Effects of Sn and Zr Additions on Phase Constitution and Aging Behavior of Ti-50 mass% Ta Alloys Quenched from β Single Phase Region*¹

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Using Ti-50Ta, Ti-50Ta-Sn and Ti-50Ta-Zr alloys, the effects of Sn and Zr additions on phase constitution in the solution treated and quenched state and aging behavior were studied by electrical resistivity and Vickers hardness measurements and X-ray diffractometry. All alloys were solution treated at 1173 K for 3.6 ks and then quenched into ice water (STQ). STQed specimens were isochronally aged at temperatures up to 1323 K in Ti-50Ta-Sn alloys and 1173 K in Ti-50Ta-Zr alloys. Shape recovery test was also performed in bent Ti-50Ta, Ti-50Ta-Sn and Ti-50Ta-Zr alloy specimens. In the STQed state, only reflections of orthorhombic α'' martensite were observed by XRD in Ti-50Ta and Ti-50Ta-4Sn alloys. In STQed Ti-50Ta-10Zr alloy, coexistence of α'' and β (bcc) phases were found by XRD. In STQed Ti-50Ta-8Sn and Ti-50Ta-20Zr alloys, only β phase was identified. In Ti-50Ta, Ti-50Ta-4Sn and Ti-50Ta-10Zr alloys, resistivity at liquid nitrogen temperature and resistivity ratio increased with isochronal aging up to a certain temperature. It is considered that these increases are due to reverse-transformation of α'' into metastable β phase. Shape-recovery test confirmed the shape memory effect of Ti-50Ta, 50Ta-4Sn and 50Ta-10Zr alloys.

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1. Introduction

In many developed countries, particularly in Japan, the proportion of the elderly population (persons aged 65 and above) is rapidly increasing.¹⁾ This worldwide trend is believed to result from progress in medical services and instruments. For example, the equipment used for replacement of failed hard tissue has developed significantly, and continues to advance steadily.²⁾

Fe-Cr-Ni austenitic stainless steels and NiTi shape memory alloys are used in these equipments because of their excellent corrosion resistance. However, nickel is highly toxic to the human body.³⁾ Thus, Ni-free stainless steels, Ti alloys, in particular β -Ti alloys and Ni-free shape memory alloys, have been developed. Many researchers actively investigated metastable β -Ti alloys with or without orthorhombic α'' -martensite using Nb, Ta, Zr and Sn as important non-toxic alloying elements. For instance, Ti-35.5Nb-5.1Ta-7.1Zr β alloy⁴⁾ and Ti-29Nb-13Ta-4.6Zr β alloy⁵⁾ were independently developed in the USA and Japan, respectively. Ti-Nb-Sn alloys are also studied as Ni-free shape memory alloys in Japan.⁶⁾

The present authors investigated the effect of Ta content on phase constitution and aging behavior of Ti-Ta binary alloys. Orthorhombic α'' -martensite was identified in Ti-40 and 50 mass% Ta alloys quenched from 1173 K. Reverse transformation of α'' -martensite to metastable β -phase was observed on isochronal aging. However, the reverse transformation started at a higher temperature than is acceptable for the human body. It is necessary to lower this starting temperature for biomedical applications. Although Sn is

widely regarded as α stabilizing additive in Ti alloys, Sn has recently been reported to lower the martensitic transformation temperature of Ti-Nb alloys.⁶⁾ Since β transus temperature decreases with increase of Zr content at the Ti rich side of Ti-Zr binary alloy, there is a possibility that Zr plays the role of the β stabilizer. The present study utilizes electrical resistivity and Vickers hardness measurements, X-ray diffractometry, and shape-recovery tests in investigating the effect of Sn and Zr additions on the phase constitution and aging behavior of a Ti-50 mass% Ta alloy with the ultimate goal of lowering the starting temperature of the reverse transformation of orthorhombic α'' -martensite.

