Isothermal Martensitic Transformations in an Aged Ni-Rich Ti–Ni Alloy Containing Coherent Ti₃Ni₄ Particles

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The time dependence nature of B2 (ordered cubic) to R (trigonal) and R to B19' (monoclinic) martensitic transformations in an aged Ni-rich Ti–Ni alloy was investigated by electrical resistivity measurements. Both B2 to R and R to B19' transformations exhibit time dependence nature in the aged alloy containing coherent lenticular Ti₃Ni₄ precipitates with an average diameter of about 110 nm. However, the successive B2-R-B19' isothermal transformation is not detected by electrical resistivity measurements. The isothermal R-B19' transformation is visualized by *in situ* scanning electron microscopy (SEM) observations. [doi:10.2320/matertrans.MT-MJ2019004]

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1. Introduction

The isothermal B2-B19', B2-R, and R-B19' martensitic transformations in Ti–Ni based alloys have been investigated in several studies.^{1–6} The kinetics of these three transformations was examined by Kustov *et al.* for Ti–50.2Ni and Ti–48Ni–2Fe (at%) alloys with various heat treatments.² They reported that the B2-B19' and R-B19' transformations have isothermal nature, whereas the B2-R transformation does not. Fukuda *et al.* found that the B2-B19' transformation in Ti–51.2 and 51.3Ni (at%) alloys and the B2-R transformation in Ti–44Ni–6Fe (at%) alloy are isothermal.^{3,4,6} These three alloys consisted of a B2 single phase quenched from 1273 K. Ji *et al.* reported that the isothermal B2-R transformation takes place in the Ti–51.3Ni (at%) alloy with holding above the martensite start temperature (M_s) of the B2-B19' transformation.⁵

Shape memory and superelastic properties have been improved by the precipitation strengthening of Ti₃Ni₄ particles.⁷ The successive B2-R-B19' transformation occurs in Ni-rich Ti–Ni alloys containing Ti₃Ni₄ particles.⁷ However, there are no reports of whether the B2-R and R-B19' transformations in aged Ni-rich Ti–Ni alloys have isothermal nature. In the present study, we investigate the time dependence nature of B2-R and R-B19' transformations in an aged Ni-rich Ti–Ni alloy containing coherent Ti₃Ni₄ particles. *In situ* scanning electron microscopy (SEM) observations are also performed to visualize the progress of the isothermal R-B19' transformation.

2. Experimental Procedure

An ingot of the Ti–51.0Ni (at%) alloy of nominal

composition was prepared by an arc melting method and remelted several times to ensure homogeneity. The ingot was heat-treated at 1273 K for 38.4 ks in a vacuum and quenched into ice water. Rectangular plates (10 × 2 × 0.2 mm) for electrical resistivity measurements and square plates (3 × 3 × 1 mm) for differential scanning calorimetry (DSC) and SEM were cut from the ingot and solution-treated at 1173 K for 3.6 ks in a vacuum with pure Zr as a getter metal, followed by quenching into ice water. The plates were aged 773 K for 3.6 ks in the same atmosphere used for the solution treatment to avoid the multistage martensitic transformation (MMT)^{8–10} and quenched into ice water. The surface of each specimen was electropolished in an electrolyte of methanol and sulfuric acid (4:1 v/v) around 273 K.

The electrical resistivity was measured by the four-probe method with a current of 100 mA and a frequency of 17 Hz. The specimen for the resistivity measurement was mounted on a Cu stage using Apiezon N grease, and the temperature of the stage was monitored throughout the measurements. The overshoot and undershoot of the temperature before isothermal holding was within 200 mK, and the fluctuation of the temperature during holding was within 10 mK. The DSC measurements were made in the temperature range between 353 and 123 K with a cooling and heating rate of 5 K min^{–1}. The characteristic temperatures of the transformation events were determined by the extrapolation method from the electrical resistivity and DSC curves. A field-emission SEM (ULTRA 55, ZEISS) equipped with an annular backscattered electron (BSE) detector and a Peltier stage (Coolstage, Deben) with a working temperature of 220–320 K were used for the *in situ* SEM observations.^{9–11} The temperature stability of the Peltier stage was about 200 mK during isothermal holding.

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3. Results and Discussion

There were two exothermic peaks derived from the B2-R and R-B19' transformations in the DSC curve of the aged alloy upon cooling. The starting temperatures of B2-R and R-B19' exothermic reactions were 289 and 238 K, respectively. These temperatures agree well with those estimated from the electrical resistivity measurements as described later. In contrast, a single endothermic peak was observed upon heating because of the difference in thermal hysteresis between the B19'-R and R-B2 transformations.^{7–10} The results confirm that there was no MMT^{8–10} in the present aged specimen.

