

Origin of 2-stage R-phase transformation in low-temperature aged Ni-rich Ti–Ni alloys

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Abstract

After aging at intermediate temperatures (400–500 °C), Ni-rich Ti–Ni alloys undergo an abnormal 3-stage martensitic transformation behavior (1-stage R and 2-stage B19'), which stems from a preferential Ti₃Ni₄ precipitation around grain boundary. On the other hand, if aged at low-temperatures (250–300 °C), they undergo 2-stage R-phase transformation, but the origin of this strange phenomenon is unclear. In the present study, we made a systematic study of this phenomenon by considering the grain boundary effect and composition effect. We found that all single crystals undergo 1-stage R-phase transformation; in contrast, the transformation behavior of polycrystals is dependent on Ni content: low-Ni (50.6Ni, 51Ni) polycrystals undergo 2-stage R-phase transformation while high-Ni (52Ni) polycrystals undergo 1-stage R-phase transformation. The abnormal 2-stage R-phase transformation is attributed to a large-scale compositional heterogeneity in B2 matrix between grain boundary region and grain interior, due to the heterogeneity in precipitate density between the grain boundary and grain interior. But for high-Ni polycrystals, precipitates are essentially homogeneously distributed across the whole grain and this leads to normal 1-stage R-phase transformation. The different transformation behavior of low-Ni and high-Ni polycrystals stems from a competition between two opposing tendencies: (1) for preferential precipitation in the grain boundary; (2) for homogeneous precipitation across the whole grain with high-Ni content. The difference between the effect of intermediate-temperature and low-temperature aging lies in the difference in the ability for long-range diffusion of Ni (from the grain interior to the grain boundary), which results in whether or not Ti₃Ni₄ precipitates can form in the grain interior. Our results lead to a unified explanation for different transformation behaviors of both low-temperature and intermediate-temperature aged alloys in terms of the kinetics of precipitation in super-saturated polycrystals.

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1. Introduction

Ti–Ni shape memory alloys have attracted considerable interest as potential candidates for novel engineering and mechanical applications, because they combine excellent functional properties (shape memory effect, superelasticity)

with good mechanical strength and ductility [1]. It is known that near-equiatomic Ti–Ni alloys may undergo three different martensitic transformations depending on the thermomechanical treatment condition: B2–R, R–B19' and B2–B19', which are the key to the above functional properties and have been extensively studied in the literature [2–5]. These three kinds of transformation are characterized by different features of transformation strain and hysteresis. B2–R transformation exhibits a small transformation strain (~1%) and hysteresis (~1–5 K). In contrast,

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R–B19' and B2–B19' transformations are associated with much larger transformation strains ($\sim 10\%$) and hysteresis ($\sim 20\text{--}70\text{ K}$).

Unlike fully annealed and quenched near-equiatom Ti–Ni alloys, which transform from B2 to B19' directly, aged Ni-rich Ti–Ni alloys normally transform in two stages (B2–R–B19') and thus show two corresponding peaks on differential scanning calorimetry (DSC) curves [6]. The appearance of R-phase prior to B19' is due to the existence of Ti_3Ni_4 precipitates formed during aging. These precipitates give a strong resistance to the formation of B19' [7], as it is associated with a large lattice deformation. On the other hand, R-phase transformation has a significant smaller lattice deformation and is much less affected by the presence of particles. Therefore, the formation of Ti_3Ni_4 particles by aging treatment favors the formation of R-phase prior to transforming to B19' [8], and thus aged Ni-rich Ti–Ni alloys normally undergo a 2-stage B2–R–B19' transformation.

Being different from the above 2-stage transformation, Ni-rich Ti–Ni alloys sometimes exhibit an abnormal “3-stage” martensitic transformation after aging at intermediate temperatures (400–500 °C). This phenomenon has attracted much attention in recent years [8–14], but it was difficult to understand why in certain cases normal 2-stage transformation appears, while in other cases 3-stage transformation occurs. By a comparative study of single crystal and polycrystal samples, Fan et al. [15] proved that grain boundaries are a necessary ingredient for the formation of 3-stage transformation, but not a sufficient condition. Ni content is also an important factor in controlling the transformation behavior: 3-stage transformation exists in low-Ni samples, but not in high-Ni samples. They proposed that the appearance of abnormal 3-stage transformation in low-Ni samples is due to the difference in the kinetics of Ti_3Ni_4 precipitation during aging between the grain boundary and grain interior. Such a difference results in a preferential precipitation around the grain boundary region and an almost precipitate-free grain interior. As a consequence, the 3-stage martensitic transformation corresponds to B2–R–B19' (two stages) in the grain boundary region, and B2–B19' (one stage) in the grain interior. Therefore, 1-stage R and 2-stage B19' transformations occur. When Ni content is high, the high Ni-supersaturation provides a large driving force for precipitation and the difference in the nucleation rate between grain boundary and grain interior becomes small. This results in a homogeneous precipitation over the whole grain; thus normal 2-stage B2–R–B19' transformation is observed. This scenario explained not only abnormal 3-stage martensitic transformation but also normal 2-stage martensitic transformation, and is consistent with all existing data reported in the literature.