2. Experimental Procedure

Ti-50 mass% Ta, Ti-50 mass% Ta-4 or 8 mass% Sn, and Ti-50 mass% Ta-10 or 20 mass% Zr (hereafter abbreviated as Ti-50Ta, Ti-50Ta-4Sn, Ti-50Ta-8Sn, Ti-50Ta-10Zr and Ti-50Ta-20Zr, respectively) were prepared in a laboratory-scale arc furnace under a high purity argon atmosphere from sponge Ti (99.8%), Ta powder (99.9%), Sn ingot (99.9%) and sponge Zr (99.5%) as raw materials. Button shaped ingots were hot-forged and hot-rolled to around 5-mm thick plates at about 1170 K. Table 1 shows alloy codes and chemical compositions of alloys. The specimens prepared from hot-rolled plates by cutting, grinding and polishing were

Table 1 Alloy code and chemical compositions (mass%) in alloys used.

Alloy code	Ta	Sn	Zr	O
50Ta	49.1	—	—	0.10
50Ta-4Sn	49.8	3.8	—	0.16
50Ta-8Sn	49.0	7.8	—	0.11
50Ta-10Zr	50.4	—	9.91	—
50Ta-20Zr	51.8	—	19.2	—

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encapsulated in quartz tubes under a roughly 3mPa atmosphere, solution-treated at 1173 K for 3.6 ks and quenched in ice water by breaking the quartz tubes (STQ).

STQed specimens were isochronally heat-treated for 3.6 ks at temperature intervals of 50 to 1323 K and 1173 K for the 50Ta-Sn and Ti-50Ta-Zr alloys, respectively. The isochronal aging helps estimate the phase transformation temperature during the heating process in Ti-50Ta-Sn and Ti-50Ta-Zr alloys.

Electrical resistivity was measured at room and liquid nitrogen temperatures (ρ_{RT} and ρ_{LN}), while Vickers hardness was measured only at room temperature using a 4.9N applied load. Phase constitution of all heat-treated specimens was determined by X-ray diffraction (XRD). Microstructures of STQed specimens were characterized by optical microscopy (OM) after mechanical polishing followed by etching with 5% HF, 25% HNO₃ and the balance H₂O.

Shape recovery tests were performed as follows: A number of specimens (about $1/30$ mm $\times$ 7 mm $\times$ 0.5 mm) were heat-treated at 1173 K for 3.6 ks, and then bent along the circumference of a round bar 25 mm in diameter. The bent specimens were heat-treated under appropriate conditions, *e.g.*, 673 K for 60 s. Radius of curvature of the specimens before and after heat treatment was measured by an image analysis software. Shape recovery ratio was calculated by the following equation:

$$\text{Shape recovery ratio (\%)} = (r_1 - r_0)/r_1 \times 100 \quad (1)$$

where r_0 and r_1 are the radii of curvature of the specimen before and after heat treatment, respectively.

3. Results and Discussion

Figures 1 and 2 show changes in resistivity at liquid nitrogen and room temperatures (ρ_{LN} , ρ_{RT}), the resistivity ratio (ρ_{LN}/ρ_{RT}), and Vickers hardness (HV) of STQed Ti-50Ta-Sn alloys and Ti-50Ta-Zr alloys as a function of Sn and Zr content, respectively. Phase constitution of each alloy is also shown in these figures. In Ti-50Ta and Ti-50Ta-4Sn, only reflections of orthorhombic α'' -martensite were identified by XRD. In Ti-50Ta-8Sn, only reflections of the β -phase were observed. In Ti-50Ta-Sn alloys, ρ_{LN} and ρ_{RT} increased monotonically with increasing Sn content due to dissolution of Sn into Ti-50Ta. ρ_{LN}/ρ_{RT} also increased monotonically with Sn content as a result of both the decrease in volume fraction of orthorhombic α'' -martensite and the increase in volume fraction of the metastable β -phase containing athermal ω . Though Sn dissolved in Ti-50Ta, HV showed a slight increase at 4 mass%Sn, remaining almost constant between 4 and 8 mass%Sn. The change in HV of the Ti-50Ta-Sn alloy is presumably caused by the decrease in volume fraction of α'' -martensite, the increase in volume fraction of the β -phase, and the decrease in volume fraction of athermal ω induced by the increase in Sn content. The present authors have obtained virtually the same results for Ti-Mo-Al alloys.⁷⁾ The above results revealed that the starting temperature of α'' -martensite transformation, M_s , is lowered by Sn addition. Thus, the stability of the β -phase presumably increases with the addition of Sn, even though Sn is a neutral additive in Ti alloys.

