperature for reverse transformation A_s is lower than the room temperature in addition to the recovery of elastic strain upon unloading. All R_{tot} shows a high recovery ratio more than 95% in the Ti5Mo(1–5)Sn, while the R_{tot} in the Ti5Mo is 73%. It is clear from the bending tests, the addition of Sn up to 5 mol% is effective to improve the shape memory effect and superelastic behavior in Ti5Mo. Both R_{sb} and R_{sme} decrease in the Ti5Mo6Sn, as a result R_{tot} is decreased rapidly. Permanent plastic deformation occurs because the finish temperature for reverse transformation A_f decreases far from the room temperature in the Ti5Mo6Sn. It is generally

Fig. 3 Stress-strain curves from cyclic tensile test in (a) Ti-5Mo-4Sn and (b) Ti-5Mo-5Sn alloys at room temperature.

Fig. 4 Effect of applied strain on superelasticity of (a) Ti-5Mo-4Sn and (b) Ti-5Mo-5Sn alloys.

accepted that superelasticity appears most significantly at a temperature about 20–30 K higher than A_f . Considering the results of convenient bending test and the decrease of transformation temperature with increasing Sn content, the suitable alloy composition to obtain a large superelastic strain at room temperature are the Ti5Mo4Sn or Ti5Mo5Sn. Therefore, the Ti5Mo4Sn and Ti5Mo5Sn were investigated hereafter.

Figure 3 shows the stress-strain curves obtained by loading and unloading cyclic tensile test at room temperature in the Ti5Mo(4–5)Sn. In the stress-strain curves of both alloys, the incomplete superelastic behavior was observed. Recovery strain with stress induced martensitic reverse transformation is denoted by ϵ_{SIMT} , total recovery strain with superelasticity is also denoted ϵ_{SE} as shown in Fig. 3(b). The ϵ_{SIMT} and ϵ_{SE} are plotted in Fig. 4 as a function of applied strain. The ϵ_{SIMT} increases with increasing applied strain up to 2% and then decreases in the Ti5Mo4Sn as shown in Fig. 4(a). The maximum superelastic strain ($= \epsilon_{SE}$) is 1.7%, where the applied strain is 5%. The ϵ_{SIMT} gradually increases with increasing applied strain up to 4% in the Ti5Mo5Sn as shown in Fig. 4(b). Finally, the maximum superelastic strain ($= \epsilon_{SE}$) is 3%, where the applied strain is 5%. From the above results, the optimum alloy composition to obtain a large superelastic strain at room temperature is

determined to be the Ti5Mo5Sn. This alloy is also expected to the improvement of the superelasticity by aging.

3.2 Effect of aging conditions on superelasticity

Acceleration of the α'' martensitic transformation by a short time aging at intermediate temperature, where ω phase never precipitated and the α laths were ready nucleated, was observed in a commercial β phase alloy Ti-10V-2Fe-3Al (by mass%).^{13,14} Superelasticity was improved by short time aging at 873 K after solution treatment in the β -type Ti-16Nb-4.9Sn alloy.⁴ These phenomena is probably common in β -Ti alloys. Thus, the Vickers hardness test and convenient bending test are performed in the Ti5Mo5Sn aged at 623–873 K. Figure 5 shows the Vickers hardness changes with the aging conditions. The HV value of specimens aged at 623, 673 K is higher than that of solution treated alloy because of the precipitation of thermal ω phase. The HV value increases slightly with an increasing aging time up to 60 s in the specimen aged at 773 and 873 K. It is supposed that a small amount of thermal ω phase which forms during heating to the aging temperature is not able to be resolved within 60 s. And then, the hardness decreased to the nearly same value of solution treated alloy. This well corresponds to the result in the Ti-10V-2Fe-3Al alloy. Therefore, the improvement of superelasticity by the aging in 773 and 873 K is expected.

Fig. 5 Changes in Vickers hardness with aging conditions in Ti-5Mo-5Sn alloys.

