Effect of Al Addition on Superelastic Properties of Aged Ti–Nb–Zr–Al Quaternary Alloys

Hiroyuki Tada^{1,*}, Tokujiro Yamamoto², Xinmin Wang³ and Hidemi Kato³

¹Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan

²Department of Mechanical Systems Engineering, Utsunomiya University, Utsunomiya 321-8585, Japan

³Institute of Materials Research, Tohoku University, Sendai 980-8577, Japan

The effect of Al content on superelastic properties of $\text{Ti}_{75-x}\text{Nb}_{15}\text{Zr}_{10}\text{Al}_x$ ($x = 0\text{--}6$ at%) quaternary β Ti alloys were investigated. And the effects of baking for coating or plating on superelastic properties were also studied. The alloys containing 3 and 4 at% of Al clearly exhibited superelastic behavior after aging at 453 and 553 K, which are appropriate temperatures for industrial coating and plating, respectively. $\text{Ti}_{72}\text{Nb}_{15}\text{Zr}_{10}\text{Al}_3$ alloy exhibited the largest recovery strain of 2.5% due to superelastic behavior even after industrial coating and plating. In this quaternary alloy system, strange non-monotonical change of superelastic behavior as a function of Al content was also found.

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1. Introduction

Superelastic TiNi alloys have been widely used as high performance materials, such as orthodontic wires, antennas of mobile phones and eyeglass frames. However, β -Ti alloys attract more attention than TiNi alloys, because they possess biocompatibility in addition to superelastic property, shape memory effect and low Young's modulus.^{1–10)} In order to produce good superelastic β -Ti alloys, the change of mechanical properties as a function of aging temperature and period have been studied intensively.^{3,11–17)} In recent years, the effect of allergenic and toxic elements on the biocompatibility of superelastic β -Ti alloys has been also studied.^{13,18–24)} Through those studies, Hosoda *et al.* reported good superelastic properties of Ti–Nb-based alloys.^{12,25)} And, Niinomi *et al.* reported that Ti–Nb–Ta–Zr alloys exhibit good process-ability and low Young's modulus as a biomaterial.^{1,26–28)}

However, many β -Ti alloys reported so far were aged at much higher temperature than practical temperature for industrial coating and plating, because most studies have focused on how to obtain good superelastic or shape memory behavior. From viewpoint of apparel demand, eyeglasses should be painted or plated at various temperatures for decoration.

Therefore, in this study, the effect of Al content and low temperature aging was investigated to develop Ni-free β -Ti alloys showing superelastic behavior, which is not degraded even after practical coating and plating process.

2. Experimental Procedures

The nominal compositions of alloys investigated in this study are tabulated in Table 1. Al was substituted for Ti in $\text{Ti}_{75}\text{Nb}_{15}\text{Zr}_{10}$, thus the alloy composition is denoted as

Table 1 Nominal alloy compositions (at%) investigated in this study.

	Ti	Nb	Zr	Al
0Al	75	15	10	0
1Al	74	15	10	1
2Al	73	15	10	2
3Al	72	15	10	3
4Al	71	15	10	4
5Al	70	15	10	5
6Al	69	15	10	6

Fig. 1 Heat treatment performed to the arc-melted ingots.

$\text{Ti}_{75-x}\text{Nb}_{15}\text{Zr}_{10}\text{Al}_x$ ($x = 0\text{--}6$). Hereafter, these alloys are referred as 0Al–6Al. The ingots were prepared by arc-melting in an Ar atmosphere. Each ingot was melted 8 times.

