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The Influence of Aluminum Content on Shape Memory Effect of Ti–7Cr–Al Alloys Fabricated Using Low Grade Sponge Titanium

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In this study, the influence of aluminum content on shape memory effect of Ti–7Cr–Al alloys fabricated using low-grade sponge titanium was investigated by measurement of electrical resistivity and Vickers hardness, along with shape-recovery testing. The results obtained are as follows.

In the STQed state, the phase constitution of non-Al added alloy, Ti–7Cr–0Al alloy, was found to consist of retained β phase and athermal ω, whereas those of Al added alloys, Ti–7Cr–1.5Al, 3.0Al and 4.5Al alloys, were found to consist of orthorhombic martensite, α'', and retained β phase. Resistivity (ρ) at liquid nitrogen (LN) and room temperature (RT) increased monotonously with Al content. Resistivity ratio (ρ_{LN}/ρ_{RT}) increased drastically at 3Al, exceeding unity.

Shape recovery was exhibited in the 1.5Al, 3.0Al, and 4.5Al alloys having been fabricated using low-grade sponge titanium as raw material. In the 3.0Al and 4.5Al alloys, shape recovery ratio was about 90% at temperatures above 523 K and recovery surface strain was at least 0.03. The resistivity change indicates that stress-induced orthorhombic martensite was produced during bending of the 4.5Al alloy.

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Keywords: *shape memory effect, low grade sponge titanium, orthorhombic martensite, metastable beta phase, electrical resistivity, reverse transformation*

1. Introduction

In many developed countries, especially Japan, the proportion of elderly in the population is increasing rapidly;[1] the ratio in Japan became 20% in September, 2004.[1] In view of this, priority must be placed on improving medical techniques and developing medical equipment. For applications in welfare and healthcare, it is also important to develop high-performance equipment along with new materials. Titanium and its alloys are attractive materials for these applications.[2] Some titanium alloys of orthorhombic martensitic structure exhibit shape memory effect and pseudoelasticity.[3] These properties are very important in medical, welfare, and healthcare applications. A shape memory effect has been confirmed in Ti–Cr–Al system alloys subjected to suitable heat treatment and with suitable phase constitution. The influence of aluminum content on shape memory effect should be investigated in detail.

In this study, the influence of aluminum content on the shape memory effect of Ti–Cr–Al alloys prepared from low-grade sponge titanium was investigated by measurement of electrical resistivity and Vickers hardness, and by X-ray diffractometry and shape-recovery testing. It is expected that a cost reduction of about 30% for Ti–7%Cr–Al alloys can be obtained by using low grade sponge titanium.[4]

2. Experimental Procedures

Ti–7 mass%Cr–0, 1.5, 3.0, and 4.5 mass%Al alloys (hereafter, abbreviated as 0Al, 1.5Al, 3.0Al, and 4.5Al) were prepared in a laboratory-scale arc furnace under a high-purity argon gas atmosphere using low-grade sponge titanium, Cr (99.99%) granules, and Al (99.999%) granules as raw materials. The alloys were melted repeatedly 4 times in order to eliminate the segregation of alloying elements. The composition of low-grade sponge titanium is shown in Table 1. The iron content of low-grade sponge titanium is higher than that of ELI grade sponge titanium. The major cause of the contamination is migration of Fe from the reduction vessel.[5] Although low-grade sponge titanium contains a small amount of Ni, about 100 mass ppm, the harmful influence on the human body is expected to be very low. Compositions of all alloys are shown in Table 2. As compared with the remaining alloys, the 0Al alloy has a lower Cr content. Although the reason for this is not clear, one of the causes may be spatter loss of Cr granules during arc melting in producing this alloy. Although the oxygen content of the alloys was not analyzed, it is estimated to be about 0.1 to 0.15 mass%, in view of the fact that the oxygen content of the low-grade sponge titanium is 0.065 mass%, which is slightly higher than the oxygen content of ELI-grade sponge titanium.[6]

Button shaped ingots were hot-forged and rolled into plates to a thickness of about 5 mm. All specimens were prepared by cutting from the hot-rolled plates and mechanical polishing.