Figure 1 shows the electrical resistivity curves measured with a cooling and heating rate of 2 K min⁻¹. During cooling, the resistivity started to gradually increase at 307 K, and then

Fig. 1 Temperature dependence of the electrical resistivity of a Ti-51.0Ni alloy aged at 773 K for 3.6 ks after solution treatment at 1173 K for 3.6 ks.

drastically increases at 290 K. The first increase corresponds to the starting temperatures of the B2-R exothermic reaction in the DSC cooling curve. There is a large decrease in resistivity from about 238 K due to the R-B19' transformation. These results are consistent with the DSC results. Figure 2 shows SEM-BSE images of the aged specimen. The average grain size of the parent B2 phase is about 20 μm in diameter (Fig. 2(a)). The lenticular Ti₃Ni₄ precipitates of about 110 nm in average diameter are homogeneously distributed around the grain boundary (Fig. 2(b)) and grain interior (Fig. 2(c)). There is no large-scale microstructural heterogeneity in the precipitation morphology, distribution and size, which is responsible for the MMT.^{8–10,12–14}

To detect the isothermal B2-R transformation, the specimen was held at set temperatures for 3.6 ks after cooling from 330 K at a rate of 2 K min⁻¹ in each holding cycle (Fig. 3(a)). There is an increase in resistivity during holding at 287 K (blue dots and line), and a transformation hysteresis of approximately 3 K between cooling and heating curves. The increase in resistivity and narrow hysteresis within 5 K are characteristic features of the B2-R transformation. These results suggest that the isothermal B2-R transformation proceeds during holding at 287 K. Figure 3(b) shows the results of isothermal holding experiments at set temperatures for 3.6 ks. $\Delta\rho$ is the difference in the electrical resistivity values between the start of the measurement and an arbitrary time at the set temperatures. The other set temperatures were 294, 280, 270, 265, 260, 255, and 250 K. The increase in resistivity is clearly observed between 294 and 270 K. Therefore, the isothermal B2-R transformation proceeds in this temperature range. However, there is no

Fig. 2 (a) Low-magnification SEM-BSE image. (b), (c) Enlarged SEM-BSE images taken from areas B and C in (a), showing the homogenous distribution of Ti₃Ni₄ precipitates around the grain boundary and interior.

Fig. 3 (a) Temperature dependence of the electrical resistivity of the aged specimen. Results of isothermal holding experiments at 294, 287, 280, 270, 265, 260, 255, and 250 K. The specimen was heated to 330 K, cooled to each temperature at a rate of 2 K min^{-1} , and then held for 3.6 ks. (b) Time dependence of electrical resistivity during holding at the temperatures indicated in (a).

change in resistivity between 265 and 250 K. The successive B2-R-B19' isothermal transformation is not detected above 250 K.

Figure 4(a) shows the results of isothermal holding experiments at set temperatures for 3.6 ks. The heating, cooling, and holding procedures were the same as those of the B2-R transformation. There was no thermal cycle effect, namely, no decrease in transformation temperatures of the B19' martensite as discussed later, because the Ti₃Ni₄ particles suppress the dislocation formation during the transformation cycles.^{1,15,16} The set temperatures were 246, 244, 242, 240, 238, and 228 K. The vertical decrease in each of the resistivity curves at the set temperatures is due to the progress of the R-B19' transformation during the holding. Figure 4(b) shows the time dependence of $\Delta\rho$ of the specimen at the set temperatures. The size and rate of the

resistivity change increase with as the set temperature is lowered above the R-B19' transformation start temperature of 238 K, whereas they decreased at 228 K. The resistivity started to decrease as soon as the holding started at all the set temperatures. This suggests that the transformation occurs without detectable incubation time in the aged specimen, although Fukuda *et al.* reported an incubation time in the isothermal B2-B19' transformation in quenched Ti-51.3 (at%) alloy.⁶ After the isothermal holding at 228 K and subsequent heating to 330 K in Fig. 4(a), the cyclic isothermal holding experiments at 238 K were completed 10 times. Figures 5(a) and (b) shows the result of first and tenth cycles, respectively. The size and rate of the resistivity change in Figs. 5(a) and (b) are fairly identical to those at 238 K in Fig. 4(a). It is confirmed that there is no thermal cycle effect upon the cyclic isothermal holding experiments.