On the other hand, if aged at low-temperatures (e.g., 200–300 °C), Ni-rich Ti–Ni alloys show another strange transformation behavior, different from the above-mentioned case for intermediate-temperature aged (400–

500 °C) samples. After aging at low-temperatures (250–300 °C), an abnormal 2-stage R and 1-stage B19' transformation (also 3-stage in total) was found in Ti-50.9 at.%Ni (in brief 50.9Ni hereafter) polycrystals [16]. This strange 3-stage transformation differs from the 3-stage transformation after aging at higher temperature in that the former undergoes a 2-stage R-transformation and 1-stage B19' transformation while the latter undergoes 1-stage R-phase transformation but 2-stage B19' transformation. The 2-stage R and 1-stage B19' transformation has been investigated by Kim et al. [16]; they attributed it to the local stress and composition heterogeneity between Ti_3Ni_4 particles. It is thought that the first peak on DSC curves on cooling is associated with R-phase transformation in the vicinity of Ti_3Ni_4 particles and the second corresponds to the R-phase transformation in regions away from precipitates. Apparently, this mechanism predicts that this peculiar phenomenon is intrinsic for all Ti_3Ni_4 -containing samples and is independent of whether or not the sample is single crystal or polycrystal. But as will be reported in the following, our experimental results showed that low-temperature aged single crystals (without grain boundary) undergo normal 1-stage R-phase transformation. Thus, this critical experimental result does not support this mechanism.

The purpose of the present paper is thus to clarify the microscopic origin of the abnormal 2-stage R-phase transformation (this will be abbreviated as “2-R transformation” hereafter). As Fan et al. pointed out, the grain boundary plays an important role in the occurrence of abnormal 3-stage martensitic transformation for intermediate-temperature aged Ni-rich Ti–Ni alloys. Inspired by Fan et al.'s [15] idea about the mechanism of intermediate-temperature aged samples [15], we consider that the existence of grain boundary may also be the key to the occurrence of 2-R transformation. To explore such a possibility, we designed our experiment as follows. First, low-temperature aging was carried out with 50.6Ni single crystals, which is the crucial test for the mechanism based on the “small-scale” heterogeneity of composition and stress between Ti_3Ni_4 particles. If 2-R transformation is due to such local heterogeneity, it can also be expected in aged single crystals. Then, the same aging treatment was applied to 50.6Ni polycrystals to clarify the effect of grain boundary on the occurrence of 2-R transformation. Furthermore, we used the same aging treatment with 51Ni and 52Ni polycrystals to investigate the effect of Ni content. As can be seen in the following, this systematic investigation proved our idea and leads to a simple explanation for the abnormal 2-R transformation.

As will be discussed later, our mechanism can provide a unified explanation for all the abnormal transformation behaviors for both intermediate-temperature aged alloys (undergoing 1-stage R and 2-stage B19' transformation) and low-temperature aged alloys (undergoing 2-stage R and 1-stage B19' transformation).

2. Experimental procedure

Following the above experimental design, 50.6Ni single crystals and 50.6Ni, 51Ni, 52Ni polycrystals (supplied by Furukawa Electric Co. Ltd.) were used in our present study. The Ni content of the samples was determined by a wet chemical method.

All the samples were small plates made by spark cutting, which are about $3 \times 3 \times 1 \text{ mm}^3$. In order to remove the affected surface layer, the samples were mechanically polished and chemically etched. Then they were sealed in quartz tubes with argon (about $1.5 \times 10^3 \text{ Pa}$) and Ti-getter was also sealed into the tubes to avoid oxidation during the subsequent heat treatment. All the sealed samples were annealed at $1000 \text{ }^\circ\text{C}$ for 1 h and water quenched at room temperature to obtain a homogeneous supersaturated solid solution. In the following, all samples were aged at $250 \text{ }^\circ\text{C}$ for different times: from 1 to 72 h for 50.6Ni single crystals and 52Ni polycrystals; from 1 to 110 h for 50.6Ni and 51Ni 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 was a mixture of 50 vol.%water, 40 vol.%nitric acid and 10 vol.%hydrofluoric acid.

The transformations were characterized by differential scanning calorimetry (DSC) with cooling and heating rates of $10 \text{ }^\circ\text{C}/\text{min}$ from -100 to $100 \text{ }^\circ\text{C}$, using a 822e calorimeter from Mettler Toledo.