Table 1 Impurity contents of low grade sponge titanium (mass ppm).

Fe	Cr	O	N	C	Al	Cl	Ni	Mn
2670	260	650	240	150	630	20	100	60

Table 2 Alloy code and chemical composition of alloys used (mass%).

Alloy code	Cr	Al	Fe
0Al	5.97	<0.1	0.18
1.5Al	7.09	1.50	0.18
3.0Al	7.02	3.05	0.40
4.5Al	6.99	4.55	0.28

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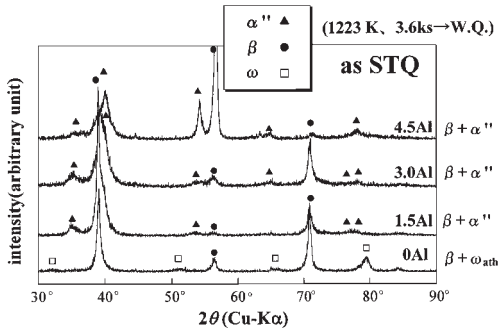

Fig. 1 X-ray diffraction profiles of Ti–7Cr–0, 1.5, 3.0 and 4.5Al alloys in STQed state.

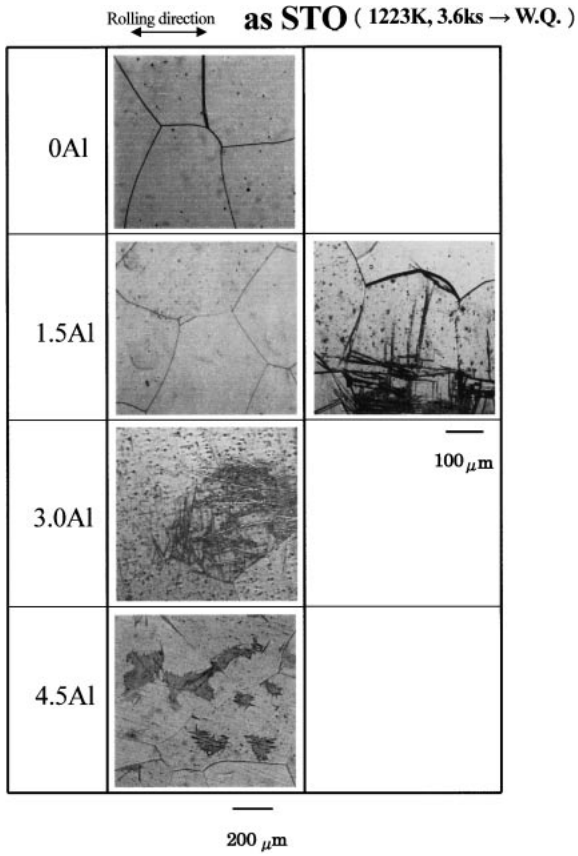

Fig. 2 Optical micrographs of Ti–7Cr–0, 1.5, 3.0 and 4.5Al alloys in STQed state.

All specimens were encapsulated in quartz tubes under a pressure of about 3 mPa. The specimens sealed in the tubes were solution-treated at 1223 K for 3.6 ks and then quenched in ice water by breaking the quartz tubes (STQ).

Electrical resistivity of these heat-treated and STQed specimens was measured at liquid nitrogen (ρ_{LN}) and room temperatures (ρ_{RT}) by the direct current 4-contact method employing a digital potentiometer. In order to avoid thermo-electromotive force at the contacts, voltages of the specimen and standard resistance were measured at positive and negative polarities of the electrical current. Vickers hardness (HV) was measured under an applied load of 4.9 N. X-ray diffraction (XRD) and optical microscopy (OM) were employed to identify the phase constitution.

