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Transformation sequence in severely cold-rolled and annealed $Ti_{50}Ni_{50}$ alloy

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Abstract

Transformation sequence of $Ti_{50}Ni_{50}$ shape memory alloy after 35% cold-rolling and subsequent recrystallization annealing have been investigated. Four transformation sequences of Stages I–IV on different annealing conditions are proposed. Stage I corresponds to an incomplete transformation, whereas Stage II represents the four-step MST with two large and two small peaks associated with $B2 \rightarrow R \rightarrow B19'$ transformation of large grains in the specimen center and that of small grains near the rolling surface, respectively. Stages III and IV are the complete $B2 \leftrightarrow R \leftrightarrow B19'$ and $B2 \leftrightarrow B19'$ transformation sequences, respectively.

Keywords: Shape memory alloy; Martensitic transformation sequence; Cold working; Annealing; Differential scanning calorimetry

1. Introduction

It is well known that the martensitic transformation of equiatomic TiNi alloy comprises a single-stage from a high temperature B2 parent phase to a B19′ martensite phase. After conducting a thermomechanical treatment or adding a third element, transformation sequence of near equiatomic TiNi SMAs can change into a two-stage from B2 to premartensite R-phase and then to B19′ upon cooling. Recently, martensitic transformation of Ni-rich TiNi SMAs was found to have more than two distinct steps, and is known as the multi-stage martensitic transformation (MST). Bataillard et al. [1,2] attributed the cause of MST to the stress fields formed around the coherent interfaces between B2 matrix and Ti_3Ni_4 precipitates. Khalil-Allafi et al. [3] found $B2 \rightarrow R$ and $R \rightarrow B19'$, and an additional step with $B2 \rightarrow B19'$ in the cooling curves of annealed Ni-rich TiNi alloys. They proposed that the MST comes from the inhomogeneous distribution of Ti_3Ni_4 precipitates. Chobak et al. [4] stated that the MST in 10% cold-worked and annealed $Ti_{49.3}Ni_{50.7}$ alloy has $B2 \rightarrow R$ and $R \rightarrow B19'$, and that the $R \rightarrow B19'$ peak consists of two transformation sub-peaks occurring at different temperatures. Su and Wu [5] have obtained a complex four-step MST in a 20% cold-rolled and annealed $Ti_{49}Ni_{51}$ alloy, and they suggested that the MST is the result of the combined effect of severe cold-working and long-time annealing. Kim et al. [6] reported a low temperature aging-induced two-stage R-phase transformation in $Ti_{49.1}Ni_{50.9}$ alloy.

According to the aforementioned studies, all the complex MSTs appear in Ni-rich TiNi alloys and their behaviors are relevant to the inhomogeneous distribution of Ti_3Ni_4 precipitates. In this study, we find a four-step MST in cold-rolled and annealed $Ti_{50}Ni_{50}$ alloy. In the $Ti_{50}Ni_{50}$ alloy, neither Ti_3Ni_4 precipitation nor non-uniform precipitation distribution is observed in the specimen. In this study, the unusual complex MST behavior obtained in specific annealing conditions is identified by DSC and the occurrence of the complicated four-stage transformation sequence in different annealing temperatures and time intervals are also demonstrated. At the same time, the other transformation sequences occurred in cold-rolled and annealed $Ti_{50}Ni_{50}$ SMA are also discussed.

2. Experimental procedure

Equiatomic TiNi alloy was prepared by the conventional vacuum arc remelting (VAR) technique. The as-melted ingots were hot-rolled at 850 °C into 2 mm thick plates then the plates were solution-treated at 850 °C for 2 h followed by quenching in water. Thereafter, the plates were wire-cut along the hot-rolling

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direction. The cut specimens were then cold-rolled along the hot-rolling direction and reached a final 35% thickness reduction. No annealing process was conducted during the cold-rolling to avoid the occurrence of recrystallization. Then, the cold-rolled plates were cut into testing specimens and annealed at 350, 500 and 650 °C salt baths for different time intervals. Transformation temperatures of cold-rolled and annealed specimens were determined by DSC tests using the TA Q10 DSC equipment at the same heating and cooling rates (10 K/min). The details of the experimental procedures are presented in our previous report [7].