Fig. 1 Changes in ρ_{LN} , ρ_{RT} , ρ_{LN}/ρ_{RT} and HV of STQed Ti-50Ta-Sn with increase in Sn content.

Fig. 2 Changes in ρ_{LN} , ρ_{RT} , ρ_{LN}/ρ_{RT} and HV of STQed Ti-50Ta-Zr with increase in Zr content.

XRD revealed the presence of both the α'' - and β -phase in Ti-50Ta-10Zr, while only the β -phase was found in Ti-50Ta-20Zr. In Ti-50Ta-Zr alloys, ρ_{LN} increased monotonically with Zr content, while ρ_{RT} showed an increase at 10 mass%Zr, decreasing slightly at 20 mass%Zr. The ρ_{LN} change is due to dissolution of Zr in Ti-50Ta, while the ρ_{RT}

Fig. 3 Changes of ρ_{LN} , ρ_{RT} , ρ_{LN}/ρ_{RT} and HV of Ti-50Ta, 50Ta-4Sn and 8Sn alloys with increase of isochronal aging temperature.

change is caused by decrease in volume fraction of α'' , increase in volume fraction of the β -phase and decrease in volume fraction of athermal ω in the β -phase induced by the increase in Zr content. Resistivity ratio ρ_{LN}/ρ_{RT} increased monotonically with Zr content. HV showed a slight increase at 10 mass%Zr and a significant increase at 20 mass%Zr. The increase in HV is believed to be due to both solution hardening induced by Zr addition and the decrease in volume fraction of α'' that accompanies the increase in Zr content.

The above results suggest that M_s is lowered by Zr addition. Thus, the β -phase of the Ti-50Ta alloy is thought to be stabilized by the addition of Zr, a neutral additive in Ti alloys.

Figure 3 shows the variation in ρ_{LN} and ρ_{RT} , ρ_{LN}/ρ_{RT} and HV for Ti-50Ta, Ti-50Ta-4Sn and Ti-50Ta-8Sn as a function of isochronal aging temperature. In Ti-50Ta, ρ_{LN} and ρ_{RT} started to increase at 573 K, reaching a maximum at 623 K. The resistivity values then decreased up to 873 K, but increased again from 873 to 973 K. A plateau was observed at around 823 K in the resistivity-isochronal aging curve. Above 973 K, resistivity exhibited a gradual increase with temperature. The resistivity ratio during isochronal aging showed similar trends with temperature. HV started to increase at 623 K, reached its maximum at 723 K, and then decreased up to 973 K. A plateau was observed at around 873 K in the HV-isochronal aging curve as well. Above 973 K, HV remained almost constant.

In the case of Ti-50Ta-4Sn, ρ_{LN} started to increase at

523 K and reached a maximum at 573 K. Upon further heating, ρ_{LN} decreased up to 723 K; ρ_{RT} also decreased from 623 to 723 K. Resistivity increased at 773 K, and gradually decreased until the temperature reached 873 K. Above 873 K, ρ_{LN} gradually increased up to 1323 K, while ρ_{RT} increased slightly up to 973 K and remained almost constant from 973 to 1032 K. The ρ_{LN}/ρ_{RT} variation during isochronal aging corresponded almost exactly to the resistivity variation except for the slight increase in ρ between 723 and 773 K. HV started to increase at 623 K and, as in the case of Ti-50Ta, reached a maximum at 723 K. However, the maximum value was higher in the case of Ti-50Ta-4Sn. HV dropped sharply at 773 K, and continued to decrease gradually up to 973 K. Above 973 K, HV kept almost constant until 1323 K. In the case of Ti-50Ta-8Sn, practically no variation in ρ_{LN} , ρ_{RT} or ρ_{LN}/ρ_{RT} was observed during isochronal aging, while HV was found to increase slightly between 623 and 773 K.