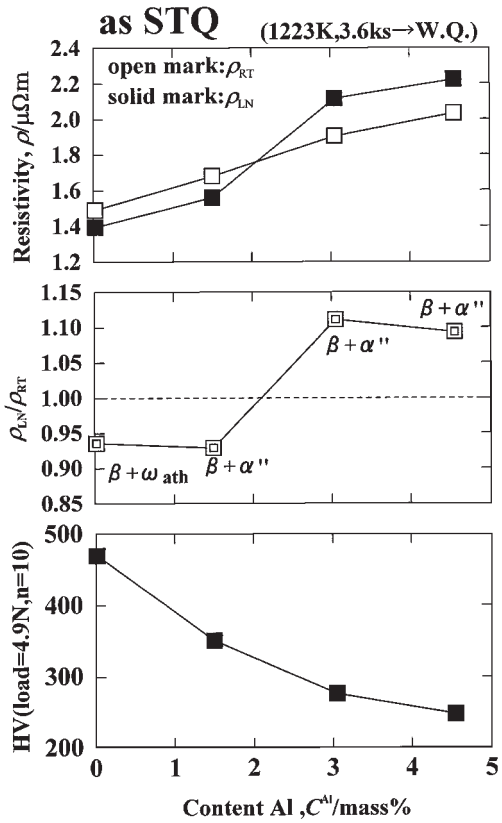

Fig. 3 Changes of resistivity (ρ_{LN} and ρ_{RT}), resistivity ratio (ρ_{LN}/ρ_{RT}) and Vickers Hardness (HV) of Ti–7Cr–Al alloys with increase of Al content in STQed state.

Shape recovery testing was performed on 1.5Al to 4.5Al alloys with orthorhombic martensite, α'', as follows. The specimens were cold-rolled (to about 0.5 mm thickness) and STQed (1223 K, 3.6 ks → W.Q.) again. They were then bent against a round bar (ϕ10 mm) at room temperature. Bent specimens were heat-treated at a suitable temperature for 60 s. The radius of curvature of the bent specimens before and after heat treatment was measured using an image analyzer. The shape recovery ratio was calculated from the surface strain eq. (2), which in turn was calculated from the radius of curvature eq. (1).

$$\text{Surface strain, } \varepsilon = d/2r \quad (1)$$

where d is the specimen thickness and r is the radius of curvature.

$$\text{Shape recovery ratio, R}(\%) = (\varepsilon_0 - \varepsilon_1)/\varepsilon_0 \times 100 \quad (2)$$

where ε_0 and ε_1 are the specimen surface strain before and after heat treatment, respectively.

Recovery surface strain was calculated by the following equation: $\varepsilon_R = \varepsilon_0 - \varepsilon_1$ (3)

A bent 4.5Al alloy was repeatedly subjected to isochronal heat treatment for 60 s at temperatures up to 723 K, in increments of 50 K. This heat treatment is a useful method, in that any phase transformation that occurs on heating can be easily detected. Resistivity at LN and RT and surface strain were measured after each isochronal heat treatment by the method described above.