Samples for transmission electron microscopy (TEM) observation were mechanically polished and then electrolytically polished with a twin-jet apparatus at room temperature. The electrolyte consisted of HClO_4 and CH_3COOH in the proportion of 1:9 in volume. The microstructures were observed with a JEM-2000EX.

3. Experimental results

3.1. DSC results of 50.6Ni single crystals aged at $250 \text{ }^\circ\text{C}$

Transformation behaviors of 50.6Ni single crystals aged at $250 \text{ }^\circ\text{C}$ for different times are shown in Fig. 1, which is a crucial test for the mechanism based on the local heterogeneity of composition and stress between Ti_3Ni_4 particles. It can be seen that all 50.6Ni single crystals undergo normal 2-stage transformation (B2–R–B19') both on cooling and heating, except for the one aged for 1 h, which shows only 1-stage transformation (B2–R).

Therefore, all single crystal samples undergo 1-stage R-phase transformation (1-R transformation), not 2-R transformation. This important finding proves that the local heterogeneity of composition and stress between particles is not responsible for the abnormal 2-R transformation, because such small-scale heterogeneity clearly exists even in aged single crystals.

3.2. DSC results of 50.6Ni polycrystals aged at $250 \text{ }^\circ\text{C}$

Fig. 2 shows the transformation behaviors of 50.6Ni polycrystals after aging at $250 \text{ }^\circ\text{C}$ for different times. Clearly, 50.6Ni polycrystals exhibit transformation behaviors that are significantly different from those of single crystals. Three peaks, marked with 1–3 on cooling, are shown in DSC curves of 50.6Ni polycrystals aged for a short time ($<60 \text{ h}$), and peak-2 gradually shifts to peak-1, until finally merging into peak-1 with increasing aging time ($>60 \text{ h}$). Furthermore, there is a high background level on the DSC curve between peaks 1 and 2, which is very different from normal transformation behavior. On heating, two peaks marked with 4 and 5 are shown in all DSC curves, irrespective of aging time.

In order to identify the nature of these peaks, partial DSC cycles were performed by cooling and heating the samples to a predefined temperature, during which only the selected transformation was allowed to occur. Fig. 3 shows the partial DSC cycles of 50.6Ni polycrystal aged at $250 \text{ }^\circ\text{C}$ for 24 h. Fig. 3(b) suggests that peak-1 corresponds to peak-5. As this pair of transformation peaks has a small hysteresis of 2 K, which is 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 peak-2' is a part of peak-4. Similarly, peak-2 and peak-2' should also be associated with B2–R and R–B2, respectively, from their narrow hysteresis. Thus, the 50.6Ni polycrystal aged at $250 \text{ }^\circ\text{C}$ for 24 h undergoes 2-stage R-phase transformation, and it is the same case for those aged up to 60 h. In the following, we denote the two stages of R-phase transformation as B2–R1 and B2–R2 on cooling, R1–B2 and R2–B2 for their reverse transformations on heating, respectively. Furthermore, it can be concluded that peak-3 corresponds to the part of peak-4 by excluding peak-2' and they represent R–B19' and B19'–R transformations from the large hysteresis (70 K). It is to be noted here that R represents both R1 and R2. That is, there is only one stage of B19' transformation following two stages of R-phase transformation, which will be explained later. For 50.6Ni polycrystals after aging for a longer time, peak-2 merges into peak-1, and thus B2–R1 and B2–R2 become one stage, B2–R. Therefore, it is easy to identify those peaks on DSC curves to represent B2–R and R–B19' on cooling; B19'–R and R–B2 on heating, which are the normal 2-stage (B2–R–B19') martensitic transformation for aged Ni-rich Ti–Ni alloys.

Therefore, 50.6Ni polycrystals show two stages of R-phase transformations (B2–R1 and B2–R2) and one stage of R–B19' after short time aging; normal 2-stage (B2–R–B19') transformations after long time aging. Most importantly, the abnormal 2-R transformation occurs only for 50.6Ni polycrystals, not for the corresponding 50.6Ni single crystals; this suggests that the occurrence of 2-R transformation should be due to the existence of grain boundaries.