3. Results

Fig. 1 shows the DSC results of $Ti_{50}Ni_{50}$ alloy cold-rolled and annealed at 350 °C from 10 s to 24 h in which the specimens have a two-stage transformation, B2 → R and R → B19′, in cooling and a single-stage B19′ → B2 in heating. All transformation peak temperatures, R^*, M^* and A^* for B2 → R, R → B19′ and B19′ → B2 transformations, respectively, as shown in Fig. 1(e), increase by prolonging the annealing time. Also from Fig. 1, both transformation enthalpies increase upon increasing the annealing time, and reach about 20 J/g after annealing for 24 h which is less than the normal $Ti_{50}Ni_{50}$ transformation energy, about 25 J/g [8]. This indicates that the cold-rolled specimen is not completely recovered and recrystallized even annealing at 350 °C for 24 h.

Figs. 2 and 3 show the 35% cold-rolled $Ti_{50}Ni_{50}$ alloy annealed at 500 and 650 °C, respectively. In Fig. 2(a and b), when the annealing time is short, there are two peaks with ΔH being about 20 J/g. Upon increasing the annealing time to 1 and 3 h, transformation becomes a complex four-step MST on cooling, as shown in Fig. 2(c and d). This four-step MST comprises two large and two small peaks upon cooling but only one large peak and one small peak upon heating. After annealing for 24 h, the four peaks in the forward transformation combine to become two large peaks and the two peaks in the reverse transformation merge to a single large peak, as shown in Fig. 2(e). When the specimen was further annealed to 96 h, the transformation sequence is the same as that of Fig. 2(e), as shown in Fig. 2(f).

As the annealing temperature is increased to 650 °C, as shown in Fig. 3, a four-step MST also appears when the annealing time is 1 min 30 s (Fig. 3(c)). These four transformation peaks gradually merge to two large peaks when the annealing time prolongs to 2 min. After annealing at 2 min 30 s, only one peak is observed. The transformation temperatures and enthalpies are almost kept constants when the annealing time is longer than 3 min, as shown in Fig. 3(f).

4. Discussion

Fig. 4(a–c) delineates all transformation temperatures shown in Figs. 1–3, respectively. There are four stages, i.e. Stages I–IV, in Fig. 4 are denoted. This result is similar to the ear-

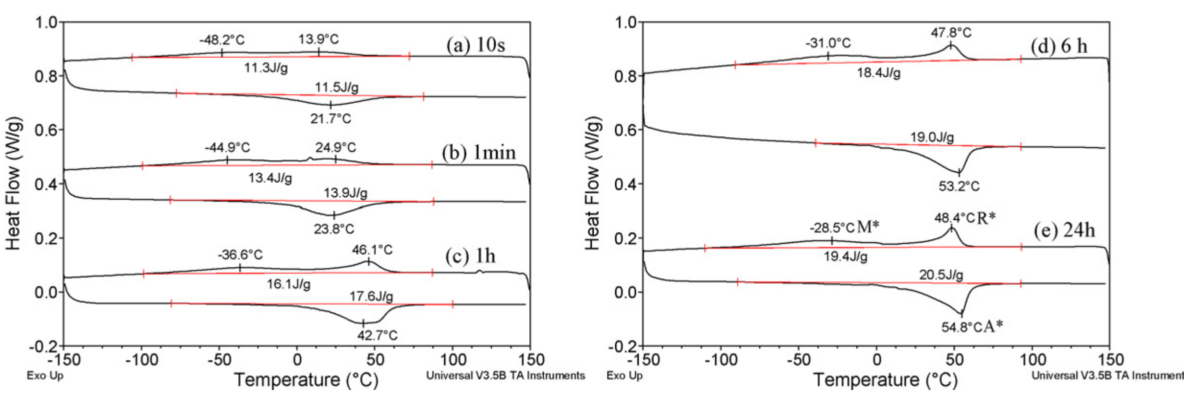

Fig. 1. DSC curves for 35% cold-rolled $Ti_{50}Ni_{50}$ alloy annealed at 350 °C for different time intervals.