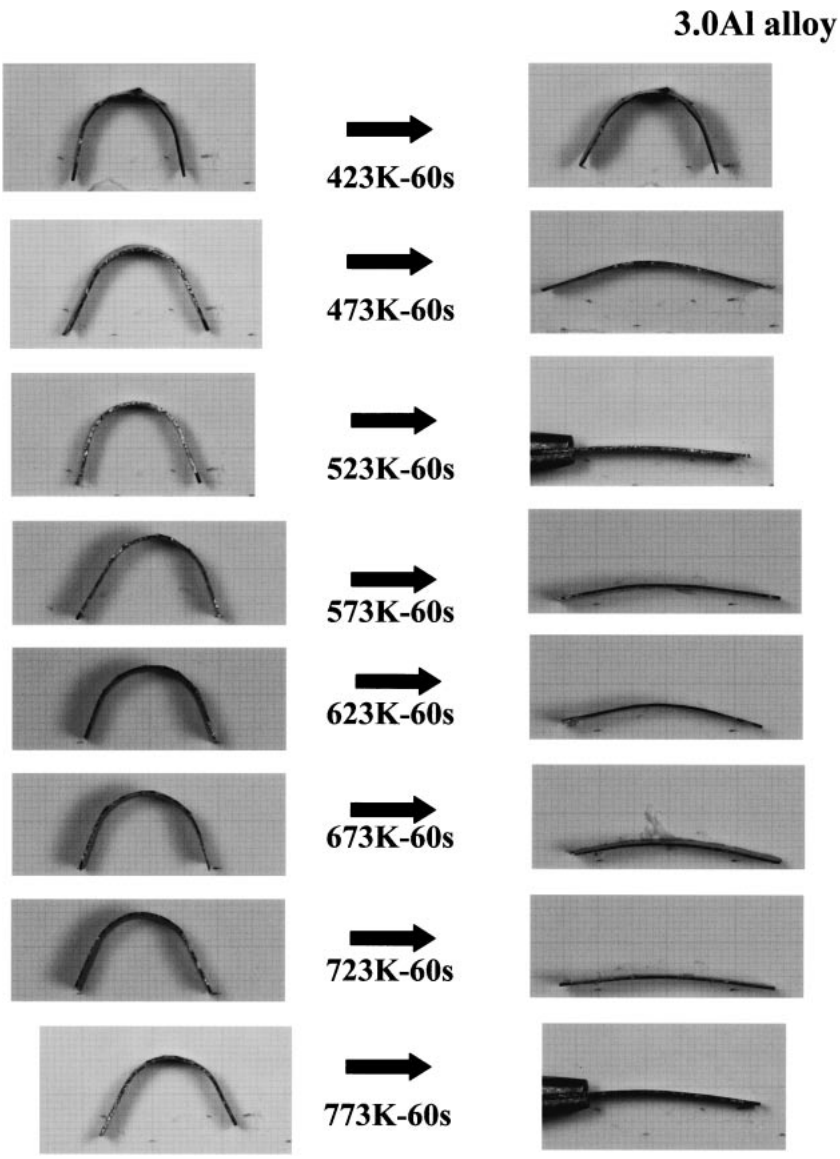

Fig. 4 Appearances of bent 3.0Al specimen in as-bent and in heat treated states, respectively.

3. Results and Discussion

Figures 1 and 2 show profiles of X-ray diffraction and optical microstructures, respectively, in the STQed state. In the 0Al alloy, peaks of retained β phase and athermal ω were identified, whereas in the 1.5Al and 4.5Al alloys, peaks of retained β phase and orthorhombic martensite, α'', were identified. In the 1.5Al, 3.0Al, and 4.5Al alloys, an acicular structure that originated in martensite was partially observed by optical microscopy, whereas no acicular structure was observed in the 0Al alloy. In the 1.5Al alloy, acicular structure was only observed near the edge of the specimen. Although the reason for this is not clear, the same structure has been observed in other titanium alloys.[7)]

Figure 3 shows changes in resistivity at liquid nitrogen and room temperatures (ρ_{LN} and ρ_{RT}), resistivity ratio, or ρ_{LN} divided by ρ_{RT} (ρ_{LN}/ρ_{RT}), and Vickers hardness (HV) with increasing Al content. Resistivity at room and liquid nitrogen temperatures increased monotonously with Al content. These increases are due to dissolution of Al in Ti. In the 3.0 and 4.5Al alloys, resistivity at liquid nitrogen temperature was higher than that at room temperature. Therefore, the resistivity ratios of these alloys exceeded unity. Vickers hardness decreased with increasing Al content, without indication of solution-hardening. The reason why solution-hardening was not observed is that addition of Al resulted in formation of orthorhombic martensite, α'', and a decrease in volume fraction of athermal ω.

The 1.5Al, 3.0Al, and 4.5Al alloys were subjected to a shape recovery test, whereas the 0Al alloy was broken during bending. Although the cause of the 0Al alloy breaking during bending is not clear, one factor is likely to be the higher HV (about 550HV) compared to the Al added alloys.