Figures 4 and 5 show the variation in the X-ray diffraction profiles of Ti-50Ta and Ti-50Ta-4Sn, respectively, during isochronal aging. In the case of Ti-50Ta, a β_{110} reflection was clearly observed on aging at 673 K. On aging at 723 K, reflections of α'' disappeared, while the intensity of β_{110}

Fig. 4 Change of X-ray diffraction profile of Ti-50Ta alloy with isochronal aging.

Fig. 5 Change of X-ray diffraction profile of Ti-50Ta-4Sn alloy with isochronal aging.

peaks increased and some reflections of the isothermal ω phase were observed. In the case of Ti-50Ta-4Sn, aging at 573 K yielded a clearly visible β_{110} reflection. On aging at 673 K, reflections of α'' disappeared, while the β_{110} reflections intensified. XRD results suggest that the increase in resistivity of Ti-50Ta and Ti-50Ta-4Sn induced by aging at or below 673 K is due to reverse transformation of α'' -martensite into the metastable β -phase containing athermal ω . Similar results have been reported for Ti-Nb alloys by the present authors.⁸⁾ Furthermore, the temperature at which the resistivity begins to increase, *i.e.*, the starting temperature of reverse transformation, is lowered by Sn addition. This is consistent with the decrease in the starting temperature of martensitic transformation induced by Sn addition.

XRD reveals that the increase in HV and decrease in resistivity in Ti-50Ta are due to isothermal ω precipitation (Fig. 4). The plateaus in the HV- and ρ -isochronal curves are due to α precipitation (Table 2). The increase in HV in Ti-50Ta-4Sn is also caused by isothermal ω precipitation. However, no isothermal ω peaks were detected because volume fraction of isothermal ω precipitates is reduced by Sn addition. It is well-known that Sn addition suppresses isothermal ω precipitation as well as Al precipitation.⁹⁾

Figure 6 shows the variation of ρ_{LN} , ρ_{RT} , ρ_{LN}/ρ_{RT} , and HV in Ti-50Ta, Ti-50Ta-10Zr and Ti-50Ta-20Zr as a function of isochronal aging temperature. The curves for Ti-50Ta are identical to those in Fig. 3. In the case of Ti-50Ta-10Zr, ρ_{LN} and ρ_{RT} started increasing at 423 K and reached a maximum at around 523 K. Above 523 K, resistivity decreased with increasing isochronal aging temperature up to 723 K, increasing sharply at 773 K and decreasing slightly at 823 K. Resistivity increased again slightly at 873 K, remaining roughly constant above 873 K. The resistivity ratio followed virtually the same trends as the resistivity. HV started to increase at 523 K and reached a maximum at 723 K. HV then decreased with increasing isochronal aging temper-

Table 2 Summary of phase constitution of isochronally aged Ti-50Ta, 50Ta-4Sn, 50Ta-8Sn, 50Ta-10Zr and 50Ta-20Zr alloys by XRD at room temperature, except for 50Ta alloys isochronally aged at 523 K.

	50Ta	50Ta-4Sn	50Ta-8Sn	50Ta-10Zr	50Ta-20Zr
1173 K	α''	α''	β	$\alpha'' + \beta$	β
1123 K	α''	α''	β	$\alpha'' + \beta$	β
1073 K	α''	α''	β	$\alpha'' + \beta$	β
1023 K	α''	α''	β	$\alpha'' + \beta$	$\beta_1 + \beta_2$
973 K	α''	α''	β	$\alpha'' + \beta$	$\beta_1 + \beta_2$
923 K	α''	α''	β	$\alpha'' + \beta$	$\beta_1 + \beta_2$
873 K	$\alpha + \beta$	α''	β	$\alpha'' + \beta + \alpha$	$\beta_1 + \beta_2$
823 K	$\alpha + \beta$	α''	β	$\alpha'' + \beta + \alpha$	$\beta_1 + \beta_2$
773 K	$\beta + \omega$	α''	β	$\alpha'' + \beta$	β
723 K	$\beta + \omega$	$\alpha'' + \beta$	β	$\beta + \omega$	β
673 K	$\alpha'' + \beta$	$\alpha'' + \beta$	β	$\beta + \omega$	β
623 K	α''	$\alpha'' + \beta$	β	$\beta + \omega$	β
573 K	α''	$\alpha'' + \beta$	β	β	β
523 K	α''	α''	β	β	β
473 K	α''	α''	β	$\alpha'' + \beta$	β
373 K	α''	α''	β	$\alpha'' + \beta$	β
323 K	—	α''	β	$\alpha'' + \beta$	β
STQ	α''	α''	β	$\alpha'' + \beta$	β