Figure 1 schematically shows the history of heat treatment performed to the arc-melted ingots. Firstly, the arc-melted ingots were sealed in a vacuumed quartz tube for homogenization at 1373 K for 3.6 ks, then followed by quenching in water. Secondly, the ingots were cold-rolled up to 80% reduction until the thickness of the rolled plates was reduced to 1 mm. The specimens for tensile tests were punched out from the cold-rolled plates. More than six sets of specimens were obtained for each alloy composition. Then, the punched-out specimens were solution-treated at 973 K for 0.6 ks in vacuumed quartz tubes, followed by quenching in

*Corresponding author, E-mail: h.tada@charmant.co.jp. Graduate Student, Tohoku University. Present address: Charmant Inc., Sabae 916-0088, Japan

Fig. 2 Stress-strain curves of the $\text{Ti}_{75-x}\text{Nb}_{15}\text{Zr}_{10}\text{Al}_x$ specimens solution-treated at 973 K for 600 s. Specimens were subjected to tensile tests until failure.

Fig. 3 Stress-strain curves of the $\text{Ti}_{75-x}\text{Nb}_{15}\text{Zr}_{10}\text{Al}_x$ specimens solution-treated at 973 K for 600 s. Specimens were subjected to loading-unloading tensile tests where the strain was no more than 4%.

water. Finally, some of the specimens were aged for 3.6 ks at 453 and 553 K. After those heat treatments, the oxidized surface of the specimens was removed by chemical etching or mechanical polishing at room temperature. The solution for etching was H_2O , HNO_3 and HF (5 : 4 : 1).

Those specimens were characterized by X-ray diffraction (XRD) using $\text{Cu K}\alpha$ radiation to identify the composing phases. Simple tensile tests were first performed for some solution-treated specimens without aging until failure to measure ultimate tensile strength, σ_{max} . The aged specimens were subjected to loading-unloading tensile tests using a strain gauge extensometer at room temperature, where a strain rate was at $5 \times 10^{-4} \text{ s}^{-1}$, to observe superelastic or shape memory behavior. The cross section of the gage was $1 \text{ mm} \times 2 \text{ mm}$, and the gage length was 10 mm. The microstructure was studied using transmission electron microscope (TEM) at an accelerating voltage of 200 kV for solution treated specimen and aged specimen. Specimens for TEM observations were prepared by twin-jet polishing using an electrolyte solution of 6 vol% perchloric acid and 94 vol% methanol.

3. Results and Discussions

3.1 The solution-treated specimens

Figure 2 shows the stress-strain curves of the $\text{Ti}_{75-x}\text{Nb}_{15}\text{Zr}_{10}\text{Al}_x$ specimens solution-treated at 973 K for 0.6 ks, measured by the simple tensile tests. σ_{max} of each alloy increased with increasing Al content. For 0Al, 1Al and 2Al specimens, the increasing rate of the stress was approximately 75 MPa per 1 at%Al. The rate for 3Al to 6Al specimens is considerably smaller than that for 0Al to 2Al. It should be noted here that all the specimens in Fig. 2 yielded twice before the stress reached σ_{max} . There are many reports that the β -type Ti alloys exhibits a stress induced martensitic transformation from parent phase (β : body centered cubic) to martensite phase (α' : orthorhombic).²⁹⁻³⁵ It has also been reported that the shape memory effect and the superelastic behavior of β -type Ti alloys are related to the transformation.^{6,35-38} Therefore, the first yielding in these specimens were induced by martensitic transformation, thus this

Fig. 4 σ_{max} , σ_{M} , σ_{re} of the $\text{Ti}_{75-x}\text{Nb}_{15}\text{Zr}_{10}\text{Al}_x$ specimens.

yield stress is denoted as σ_{M} hereafter. The second yield stress, σ_{y} , is of the specimen consisting of stress-induced martensite phase.

In order to observe superelastic and shape memory behavior precisely, other solution-treated specimens were also subjected to loading-unloading tensile tests where the strain was no more than 4%. The stress-strain curves for loading-unloading tests were also shown in Fig. 3. σ_{M} increased monotonically with increasing Al content. The specimens with Al content of more than 4 at% exhibited superelastic behavior. 6Al specimen also exhibited superelastic behavior, but the amount of recovery strain was smaller than specimen 4Al and 5Al. Both shape memory effect and slight superelastic behavior were exhibited for 3Al specimen. For those specimens exhibiting superelastic behavior, the reverse transformation stress, σ_{re} , also increased with increasing Al content.