Figures 4 and 5 show examples of the shape recovery tests for the 3.0 and 4.5Al alloys, respectively. In the 3.0Al and 4.5Al alloys, shape recovery started at 423 K, and above 523 K the bent specimen almost completely recovered its original shape. In the 3.0Al alloy, above 573 K, the specimen is slightly curved, especially at 623 K. In the 4.5Al alloy, the specimen after 623 K treatment for 60 s is also slightly

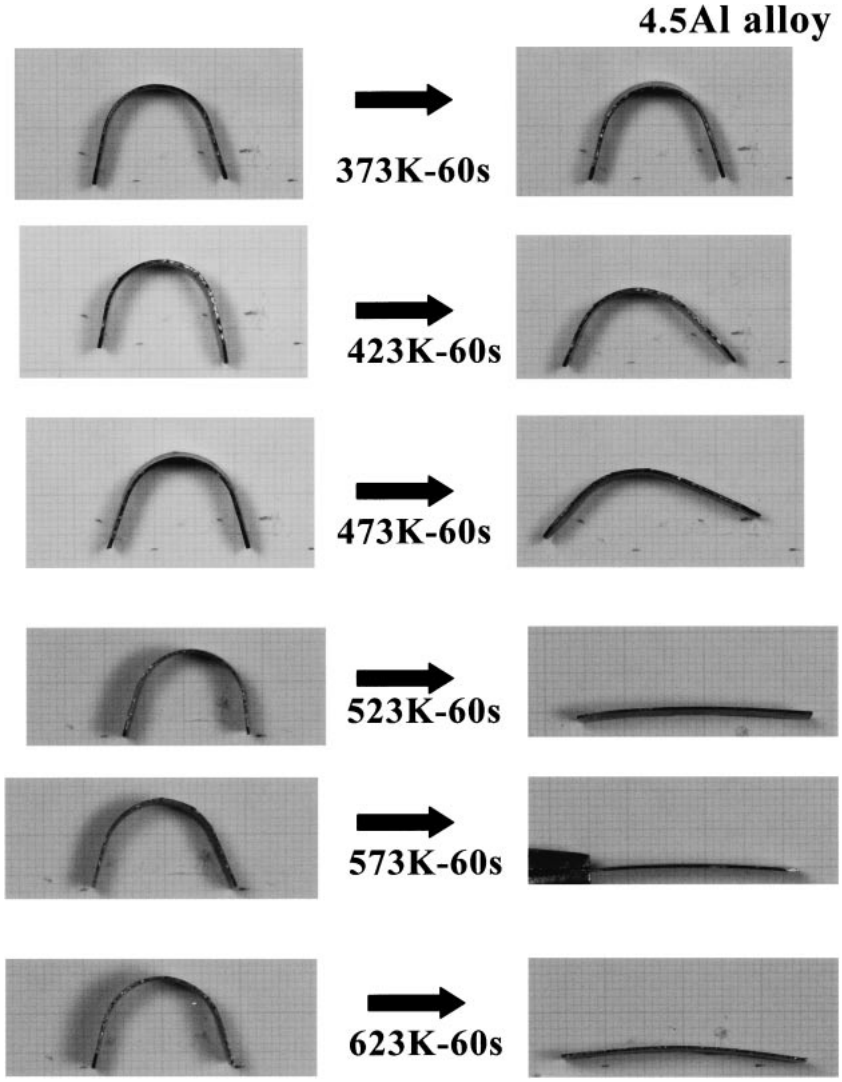

Fig. 5 Appearances of bent 4.5Al specimen in as-bent and in heat treated states, respectively.

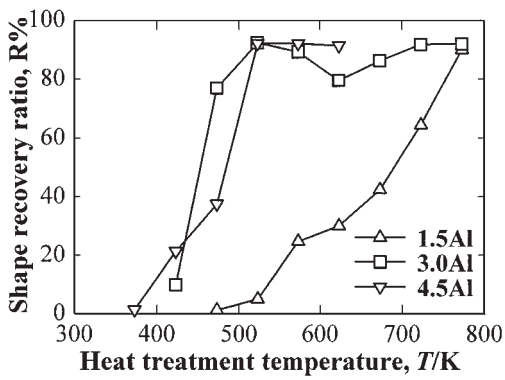

Fig. 6 Relationships between shape recovery ratio and heat treatment temperature in 1.5, 3.0 and 4.5Al alloys.

curved. Figure 6 shows the relationship between shape recovery ratio and heat treatment temperature in the three Al-added alloys. All alloys showed about a 90% shape recovery ratio; at 773 K in the 1.5Al alloy and at 523 K in the 3.0 and 4.5Al alloys. Lowering of the 90% recovery temperature is due to a decrease in the finish temperature of the reverse transformation of orthorhombic martensite, α'', to the β phase with increasing Al content. In general, start and finish temperatures of martensite transformation of the Ti alloys decrease with increasing Al content.[8)]