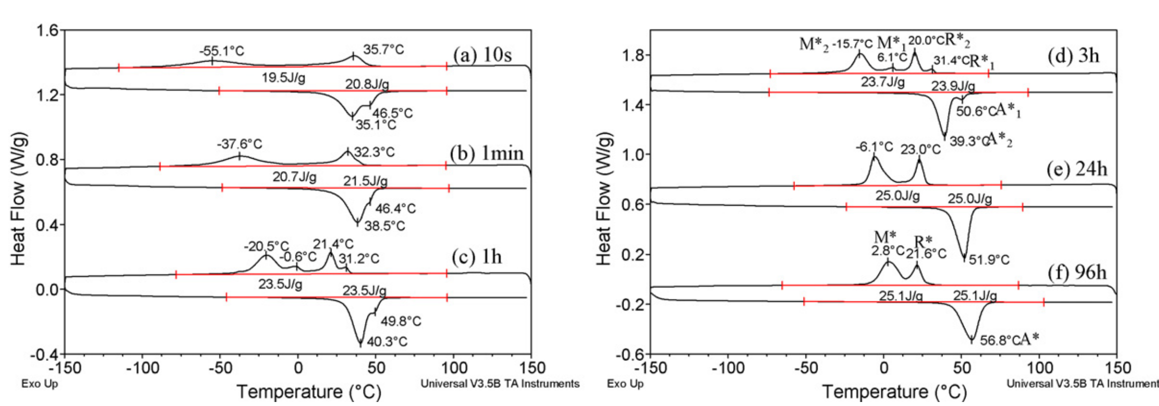

Fig. 2. DSC curves for 35% cold-rolled $Ti_{50}Ni_{50}$ alloy annealed at 500 °C for different time intervals.

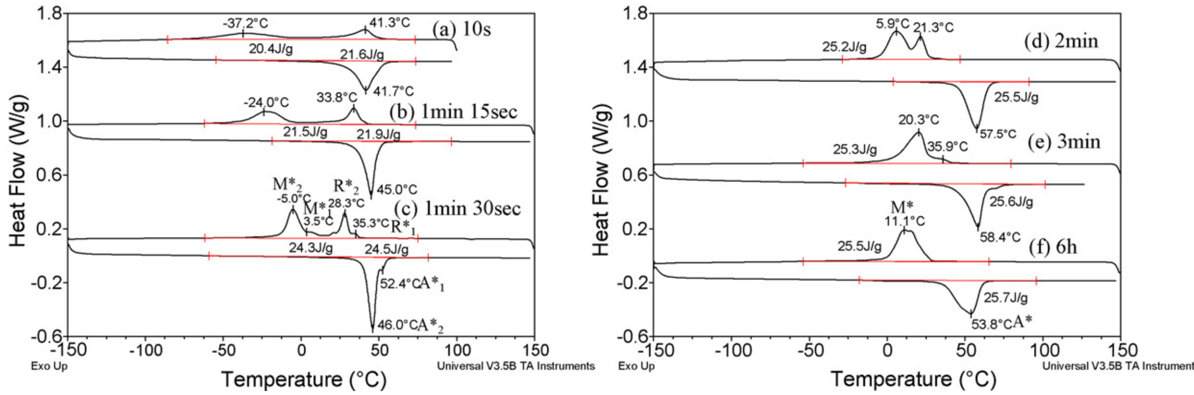

Fig. 3. DSC curves for 35% cold-rolled $Ti_{50}Ni_{50}$ alloy annealed at 650 °C for different time intervals.

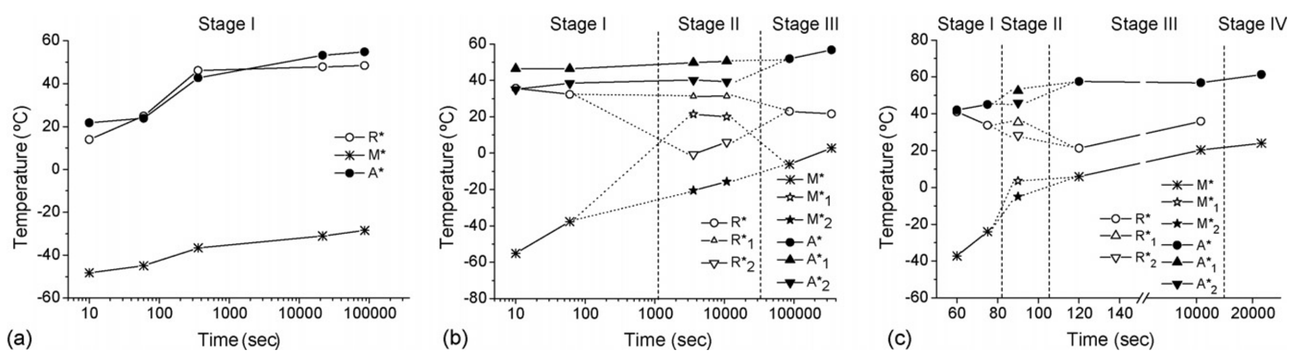

Fig. 4. Evolution of transformation peak temperatures of Figs. 1–3 for 35% cold-rolled $Ti_{50}Ni_{50}$ alloy annealed at (a) 350 °C, (b) 500 °C, and (c) 650 °C.

lier report [9] though it is more complicated in this study. Stage I corresponds to the “incomplete” B2 → R → B19′ and B19′ → B2 or B2 ↔ R ↔ B19′ transformation sequence. Stage II represents the four-step MST. Stages III and IV relate to the “complete” B2 ↔ R ↔ B19′ and B2 ↔ B19′ transformation sequences, respectively. Here, the “complete” and “incomplete” mean that the transformation enthalpies shown in Figs. 1–3 are near or much less than 25 J/g, respectively. They also mean that the recovery and recrystallization annealing are “completed” or “incompleted”, respectively. Transformation behaviors of Stages I–IV are summarized in Table 1.

