Understanding of multi-stage R-phase transformation in aged Ni-rich Ti–Ni shape memory alloys

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Abstract

An abnormal three-stage martensitic transformation behavior (one-stage R and two-stage B\textsubscript{19}′) has been found in Ni-rich Ti–Ni alloys when aged at intermediate temperatures (350–500 °C). This strange behavior was successfully explained by considering the kinetics of Ti\textsubscript{3}Ni\textsubscript{4} precipitation in polycrystalline samples. However, it was found that R-phase transformation occurs in two stages, when aging is done at low temperatures (250–300 °C). In order to find the origin of this abnormal phenomenon, we made a comparative study with Ni–49.4 at.% Ti single crystals and polycrystals, which were aged at 250 °C for different time. Differential scanning calorimetry showed that all single crystals undergo normal one-stage R-phase transformation, while polycrystals exhibit the abnormal two-stage R-phase transformation after short time aging. These different transformation behaviors can be understood by considering the kinetics of precipitation in supersaturated solid solution. The abnormal two-stage R-phase transformation is attributed to a large-scale heterogeneity of Ni-content between grain boundary region and grain interior, resulted from the preferential precipitation in grain boundary regions. Therefore, it is suggested that there is a unified scenario for seemingly different transformation behaviors of both low-temperature-aged and intermediate-temperature-aged Ti–Ni alloys.

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1. Introduction

Ti–Ni alloys of near-equiatomic composition are technologically important materials because they combine excellent functional properties (shape memory effect, superelasticity) with good mechanical strength and ductility \cite{1}. It is known that near-equiatomic Ti–Ni alloys may undergo three different martensitic transformations depending on thermomechanical treatment condition: B\textsubscript{2}-R, R-B\textsubscript{19}′ and B\textsubscript{2}-B\textsubscript{19}′, which are the key to the above functional properties and have been extensively discussed in literature \cite{2–6}. These three kinds of transformations are characterized by different features of transformation strain and hysteresis. B\textsubscript{2}-R, called R-phase transformation, exhibits small transformation strain (\sim 1\%) and hysteresis (\sim 2–5 K). In contrast, R-B\textsubscript{19}′ and B\textsubscript{2}-B\textsubscript{19}′ are characterized by much larger transformation strain (\sim 10\%) and hysteresis (\sim 20–70 K).

Unlike, fully annealed and quenched near-equiatomic Ti–Ni alloys, which transform from B\textsubscript{2} to B\textsubscript{19}′ directly, the aged Ni-rich Ti–Ni alloys normally transform in two stages (B\textsubscript{2}-R-B\textsubscript{19}′), and thus, show two distinct peaks on differential scanning calorimetry (DSC) curves, which are well documented in literature \cite{7}. In addition to the generation of R-phase transformation, an abnormal three-stage (one-stage R and two-stage B\textsubscript{19}′) martensitic transformation in intermediate-temperature-aged Ni-rich Ti–Ni alloys was reported from time to time. The debate about the origin of this three-stage martensitic transformation has been going on for a long time and several explanations were given based on different experimental observations \cite{1,8–12}. Recently, by further studies, Fan et al. proved that those preceding mechanisms are not the ultimate origin of this abnormal phenomenon and they attributed it to the inhomogeneous precipitate distribution between grain boundary and grain interior \cite{13}. In addition, three-stage martensitic transformation are identified to be B\textsubscript{2}-R-B\textsubscript{19}′ in grain boundary region, and B\textsubscript{2}-B\textsubscript{19}′ in grain interior by doing partial differential scanning calorimetry cycles. This scenario successfully explained this abnormal phenomenon...
and is consistent with all the existing data reported in literature.

As mentioned in the above, both the normal two-stage martensitic transformation and the abnormal three-stage transformation of intermediate-temperature-aged alloys involve only one stage of R-phase transformation. However, an abnormal two-stage R-phase transformation was found in Ti–50.9 at% Ni polycrystals aged at low temperatures (250–300 °C). By investigation with DSC, X-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques, Kim et al. attributed it to the local stress and composition heterogeneity between Ti3Ni4 particles [14]. Apparently, this mechanism expects that this strange phenomenon is intrinsic for all Ti3Ni4-containing samples and is independent of whether or not the sample is single crystal or polycrystal. As reported in the following, this mechanism is not consistent with the fact that 250 °C-aged Ti–50.6 at% Ni (this will be abbreviated as 50.6Ni, hereafter) single crystals all undergo normal one-stage R-phase transformation in our experiment.

Since, grain boundary plays an important role in the occurrence of abnormal three-stage martensitic transformation, as Fan et al. pointed out, we consider that this abnormal two-stage R-phase transformation may be due to the existence of grain boundary. Based on this idea, we designed the following experiment. At first, low-temperature aging is done with 50.6Ni single crystals, which is the crucial test for the mechanism based on the local heterogeneity of composition and stress between Ti3Ni4 particles. Then, the same aging treatment is done with 50.6Ni polycrystals to clarify the effect of grain boundary on this abnormal phenomenon. As can be seen in the following, our experimental results directly to a simple explanation for the abnormal two-stage R-phase transformation in low-temperature-aged alloys. In addition, it is suggested that there is a unified scenario for both the abnormal three-stage martensitic transformation in intermediate-temperature-aged alloys and the above two-stage R-phase transformation in low-temperature-aged alloys.