Figures 7 and 8 show changes in surface strain and shape recovery ratio of the 3.0Al and 4.5Al alloys in heat treatment with increasing temperature. Surface strains of both alloy specimens in the as-bent state are also shown in these figures. In the 3.0Al and 4.5Al alloys, the surface strain in the as-bent state was not a constant value; *e.g.* in the 4.5Al alloy, surface strain in the as-bent state decreased with heat treatment temperature. However, this phenomenon is not related to heat treatment temperature; after bending of the specimens, the shape recovery test was performed on a specimen that had been chosen at random from all the bent specimens. The reason why surface strain in the as-bent state was not constant is that the deformation force was not constant, because this deformation was performed by hand. Surface strains of as-bent specimens fall within the range of 0.035 to 0.040. In the 3.0Al alloy, after heat treatment above 523 K, the surface strain was about 0.03; therefore, the recovery strain was about 0.03 and above. In the 4.5Al alloy, after heat treatment

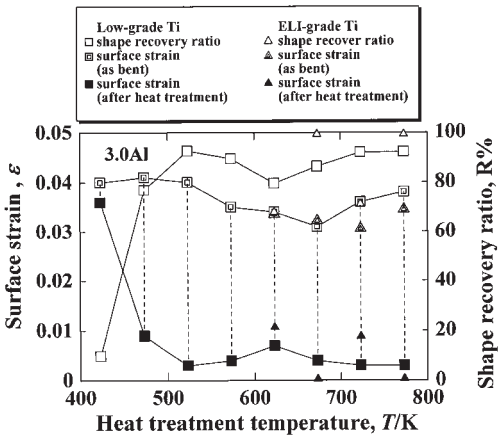

Fig. 7 Changes in surface strain and shape recovery ratio of 3.0Al alloy in heat treated state with increase of heat treatment temperature. Surface strains of specimen in as bent state are also shown in this figure. Furthermore, those surface strains and shape recovery ratio of Ti–7Cr–3.0Al alloy prepared from ELI-grade sponge titanium are shown in this figure, too.

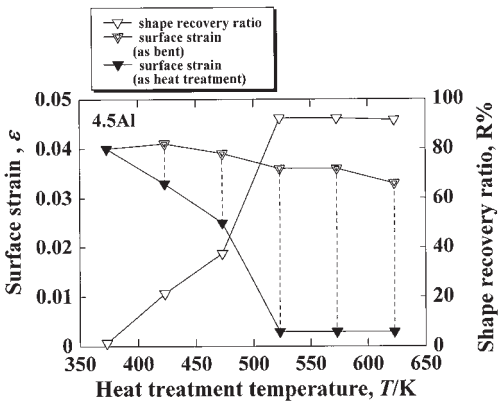

Fig. 8 Changes in surface strain and shape recovery ratio of 4.5Al alloy in heat treated state with increase of heat treatment temperature. Surface strains of specimen in as bent state are also shown in this figure.

above 523 K, surface strain became about 0.003; therefore, recovery strain was about 0.03. In the 1.5Al alloy, recovery strain was a value of 0.03 to 0.04 (results not shown). Thus, in the 1.5Al, 3.0Al, and 4.5Al alloys, recovery surface strain is at least 0.03. Furthermore, although these alloys had been prepared from low-grade sponge titanium, the shape memory effect of these alloys is comparable with that of Ti–Cr–Al system alloys prepared from ELI-grade sponge.[5] For example, as shown in Fig. 7, the shape recovery ratio and surface strain of the 3.0Al alloy prepared from low-grade sponge Ti in the as-bent state and the heat treated state are almost equal to those of the 3.0Al alloy prepared from ELI-grade sponge Ti, indicated by triangles in the figure. When the iron content increases above a certain value, it is expected that the shape memory effect will not appear, although the structure includes α'' and β phases.