From the DSC results of Figs. 1–3 for specimens annealed for short time intervals, there occurred only “incomplete” B2 → R, R → B19′ and B19′ → B2 transformation peaks, shown as Stage I in Fig. 4. This reflects that the recrystallization of the cold-rolled specimen is not completed when the annealing temperature is too low or the annealing time is too short. From the DSC results of Figs. 1–3, the four-step MST can only be observed in some specific annealing conditions, for example annealing at 500 °C × 1 h, 500 °C × 3 h and 650 °C × 1 min 30 s, i.e. at Stage II in Fig. 4. In our previous study [7], we disclosed that the grain size distribution along the specimen’s thickness direction is inhomogeneous due to the cold rolling effect, in which the grain size at the central region is apparently larger than that near the rolling surface. Two small peaks in the four-step MST are related to the B2 → R → B19′ transformation of large grains and the other two large peaks are also associated with the B2 → R → B19′ transformations, but now they correspond to small grains near the rolling surface. The further discussion about the effect of grain size on multiple-stage transformation of cold-rolled and annealed equiatomic TiNi alloy was reported in Ref. [7].

When the specimen annealed at 500 °C × 24 h or 650 °C × 2 min, the four-step MST now converts to a “complete” B2 ↔ R ↔ B19′, which is Stage III in Fig. 4. This is because the severely cold-rolled specimen has completely recrystallized under these annealing conditions and the transformation enthalpies increase to 25 J/g. In Stage III, though the annealing is sufficient, the residual defects/dislocations remain in the specimen that can induce the premartensite transformation and develop B2 → R transformation peaks [10]. Meanwhile, the average grain size at the central region and that near the rolling surface approaches uniformity in Stage III [7], the four-step MST obtained in Stage II fades out. Therefore, upon cooling, it has B2 → R → B19′ transformation sequence in Stage III. However, the difference of peak temperatures corresponding to B2 → R

Table 1
The transformation sequence of Stages I–IV in Fig. 4

	Transformation sequence
Stage I	Incomplete B2 → R → B19′ and B19′ → B2 or B2 ↔ R ↔ B19′
Stage II	Four-step MST
Stage III	Complete B2 ↔ R ↔ B19′
Stage IV	B2 → B19′

and R → B19′ is about 20–30 °C. This temperature difference is too small to induce R-phase in the reverse transformation [10], therefore, on heating, it has B19′ → B2 transformation sequence in Stage III.

As the annealing time at 650 °C is longer than 2 min, i.e. at Stage IV in Fig. 4, the grain size in the whole specimen is more uniform and only B2 ↔ B19′ transformation sequence is obtained. This comes from the fact that the annealing is completed and all of the defects/dislocations induced from cold-rolling have been fully annihilated. From Fig. 4, we can also notice that the growth rate of recrystallized grains of the specimen annealed at a higher temperature is faster than that annealed at lower temperatures. This is due to the grain growth involving the migration of high angle grain boundaries and its kinetics will be strongly influenced by the temperature dependence of boundary mobility [11].

5. Conclusions

Transformation behaviors of $Ti_{50}Ni_{50}$ shape memory alloy after 35% cold-rolling and subsequent recrystallization annealing are investigated in this study. Four transformation sequences, i.e. Stages I–IV, in different annealing conditions are proposed. Stage I corresponds to the "incomplete" B2 → R → B19′ and B19′ → B2 or B2 ↔ R ↔ B19′ transformation sequence due to the incomplete recovery and recrystallization. Stage II represents the four-step MST with two large and two small peaks in the cooling curve which are associated with the large grains in the specimen center and that of small grains near the rolling surface, respectively. Stages III and IV relate to the "complete" B2 ↔ R ↔ B19′ and B2 ↔ B19′ transformation sequence, respectively, since the completed recovery and recrystallization with their transformation enthalpies are about 25 J/g. In Stage III, the average grain size at the central region and that near the rolling surface approaches uniformity, the four-step MST fades out. The residual defects/dislocations in the specimen in Stage III still can induce R-phase and therefore B2 ↔ R ↔ B19′ transformation sequence can be obtained. After sufficiently annealing in Stage IV, most defects/dislocations are annihilated and only B2 ↔ B19′ can be obtained.

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