2. Experimental procedure

In the present study, 50.6Ni single crystals and polycrystals were used and Ni-content of the samples was determined by chemical analysis.

All the samples were small plates made by spark-cutting, which were about 3 mm × 3 mm × 1 mm. In order to remove the affected surface layer, samples were mechanically polished and chemically etched. Then they were sealed into quartz tubes filled with argon (about 1.5 × 10^3 Pa) and Ti-getter was also sealed into the tubes to avoid oxidation during the subsequent heat treatment. All the sealed samples were annealed at 1000 °C for 1 h, followed by water quench to the room temperature to obtain a homogeneous supersaturated solid solution. In the following, all samples were aged at 250 °C for different time: from 1 to 72 h for 50.6Ni single crystals; from 1 to 110 h for 50.6Ni polycrystals. After the above heat treatment, the samples were slightly chemically etched again to remove the surface layer that might be oxidized during the heat treatment. The etching agent is a mixture of 50 vol% water, 40 vol% nitric acid and 10 vol% hydrofluoric acid.

The transformations are characterized by differential scanning calorimetry with the cooling and heating rate of 10 °C/min from –100 to 100 °C, using an 822e calorimeter from METTLER TOLEDO.

3. Experimental results

3.1. DSC results of the 50.6Ni single crystals aged at 250 °C

Fig. 1 shows the transformation behaviors of 50.6Ni single crystals aged at 250 °C for different time. It can be seen that 50.6Ni single crystals undergo normal two-stage transformation (B2-R-B19′), both on cooling and heating, except for the one aged for 1 h, showing only one-stage transformation (B2-R). Therefore, all single crystal samples undergo normal one-stage R-phase transformation, not two-stage R-phase transformation. This important finding proves that the local heterogeneity of composition and stress between particles is not responsible for the abnormal two-stage R-phase transformation, because such small-scale heterogeneity apparently exists in aged single crystals.

3.2. DSC results of 50.6Ni polycrystals aged at 250 °C

Fig. 2 shows the transformation behaviors of 250 °C-aged 50.6Ni polycrystals. Clearly, 50.6Ni polycrystals exhibit transformation behaviors of great difference with those of single crystals. Three peaks, marked with 1–3 on cooling, are found on DSC curves of 50.6Ni polycrystals aged for short time, and peak-2 gradually shifts to peak-1, until finally, merges into peak-1 with increasing aging time. On heating, two peaks marked with 4 and 5 are shown on all DSC curves, irrespective of aging time.

In order to identify the nature of these peaks, partial DSC cycles are performed with 50.6Ni polycrystal aged at 250 °C for 24 h, shown in Fig. 3. Fig. 3(b) suggests that peak-1 corresponds exactly with peak-5. As this pair of transformation has a small hysteresis of 2K, which is the typical characteristic of R-phase transformation, it can be deduced that peak-1 and peak-5 represent B2-R and R-B2, respectively. With further cooling, Fig. 3(c) indicates that peak-2 and peak-2′ is another pair of transformations and similarly, they should also be associated with B2-R and R-B2, respectively, from their narrow hysteresis. Therefore, 50.6Ni polycrystal aged at 250 °C for 24 h undergoes two-stage R-phase transformation, and this behavior persists up to 60 h of aging time. In order to characterize the two stages of R-phase transformation, we denote them as B2-R1 and B2-R2 on cooling; R2-B2 and R1-B2, respectively, for their reverse transformations on heating. For 50.6Ni polycrystals aged for longer time, it is easy to identify that peaks on DSC curves represent B2-R and R-B19′ on cooling; R-B19′ and B19′-B2 on heating, which are the normal two-stage martensitic transformations for aged Ti–Ni alloys.

Therefore, two stages of R-phase transformation (B2-R1 and B2-R2) occur in aged 50.6Ni polycrystals. Comparing with the
transformation behavior of 50.6Ni single crystals, it is suggested that the occurrence of two-stage R-phase transformation is due to the existence of grain boundary.

4. Discussion

4.1. Origin of the abnormal two-stage R-phase transformation behavior

Concerning the origin of two-stage R-phase transformation, Jim et al. speculated that the local heterogeneity of composition and stress between Ti₃Ni₄ particles is responsible for it. This mechanism implies that two-stage R-phase transformation is intrinsic for all Ti₃Ni₄-containing samples; no matter they are single crystals or polycrystals. However, all 50.6Ni single crystals, in our experiment, show normal one-stage R-phase transformation, independent of aging time. This important result suggests that the occurrence of two-stage R-phase transformation is not due to the local heterogeneity of composition and stress between particles, because such local heterogeneity definitely exists in aged single crystals. The contrasting transformation behaviors of 50.6Ni single crystals and polycrystals indicate that this abnormal phenomenon is attributed to the existence of grain boundary, which can be understood by considering the nucleation kinetics of supersaturated solid solution.

