Effect of Thermal Cycling on Multistage Martensitic Transformation in Aged Ti–50.8 at% Ni Alloy

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The effect of thermal cycling on multistage martensitic transformation (MMT) in aged Ti–50.8 at% Ni alloy was investigated. The specimens were solution-treated at 1273 K for 3.6 ks and then aged at 773 K for 3.6 ks in vacuum without atmosphere regulation. Upon cooling, the aged specimens clearly showed quadruple-stage transformation denoted as B2 → R → M1 → M2 → M3. The peak temperatures of exothermic reaction R → M1, M1 → M2, and M2 → M3 (corresponding to the R-phase, M1 and M2 transformations, respectively) in the differential scanning calorimetry (DSC) cooling curve were rather stable up to 100 thermal cycles, since there were fine Ti3Ni4 precipitates with high distribution density in the intermediate and grain boundary regions. These precipitates prevented the formation of dislocations during thermal cycling. On the other hand, the peak temperature of exothermic reaction M3 → M2 (corresponding to the M3 transformation) drastically decreased with increasing the number of thermal cycles since there were large Ti3Ni4 precipitates with low distribution density. Many dislocations were observed in the central regions of grains after 100 thermal cycles. [doi:10.2320/matertrans.M2013309]

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1. Introduction

Complex multistage martensitic transformation (MMT) behaviors have been observed in aged Ni-rich Ti–Ni shape memory alloys.1–16) Different explanations for MMT have been proposed on the basis of several experimental studies, in which the size and distribution of Ti3Ni4 precipitates were heterogeneous.3,9,11,14–16) The transformation sequence during MMT is also disputed.7,9,14) The present authors have previously reported the transformation sequence during the quadruple-stage transformation in Ti–50.8 at% Ni, as determined by in-situ SEM.16) In the quadruple-stage transformation upon cooling, the R-phase transformation occurred in the intermediate and grain boundary regions. The first martensitic transformation, which corresponded to the M1 peak in the DSC cooling curve, took place in the intermediate region of the grain via the R phase. The second martensitic transformation, which corresponded to the M2 peak, occurred around the grain boundary via the R phase. The final transformation, which corresponded to the M3 peak, appeared directly from the B2 phase at the grain center. Heterogeneity in distribution and size of the Ti3Ni4 precipitates was observed from the grain boundary to the grain center in these specimens. The apparent diameter of Ti3Ni4 precipitates in the grain interior was much larger than that at the grain boundary, whereas the precipitate density at the grain interior was lower than that at the boundary.

The effect of thermal cycling on the transformation behavior in Ti–Ni alloys has been studied extensively.17–22) A shift in transformation temperatures in solution-treated alloys was observed irrespective of Ni content, while aged Ni-rich alloys with densely fine Ti3Ni4 precipitates did not show such a shift up to 100 cycles.17) In the former case, numerous dislocations were observed after thermal cycling,17–19) whereas there was no obvious increase in dislocation density in the latter case since the fine precipitates prevented the formation of dislocations during thermal cycling.17–19) As mentioned above, specimens undergoing MMT also display heterogeneity in size and distribution of Ti3Ni4 precipitates from grain boundary to interior.3,9,11,14–16) These facts indicate that a different thermal cycling effect can be expected in each transformation event (i.e., in M1, M2 and M3 transformations). In other words, the effect of precipitation morphology on transformation behavior can be observed systematically in an identical specimen.

The present study is conducted to investigate the effect of thermal cycling on MMT behavior in aged Ni-rich Ti–Ni alloys by means of DSC measurements and TEM observations.

2. Experimental Procedure

A commercially available Ti–50.8 at% Ni alloy rod 3 mm in diameter was cut into disks of about 1 and 0.2 mm in thickness for DSC measurements and TEM observations, respectively. The disk specimens were solution-treated in vacuum of 2.5 × 10–4 Pa at 1223 K for 3.6 ks and then quenched in ice water. Details such as heat treatment atmosphere are described elsewhere.6,11,15,16) Some specimens were aged at 773 K for 3.6 ks and then quenched into ice water. The solution-treated and aged specimens were subjected to thermal cycling in the temperature range between 77 and 373 K by alternately dipping them into liquid nitrogen and boiling water for 1 min at a time. The transformation temperatures and their variations after thermal cycling were measured by using DSC equipment (Shimadzu DSC-60) with a cooling and heating rate 0.17 K/s for the 1st,
5th, 10th, 25th, 50th and 100th cycles. For simplicity, the temperatures at which DSC peaks appeared were regarded as the transformation temperatures of the corresponding phase transformations. For instance, the temperatures of the R-phase transformation and its reversion are denoted by \( R^* \) and \( AR^* \), respectively. In the same way, the notations \( M^* \) and \( A^* \) correspond to the temperatures of a martensitic transformation and its reversion. The TEM specimens were electropolished in HNO\(_3\)/CH\(_3\)OH (1:3 v/v). TEM and STEM observations were carried out in a FEI Technai-F20 microscope operated at 200 kV. Annular dark-field scanning transmission microscope (ADF-STEM) imaging was applied since this technique is less sensitive to specimen misalignments under significant strain, such as in the case of complex dislocation arrangements induced by thermal cycling and coherent Ti\(_3\)Ni\(_4\) precipitates. In other words, ADF-STEM imaging is a reliable technique for observation of dislocations.