To investigate phase transformation of a bent specimen, the electrical resistivity of a bent 4.5Al specimen was measured by isochronal heat treatment up to 723 K under the

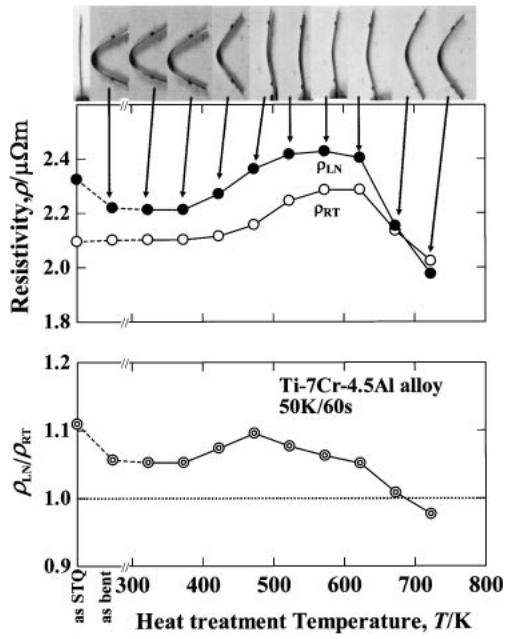

Fig. 9 Changes in resistivity (ρ_{LN} and ρ_{RT}), resistivity ratio (ρ_{LN}/ρ_{RT}) of shape-recover test 4.5Al specimen with increase in temperature of heat treatment (50 K/60 s). Change in appearance of 4.5Al specimen with increase in temperature of heat treatment is also shown in this figure.

same heat treatment conditions as employed in the shape recovery test. The results are shown in Fig. 9. Resistivity at LN (ρ_{LN}) and resistivity ratio (ρ_{LN}/ρ_{RT}) decreased drastically under bending. The reason why these values decreased is that stress- or strain-induced α'' martensite was formed by bending.[9,10] If only dislocations were introduced by bending, resistivity would have increased because of the increased probability of electron scattering by dislocations. The resistivity ratio started to increase at 423 K, which is the start temperature of reverse transformation of orthorhombic martensite, α''. The maximum value of resistivity at LN is larger than that in the as-STQed state. This result suggests that heat treatment reversely transformed into the beta phase both α'' martensite that had been transformed during quenching and that which had been stress- or strain-induced. A very interesting phenomenon of shape change was observed above 623 K: the specimen began to bend to the as-bent shape. The same phenomenon has previously been observed in Ti–Mo system alloys and reported by some investigators.[10] The reason why bent specimens of the 3.0Al and 4.5Al alloys were curved slightly after heat treatment at temperatures above 623 K is considered to be the same reason for the change in shape of the bent specimen with increasing isochronal heat treatment temperature above 623 K. In the same temperature range at which this interesting shape change was observed, resistivity at LN and RT and the resistivity ratio decreased drastically. These decreases are thought to be due to precipitation of isothermal ω as a result of the isochronal heat treatment. The mechanism of the reverse bending is not yet clear. This phenomenon is probably attributed to strain fields of isothermal ω precipitation. However, further investigation is necessary.

4. Conclusions

Using Ti–7Cr–Al alloys prepared from low-grade sponge titanium, the influence of Al content on shape memory effect was studied by measurement of electrical resistivity and Vickers hardness, and by X-ray diffractometry and shape-recovery testing.

In the STQed state, phase constitutions of the Al added alloys, Ti–7Cr–1.5Al, 3.0Al, and 4.5Al, were found to consist of orthorhombic martensite, α'', and retained β phase. Resistivity at LN and RT was found to increase monotonously with Al content. The resistivity ratio (ρ_{LN}/ρ_{RT}) increased drastically at 3Al and exceeded unity.

Shape recovery was observed in the 1.5Al, 3.0Al, and 4.5Al alloys having been fabricated using low-grade sponge titanium as raw material. In the 3.0Al and 4.5Al alloys, the shape recovery ratio was about 90% at temperatures above 523 K and the recovery surface strain was at least 0.03. The resistivity change revealed that stress-induced orthorhombic martensite was produced during bending of the 4.5Al alloy.

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