Fig. 4 [13] shows the schematic illustration for the relation between nucleation rate and supersaturation degree in grain boundary and interior region. It can be seen that when supersaturation is low, the nucleation rate in grain boundary region is significantly larger than that in grain interior; for instance, \( I_{GB} \) is nine times of \( I_{GI} \) for 50.6Ni polycrystals. Thus, the precipitates are preferentially distributed in grain boundary region,
and accordingly, the Ni-content in grain boundary region is lower than that in grain interior. In addition, by referring to the phase diagram of Ti–Ni system, it can be seen that the solubility of Ni in Ti–Ni alloys decreases as the temperature decreases. Thus, for samples of the same composition, the supersaturation is larger when aging is done at low temperatures than that at intermediate temperatures, and this gives rise to much more precipitation in grain interiors of low-temperature-aged samples than the case of intermediate-temperature-aged samples, which are almost precipitate-free in grain interiors [13]. Therefore, R-phase transformation first occurs in low-Ni grain boundary region, followed by that in high-Ni grain interior. Therefore, the abnormal two-stage R-phase transformation originates from a large-scale heterogeneity of Ni-content between grain boundary region and grain interior, which results from the preferential precipitation in grain boundary region when Ni-content is low.

4.2. Unified explanation for different transformation behaviors of both low-temperature-aged and intermediate-temperature-aged Ni-rich Ti–Ni polycrystals

In the following, we will show that both the abnormal three-stage martensitic transformation in intermediate-temperature-aged alloys and the abnormal two-stage R-phase transformation in low-temperature-aged alloys can be understood by a unified explanation.

For low-Ni-content polycrystals aged at intermediate temperatures, low-Ni leads to a preferential precipitation along grain boundary, while leaving grain interior essentially precipitate-free, which is due to the low supersaturation when aging is done at intermediate temperatures. So grain boundary portion undergoes B2-R-B19' two-stage transformation and grain interior undergoes a direct B2-B19' transformation, which gives rise to the abnormal three-stage martensitic transformation.
Fig. 3. Partial DSC cycles and full cycle for Ti–50.6 at% Ni polycrystal aged at 250 °C for 24 h after solution treatment at 1000 °C for 1 h, followed by water quenching.

For low-Ni polycrystals, aged at low temperatures for short time, although low-Ni leads to preferential precipitation in grain boundary region, which results in a large-scale heterogeneity of Ni-content between grain boundary region and grain interior nucleation, a certain amount of precipitates are nucleated in grain interior, because of the comparatively high superasturation when aging is done at low temperatures than that at intermediate temperatures. Thus, low-Ni grain boundary portion firstly undergoes B2-R1, followed by B2-R2 in high-Ni grain interior, and this gives rise to the abnormal two-stage R-phase transformation.

Therefore, both the abnormal three-stage martensitic transformation in intermediate-temperature-aged polycrystals and two-stage R-phase transformation in low-temperature-aged polycrystals are due to a large-scale heterogeneity of precipitate distribution between grain boundary region and interior, which is resulted from the preferential precipitation in grain boundary regions when Ni-content is low.

5. Conclusions

In order to find the origin of abnormal two-stage R-phase transformation in low-temperature-aged Ni-rich Ti–Ni alloys, we investigated the transformation behaviors of 50.6Ni single crystals and polycrystals, which were aged at 250 °C after solution treatment, with DSC technique. We obtained following conclusions.

(i) All 50.6Ni single crystals undergo normal one-stage R-phase transformation. This indicates that the local heterogeneity of composition and stress between Ti3Ni4 particles is not responsible for the occurrence of two-stage R-phase transformation, for such heterogeneity, definitely exists in aged single crystals. Comparing with that of single crystal, 50.6Ni polycrystals undergo two-stage R-phase transformation, which suggests that this abnormal phenomenon is due to the existence of grain boundary.

(ii) By considering the kinetics of precipitation, two-stage R-phase transformation is attributed to a large-scale heterogeneity of Ni-content in the matrix between grain boundary region and grain interior, created by the preferential precipitation in grain boundary regions. Thus, B2-R1 firstly occurs in low-Ni grain boundary region and then B2-R2 occurs in high-Ni grain interior. For single crystals, Ti3Ni4 particles are homogeneously distributed across the whole samples, so R-phase transformation occurs in one stage.

(iii) There is a unified explanation for both the abnormal three-stage martensitic transformation (B2-R-B19′ in grain boundary, B2-B19′ in grain interior) in intermediate-temperature-aged alloys and the above two-stage R-phase transformation in low-temperature-aged alloys, and both of them are due to the large-scale heterogeneity of precipitate distribution between grain boundary region and grain interior, which are determined by the precipitation kinetics of supersaturated solid solution in polycrystalline state.

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