Fig. 6 Effect of aging time on shape recovery properties estimated from convenient bending test of Ti-5Mo-5Sn alloys.

The effect of short time aging at 773 and 873 K on superelasticity is investigated by the convenient bending test as shown in Fig. 6. There is little change in R_{sb} of the specimens aged at 773 K. On the other hand, the R_{sb} gradually increases with an increasing aging time up to 300 s and then decreases in the specimen aged at 873 K. Thus, optimum aging condition to obtain a large superelastic recovery strain is at 873 K for 300 s in the Ti5Mo5Sn.

The quantitative measurement of superelastic strain is performed in Ti5Mo5Sn aged at 873 K for 300 s by loading and unloading cyclic tensile test as shown in Fig. 7. It is understood that the superelastic behavior is clearly appeared upon unloading in comparison to the specimen solution treated as shown in Fig. 3(b). The maximum superelastic strain is 3.5%, where the applied strain is 5%. In order to clarify the effect of aging on superelasticity, the ϵ_{SIMT} and ϵ_{SE} are plotted in Fig. 8 as a function of applied strain. The ϵ_{SIMT} gradually increases with increasing applied strain up to 4% and decreases in the solution treated specimen. On the other hand, ϵ_{SIMT} consistently increases with increasing applied

Fig. 7 Stress-strain curves obtained from cyclic tensile test at room temperature in Ti-5Mo-5Sn alloy aged at 873 K for 300 s after solution treatment.

Fig. 8 Effect of applied strain on superelasticity of Ti-5Mo-5Sn alloy solution treated and aged at 873 K for 300 s after solution treatment.

strain in the aged specimen. It is clear in Fig. 8 that increase in ϵ_{SIMT} contribute to improve total recovery strain ϵ_{SE} in the aged specimen. The improvement of superelasticity by aging is attributable to the increment of recovery strain associated with the reverse transformation of stress induced martensite. The relationship between microstructure and improvement of superelasticity by aging should be investigated in detail. This is now under study and will be reported in due course.

Since the stability of superelasticity is very important for biomedical applications, the cyclic tensile test is performed in the Ti5Mo5Sn alloy aged at 873 K for 300 s. Figure 9 shows the stress-strain curves during loading and unloading cyclic tensile tests in the Ti5Mo5Sn aged at 873 K for 300 s. It is noted that the stable superelastic curves with recovery strain of 3% were obtained after the 5th cycles. The recovery strain of 3% is consistently obtained up to the 15th or more. It is concluded that the newly developed Ti-Mo-Sn alloys are promising as a substitute for Ti-Ni alloys in the biomedical field.

Fig. 9 Stress-strain curves of Ti–5Mo–5Sn alloy aged at 873 K for 300 s after solution treatment, where loading and unloading are repeated 15 times.

4. Conclusions

In order to develop biomedical shape memory and superelastic alloy, the effects of Sn content and aging conditions on superelasticity in biomedical Ti–Mo–Sn alloys were investigated. The obtained results are as follows;

- (1) The martensitic transformation temperature decreases with increasing Sn content. The addition of Sn to the Ti–Mo is effective to improve shape memory effect and superelastic behavior.
- (2) The superelasticity with a recovery strain of 3% is obtained in Ti–5Mo–5Sn alloy solution-treated at 1273 K for 1.8 ks.
- (3) The short time aging is effective to improve the superelasticity. The maximum superelastic strain of 3.5% and the stable superelastic strain of 3% are obtained in Ti–5Mo–5Sn alloy aged at 873 K for 300 s after solution treatment.
- (4) The recovery strain with stress induced martensitic transformation (ε_{SMT}) increases with increasing applied strain in Ti–5Mo–5Sn alloy. The amount of an increase ε_{SMT} in the aged alloy is large than that in the solution treated alloy, accordingly superelastic strain ε_{SE} has increased in the aged alloy.

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