3. Results and Discussion

Figure 1 shows DSC curves for a solution-treated specimen subjected to thermal cycling between 77 and 373 K for 100 cycles. Single-stage martensitic transformation and its reverse transformation take place upon cooling and heating, respectively. \( M^* \) and \( A^* \) clearly decrease with increasing thermal cycling, as previously reported.\(^{17,19-21}\)

Figure 2 shows DSC curves for an identical aged specimen subjected to thermal cycling between 77 and 373 K for 100 cycles. Quadruple transformation occurs upon cooling, as mentioned in the introduction. There appear to be four exothermic peaks and three endothermic peaks in the DSC cooling and heating curves, respectively, even after 100 thermal cycles. Based on the partial DSC cycling experiments and in-situ SEM observations in the author’s previous study,\(^{10}\) the \( R^* \) and \( AR^* \) peaks are attributed to the R-phase transformation and its reversion. Similarly, the \( M1^* \) and \( A1^* \) peaks correspond to the first martensitic transformation and its reversion. The \( M2^* \) and \( A2^* \) peaks are identified with the second martensitic transformation and its reversion, although the \( A2^* \) and \( AR^* \) peaks overlap. Therefore, the \( A2^* \) and \( AR^* \) peaks are denoted as \( A2^* + AR^* \) below. The \( M3^* \) and \( A3^* \) peaks correspond to the third martensitic transformation and its reversion. The \( R^* \), \( M1^* \), \( M2^* \) and \( M3^* \) peaks upon cooling and \( A1^* \), \( A2^* + AR^* \) and \( A3^* \) peaks upon heating in the aged specimen are summarized as functions of the number of thermal cycles in Figs. 3(a) and 3(b), respectively. \( M^* \) and \( A^* \) for the solution-treated specimen are also plotted. The amount of decrease \( \Delta M^* \) reached about 20 K after 100 thermal cycles in the solution-treated specimen. In contrast, the amount of \( \Delta A^* \) was about 9 K after 100 thermal cycles. These variations in transformation temperatures indicate that the influence of thermal cycling is more pronounced in forward transformation than in reverse transformation. It has been pointed out that martensitic transformation depends on the formation of new martensite plates, whereas the reversion proceeds as thermoelastic transformation by shrinkage of existing plates.\(^{18}\) Thus, forward transformation is considered to be sensitive to local stress fields due to lattice defects in the parent phase and mutual interaction between martensite plates themselves. In the aged specimen, \( R^* \) is almost constant even after 100 thermal cycles. This result is consistent with previous reports.\(^{16,18,25}\) \( M1^* \) and \( M2^* \) decrease slightly with increasing the number of thermal cycles. The decreases,
ΔM1* and ΔM2*, amount to about 6 K, whereas ΔM3* is about 23 K after 100 thermal cycles. This value is comparable to ΔM* of the solution-treated specimen. These differences between M1*, M2* and M3* are attributable to the heterogeneous microstructure with variations in size and distribution density of Ti3Ni4 precipitates in the aged specimen, as mentioned above. After 100 thermal cycles, ΔA1*, Δ(A2* + AR*) and ΔA3* are 3, 3 and 11 K, respectively. These results suggest that the influence of thermal cycling is also more pronounced in forward transformation than in reverse transformation in the aged specimen with heterogeneous microstructure.

Figure 4(a) shows a bright-field TEM image of the aged specimen after 100 cycles. There is a grain boundary at the center of the micrograph. The incident electron beam was nearly parallel to the [111]B2 in both grains, since the
present rod specimen had (111)B2 fiber texture. The specimen was electropolished at 240 K, which was a temperature level between $M1^*$ and $M2^*$. Since TEM observations were performed at room temperature, it was expected from the DSC heating curve in Fig. 2 that the martensitic phase corresponding to $M1^*$ be retained in the specimen. In fact, the M1 martensitic phase (dark in the image) is observed at the intermediate area in each parent phase grain. On the other hand, there are R-phase and parent phase along the grain boundary (M2) and at the grain interior (M3), respectively. These phases were confirmed by electron diffraction experiments. There is also clear heterogeneity in distribution and size of the Ti$_3$Ni$_4$ precipitates in the direction from grain boundary to grain interior. The apparent diameter of Ti$_3$Ni$_4$ precipitates from grain boundary to grain center is estimated to be about 120–650 nm. It is recognized that the precipitation size decreases with increasing the degree of supersaturation of solute elements. It is suggested that the ratio of Ni to Ti (Ni/Ti) around the grain boundary is larger than that in the grain interior. Figures 4(b) and 4(c) are magnified ADF-STEM images of areas B and C in (a), respectively. Although a few dislocations indicated by arrows around the grain boundary can be seen in Fig. 4(b), there are no notable differences between the states before$^{6,11,14,15}$ and after 100 thermal cycles. In other words, the formation of dislocations during thermal cycling is prevented by the presence of fine precipitates,$^{17}$ and thus the decrease in transformation temperatures is less pronounced. On the other hand, there are many of dislocations in the grain interior, as seen in Fig. 4(c). Dislocations become entangled and their density increases toward the central regions of grains. The substantial decrease in $M3^*$ and $A3^*$ is concluded to be due to dislocations induced by thermal cycling.$^{17,19}$ The obtained results clearly indicate that a different thermal cycling effect takes place in each transformation event in the MMT.

4. Conclusion

The effect of thermal cycling on quadruple-stage transformations in aged Ti-50.8 at% Ni alloy was investigated. Different thermal cycling effects were observed at each transformation event. The forward and reverse transformation temperatures $R^*$, $AR^*$, $M1^*$, $A1^*$, $M2^*$ and $A2^*$ were rather stable after 100 thermal cycles. In contrast, $M3^*$ and $A3^*$ decreased notably with increasing thermal cycling. These changes in transformation behavior were consistent with changes in microstructure. In particular, the induced dislocations increased locally in the grain interior, where the size and density of Ti$_3$Ni$_4$ precipitates were much greater and lower than those at the grain boundary, respectively. This also supported the observation that the third martensitic transformation took place in the grain interior in the quadruple-stage transformation.

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