Fig. 4 (a) Temperature dependence of the electrical resistivity of the aged specimen. Results of isothermal holding experiments at 246, 244, 242, 240, 238, and 228 K for 3.6 ks. (b) Time dependence of the electrical resistivity during holding at the temperatures indicated in (a).

Thus, the present results are sufficiently reliable and reproducible for investigating the isothermal R-B19' transformation.

It is hard to discuss directly and quantitatively the differences and similarities of the time dependence nature of transformations in solution treated and aged alloys, since it is difficult to prepare and adjust the solution treated and aged alloys with the same B2-R and R-B19' transformation temperatures. Comparing Fig. 3 in the present study with Figs. 2 and 3 in the Ref. 4), the resistivity increment size and rate in the present aged alloy held at 287 K is larger than that in the solution treated Ti-44Ni-6Fe held at 150 K.⁴⁾ These temperatures were located at the middle point of the starting and finishing temperatures of abrupt resistivity change with negative temperature coefficient. Comparing Fig. 4 in the present study with Figs. 1 and 2 in the Ref. 3), the resistivity decrement size and ratio with the R-B19' transformation in the aged alloy held at 238 K for 3.0 ks is quite larger than those with B2-B19' transformation in the solution treated Ti-51.2 Ni held at 155 K for 3 ks.³⁾ The former temperature was the same as the starting temperatures of R-B19' exothermic reactions in the aged alloy as mentioned above. The latter one was 1 K lower than the starting temperatures of B2-B19' exothermic reactions in the solution treated alloy.³⁾ These facts suggest that both the isothermal transformations are easy to progress in the aged alloy with coherent precipitates.

Fig. 5 Results of cyclic isothermal holding experiments at 238 K. (a) First cycle. (b) Tenth cycle. See text in details.

In other words, the coherent strain and/or stress between precipitates and matrix play an important role in the acceleration of isothermal transformations.

Figures 6(a)–(d) show a series of *in situ* SEM-BSE images during isothermal holding at 240 K, which is 2 K higher than the R-B19' transformation start temperature shown in Fig. 1. The distribution and size of the Ti_3Ni_4 precipitates were homogeneous between the grain boundary and the grain interior (Figs. 2(a)–(c)), although the precipitates were not visible in the low-magnification images. There are non-metallic inclusions with dark contrast at the grain boundary on the left-hand side. The energy-dispersive X-ray analysis identifies the inclusion as $\text{TiC}(\text{O})$.¹⁷⁾ The R-phase transformation was also not visible because its transformation strain is small compared with those of the B2-B19' and R-B19' martensitic transformations. After holding for 1.8 ks, the B19' phase appears as bright contrast^{9,10)} at the grain interior and boundary (arrows, Fig. 6(b)). Upon continuous holding for up to 10.8 ks, the amount of martensitic phase increases with increasing holding time (Figs. 6(c) and (d)). These observations clearly show that the R-B19' transformation exhibits time dependence nature in an aged Ni-rich Ti-Ni alloy containing coherent particles of Ti_3Ni_4 from the metallographic point of view. So far as we know, the present results are the first visualization of isothermal nature of R-B19' transformation in Ti-Ni alloys, although there are coherent precipitates in the matrix.

In summary, the present results confirm that both B2-R and R-B19' martensitic transformations in an aged Ni-rich Ti-Ni alloy have isothermal nature, although the effect of coherency

Fig. 6 Series of *in situ* SEM-BSE images during isothermal holding at 240 K for (a) 0, (b) 1.8, (c) 3.6, and (d) 10.8 ks. Arrows indicate the B19' phase.

between precipitates and matrix on the isothermal behaviors should be further investigated in details.

4. Conclusions

The time dependence nature of B2 to R and R to B19' martensitic transformations in an aged Ni-rich Ti–Ni alloy containing coherent lenticular Ti_3Ni_4 precipitates with an average diameter of about 110 nm was investigated by electrical resistivity measurements and *in situ* SEM observations. The results are summarized as follows:

- (1) The starting temperatures of B2–R and R–B19' transformations were 289 and 238 K, respectively.
- (2) The isothermal B2–R transformation proceeds between 294 and 270 K. The successive B2–R–B19' isothermal transformation is not detected by electrical resistivity measurements between 265 and 250 K.
- (3) The isothermal R–B19' transformation occurs below 246 K without detectable incubation time. The time dependence nature of R–B19' transformation is clearly visualized by *in situ* SEM observations. The isothermal B19' phase nucleates at both grain interior and boundary.

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