Figure 4 summarizes σ_{max} , σ_{M} and σ_{re} , shown in Figs. 2 and 3. For less than 2 at%Al, σ_{max} increased with increasing Al content. However, σ_{max} was almost stable for the specimens with Al content of more than 2 at%. On the

Fig. 5 XRD patterns of the $\text{Ti}_{75-x}\text{Nb}_{15}\text{Zr}_{10}\text{Al}_x$ specimens solution-treated at 973 K for 600 s.

contrary, σ_M increased with increasing Al content without saturation. As a consequence, σ_M was comparable to $\sigma_{\max}$ for 6Al specimen. Thus, it is expected that stress induced martensitic transformation is not observed for the specimen with Al content more than 7 at% Al, because the specimen yields before the tensile stress reaches σ_M . For 0Al, 1Al and 2Al specimens, σ_{re} could not be measured because reverse martensitic transformation temperature is higher than room temperature. Thus, it is implied that the specimens show shape memory effect when Al content is no more than 2 at%. For 3Al specimen, σ_{re} was measured at just above 0 MPa stress. Therefore, the M_s temperature of 3Al specimen was estimated to be near room temperature. This is the reason the 3Al specimen exhibited both shape memory effect and superelastic behavior at room temperature.

Figure 5 shows the XRD patterns of the solution-treated specimens. The diffraction peaks of both α'' -Ti and β -Ti phases were observed in those patterns of 0Al, 1Al, 2Al and 3Al alloys. However, the amount of the α'' -Ti phase decreases with increasing Al content, as the intensity of the diffraction peaks of the α'' -Ti phase becomes low. Specimens with Al content of more than 4 at% consisted of almost only of the β -Ti phase. These results roughly coincide with the loading-unloading tensile tests performed to the solution-treated specimens as shown in Fig. 3.

In this study, σ_M increased with increasing Al content at room temperature for the solution-treated specimens. This result implies that martensitic transformation start temperature decreases with increasing Al content. The transition temperature from α to β for Ti alloy was changed by addition of alloying element. Al has been classified as α stabilizer because it raises the transformation temperature. However, there are some report have shown the influence of Al addition as a β stabilizer.^{39–41)} Our implication agrees with the results that martensitic transformation start temperature decreases with increasing the content of the ternary element added to Ti–Nb-based alloys.

3.2 Effects of aging corresponding to coating and plating

The loading-unloading tensile tests were conducted to investigate the effects of aging corresponding to coating and plating on superelastic properties. The specimens with Al content of 2 to 5 at% were chosen, because 3Al and 4Al

specimen exhibited good superelastic property among all the specimens in this study. Some of these specimens were aged at 453 K for 3.6 ks, representing industrial coating condition. Other specimens were aged at 553 K for 3.6 ks, representing industrial plating condition.

The stress–strain curves obtained by the loading-unloading tests are shown in Fig. 6. 2Al specimen exhibited superelastic behavior after aging at 453 K, however, the behavior was not observed for 2Al specimen aged at 553 K. 5Al specimen, which exhibited superelastic behavior before aging, lost the behavior after aging. In contrast, 3Al and 4Al exhibited superelastic behavior after aging. Among those specimens, 3Al specimen after aging at 453 K showed the best superelastic behavior with about 2.5% of recovery strain.