Fig. 6 Changes of ρ_{LN} , ρ_{RT} , ρ_{LN}/ρ_{RT} and HV of Ti-50Ta, 50Ta-10Zr and 20Zr alloys with increase of isochronal aging temperature.

ature up to 923 K, above which it remained roughly constant at about 210 HV. This corresponds almost exactly to the values obtained for STQed specimens. Though ρ varied between 773 and 873 K, a clear plateau was not observed in the HV-isochronal aging curve. In the case of Ti-50Ta-20Zr, ρ_{LN} started to decrease at 423 K and reached a minimum at

Fig. 7 Change of X-ray diffraction profile of Ti-50Ta-10Zr alloy with isochronal aging.

around 473 K, above which it increased up to 573 K. However, no change in ρ_{RT} was observed in the same temperature range. ρ_{LN} started to decrease again at 523 K, while ρ_{RT} started to decrease at 673 K. ρ_{LN} and ρ_{RT} reached their minima at around 723 K and increased up to 823 K. Resistivity decreased again until 923 K and then increased up to 1073 K. Above 1073 K, resistivity remained almost constant. The resistivity ratio ρ_{LN}/ρ_{RT} varied in almost exactly the same manner as ρ_{LN} . HV began to increase at 523 K, reaching its maximum at 723 K. HV decreased from 723 to 1023 K. Above 1023 K, HV remained almost constant at about 250 HV.

Figures 7 and 8 show the variation in the X-ray diffraction profiles of Ti-50Ta-10Zr and Ti-50Ta-20Zr, respectively, during isochronal aging. In the case of Ti-50Ta-10Zr, β -phase peaks intensified on aging at 473 K. No α'' peaks were observed at 573 K, rather, isothermal ω peaks were observed. At 773 K, the ω peaks disappeared, while α'' peaks reemerged. α reflection was first identified at 823 K. XRD of Ti-50Ta-10Zr suggests that the increase in ρ_{LN} , ρ_{RT} and ρ_{LN}/ρ_{RT} between 373 K and roughly 523 K is due to reverse transformation of α'' into the metastable β -phase. Isothermal ω precipitation increased HV. However, it is believed that α precipitation did not result in precipitation hardening because HV decreased monotonically in the temperature range where the α -phase precipitated (Fig. 7 and Table 2).

In the case of Ti-50Ta-20Zr, though ρ , ρ_{LN}/ρ_{RT} , and HV all varied between 423 and 773 K, only β -phase peaks were

Fig. 8 Change of X-ray diffraction profile of Ti-50Ta-20Zr alloy with isochronal aging.

observed in this temperature range. The reasons for these results are not clear at present, but they may be ascribed to the decrease in isothermal ω -phase precipitates caused by Zr addition, in a similar manner to Al and Sn addition.⁸⁾ Phase separation of β into β_1 and β_2 was identified at 823 K; the separation became clear at 873 K. HV in Ti-50Ta-20Zr decreased more gradually than in Ti-50Ta and Ti-50Ta-10Zr between 823 and 923 K (Fig. 6). This gradual decrease is attributable to the phase separation of the β -phase. Phase constitutions identified by XRD in isochronally aged Ti-50Ta, Ti-50Ta-4Sn, Ti-50Ta-8Sn, Ti-50Ta-10Zr and 20Zr are summarized in Table 2. Table 2 shows that the phenomenon of reverse transformation of α'' -martensite was observed in Ti-50Ta, Ti-50Ta-4Sn and Ti-50Ta-10Zr, in order of decreasing transformation starting temperature. Thus, shape-recovery tests were performed on these alloys.