As far as the specimens were aged in the same condition, the superelastic behavior should monotonically depend on the Al content. However, only 3Al and 4Al specimens exhibited superelastic behavior by aging at 453 and 553 K, while 2Al and 5Al specimens did not. In addition, it is noticed that the stress for martensitic transformation (σ_M) of 3Al and 4Al specimens decrease with increasing the aging temperature. Superelastic behavior is observed when reverse martensitic transformation temperature is lower than room temperature. Martensitic transformation temperature and reverse martensitic transformation temperature of β -Ti alloys depends on the composition of the β -Ti phase and the morphology of the ω phase often precipitating in the β -Ti phase.^{3,13,14,42)} It has been also reported that the ω phase was suppressed by Al addition.³⁹⁾

TEM bright field images taken along $[110]_\beta$ orientation were shown in Fig. 7. Figures 7(a) and 7(b) show the microstructure of the specimen solution-treated at 973 K for 0.6 ks and aged at 553 K for 3.6 ks, respectively. The corresponding selected area electron diffraction (SAED) patterns are also shown in the insets for each micrograph. Figure 7(c) indicates the key diagram of the diffraction spots of the β and ω phases. In addition to the primary diffraction spots from the β matrix, clear extra spots at $1/3 \{112\}$ positions representing the ω phase was observed in the SAED pattern of the specimen aged at 553 K. This indicates that the increase of σ_M after aging at 553 K is due to the precipitating the thermal ω phase. It could be suggested that the precipitation of ω phase was suppressed more by the addition of Al for 3Al and 4Al specimen compared with 2Al specimen. In other word, the aging was much more sensitive to 2Al specimen than to 3Al and 4Al specimen. Unfortunately, the microstructure inducing the unique change in superelastic properties by aging $\text{Ti}_{72}\text{Nb}_{15}\text{Zr}_{10}\text{Al}_3$ specimen has not been observed yet.

Q. Li *et al.* has reported that the first yielding stress (σ_M) remain stable at 380 MPa in $\text{TiNb}_{24}\text{Zr}_2$ alloy aged at 573 K for 7.2, 10.8 and 14.4 ks.¹⁴⁾ They described this phenomena is related with the balance of two phenomena. One is suppression of β matrix extent and the other is increasing the amount of β stabilizing elements. Both phenomena were caused by the aged ω phase precipitation. H. Y. Kim *et al.* has reported that dispersed ω particle mechanically suppress the martensitic transformation.¹¹⁾ J. song *et al.* has reported that Ti–9.8Mo–3.9Nb–2V–3.1Al (mass%) alloy lost a superelastic behavior when the alloy was aged at 473–523

Fig. 6 Stress-strain curves of (a) solution-treated specimens, (b) specimens aged at 453 K for 3.6 ks and (c) specimens aged at 553 K for 3.6 ks.

Fig. 7 Bright field TEM micrographs and the corresponding SAED patterns of (a) the solution-treated $\text{Ti}_{72}\text{Nb}_{15}\text{Zr}_{10}\text{Al}_3$ specimen and (b) the specimen aged at 553 K for 3.6 ks. (c) Key diagram of the diffraction spot of the β and ω phases.

and 773–823 K. Even though the alloy demonstrated the superelastic behavior after aging at 673, 873, 973 K.⁴³⁾ They estimated that the phenomena related to a precipitating and coarsening of α and ω phase. However, the effects of aging temperature of these specimens are still not clear completely yet. In order to detailed investigation, long period aged

specimens are preparing. Thus, it is expected to precipitate the microstructure clearly which is considered to cause this strange phenomena. This non-monotonical change of superelastic behavior as a function of Al content and aging temperature is still under investigation and will be discussed elsewhere.

4. Conclusions

Ti–Nb–Zr–Al alloys which exhibit superelastic behavior after industrial coating and plating were developed, and their mechanical properties were investigated.

3Al (Ti₇₂Nb₁₅Zr₁₀Al₃) and 4Al (Ti₇₁Nb₁₅Zr₁₀Al₄) specimens exhibited superelastic behavior even after aging at industrial coating and plating temperature, 453 and 553 K, while other specimens did not. The largest recovery strain due to superelastic behavior was about 2.5% and was observed for 3Al specimen.

The superelastic behavior of the Ti–Nb–Zr–Al alloys after aging did not change monotonically as a function of Al content. Superelastic behavior could not be observed after aging at 453 and 553 K for 2Al and 5Al specimens. Only 3Al and 4Al specimens exhibited superelastic behavior after aging in the same condition.

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