Figure 9 shows appearances of bent Ti-50Ta, Ti-50Ta-4Sn and Ti-50Ta-10Zr before and after heat treatment at appropriate temperatures. Figure 10 shows the variation in shape recovery ratio of bent Ti-50Ta, Ti-50Ta-4Sn and Ti-50Ta-10Zr specimens as a function of heat treatment temperature. The radius of curvature of each specimen was measured using image analysis software (Fig. 9). Based on these measurements, the shape recovery ratio was calculated using eq. (1). Shape recovery started at around 673 K in Ti-50Ta. Shape-recovery of Ti-50Ta-4Sn and Ti-50Ta-10Zr began at around 523 and 473 K, respectively. The maximum recovery ratios were about 70%, 60%, and 90% in the case of

Fig. 9 Appearances of bent Ti-50Ta, 50Ta-4Sn and 50Ta-10Zr alloys before and after heat treatment at appropriate temperatures.

Fig. 10 Change of shape recovery ratio of bent Ti-50Ta, 50Ta-4Sn and 50Ta-10Zr alloys with heat treatment temperature.

Ti-50Ta, Ti-50Ta-4Sn, and Ti-50Ta-10Zr, respectively. Thus, the present study revealed that Ti-50Ta-10Zr possessed the lowest shape recovery temperature and the highest maximum shape recovery ratio.

Figure 11 shows the relationship between aluminum equivalence, C_{EAL} , and shape recovery starting temperature, T_{SR} . The aluminum equivalence was calculated by using the following equation: $Al(\text{mass}\%) = Al(\text{mass}\%) + \{Sn(\text{mass}\%)\}/3 + \{Zr(\text{mass}\%)\}/6$.¹⁰⁾ Though there are only

Fig. 11 Relationship between aluminum equivalence, C_{EAL} and shape recovery starting temperature, T_{SR} .

three data points, these points tend to follow a highly linear relationship. Furthermore, when this linear relationship is extrapolated to 273 K, a C_{EAL} of approximately 3.3 mass% is obtained. Recalculation based on the C_{EAL} values yields Sn and Zr contents of about 9.9 mass% and 19.9 mass%, respectively. These values agree with the present results, particularly with those for Ti-50Ta-Zr alloys. Thus, starting temperature of shape recovery of Ti-50Ta-Zr alloys can be easily and accurately predicted by using Fig. 11.

4. Conclusion

Effects of Sn and Zr on phase constitution and isochronal aging behavior were investigated by electrical resistivity and Vickers hardness measurements, and X-ray diffractometry. Furthermore, shape recovery tests were performed on bent Ti-50Ta, Ti-50Ta-4Sn and 50Ta-10Zr specimens. The results were as follows:

Only orthorhombic martensite- α'' reflections were observed in Ti-50Ta and Ti-50Ta-4Sn. β reflections were only observed in Ti-50Ta-8Sn and Ti-50Ta-20Zr. The α'' and β dual-phase was identified in only Ti-50Ta-10Zr. Resistivity and resistivity ratio increased monotonically with the content of the second alloying additive, except in the case of the electrical resistivity of Ti-50Ta-20Zr. Vickers hardness of solution-treated and quenched samples was not changed significantly by the ternary addition, except in the case of Ti-50Ta-20Zr.

It was observed that resistivity and resistivity ratio of Ti-50Ta, 50Ta-4Sn, and 50Ta-10Zr increased because of reverse transformation of α'' into the metastable β -phase on isochronal aging below 673 K. In Ti-50Ta and Ti-50Ta-10Zr, Vickers hardness increased with isothermal ω precipitation. In Ti-50Ta-20Zr, isochronal aging-induced β -phase separation into $\beta_1 + \beta_2$ was detected by XRD. Starting temperature of reverse transformation of α'' was lowered in order of Ti-50Ta, Ti-50Ta-4Sn, and 50Ta-10Zr.

Shape recovery, *i.e.*, the shape memory effect, was observed in Ti-50Ta, Ti-50Ta-4Sn, and Ti-50Ta-10Zr. Starting temperature of shape recovery was lowered in order of Ti-50Ta, Ti-50Ta-4Sn, and Ti-50Ta-10Zr.

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