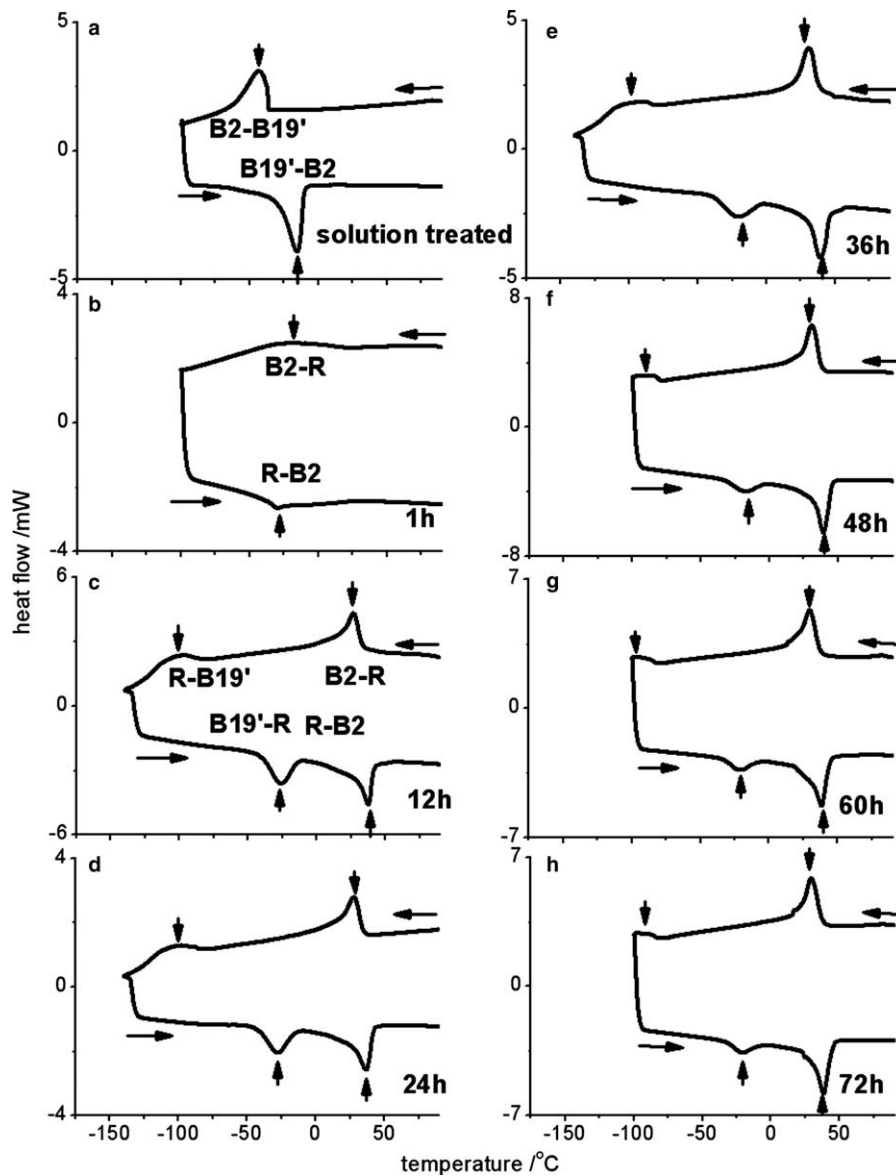


Fig. 1. DSC curves of Ti-50.6at.%Ni single crystals: (a) annealed at 1000 °C for 1 h and water quenched; (b–h) aged at 250 °C for 1, 12, 24, 36, 48, 60, 72 h, respectively, after solution treatment.

3.3. Effect of Ni content on the transformation behavior after low-temperature aging

In this part, we report the transformation behaviors of 51Ni and 52Ni polycrystals, which are of higher Ni content than 50.6Ni polycrystal. By comparing the transformation behaviors of 50.6Ni, 51Ni and 52Ni polycrystals, the effect of Ni content on transformation behaviors can be identified.

Fig. 4 shows the DSC curves of 51Ni polycrystals aged at 250 °C for different times. It can be seen that there are two peaks both on cooling and on heating when aging time is short, and they are marked with 1, 2 and 3, 4, respectively. With increasing aging time, peak-2 gradually shifts to peak-1 until finally merging into peak-1, and peak-3 shifts to peak-4 until merging into peak-4, which is similar to the case of 50.6Ni polycrystals. By doing partial DSC

cycles, we found that peak-1 corresponds to peak-4 and they represent B2–R1 and R1–B2; peak-2 and peak-3 are associated with B2–R2 and R2–B2. Thus, like 50.6Ni polycrystals, 51Ni polycrystals undergo two stages of R-phase transformation, and this is the same case for samples aged up to 48 h. In addition, we can see that the two R peaks of 51Ni polycrystals are closer to each other than those of 50.6Ni polycrystals; this indicates the tendency for merging of the two R peaks with increasing Ni content, which is confirmed by the fact that 52Ni polycrystals shows only one stage of R-phase transformation in the following part. For 51Ni polycrystals aged for longer time, the only one peak both on cooling and heating represents B2–R and R–B2, respectively, which is the normal 1-stage R-phase transformation for aged Ti–Ni alloys. In addition, as a result of high-Ni content, the subsequent R–B19' transformation temperature is out of our DSC measurement

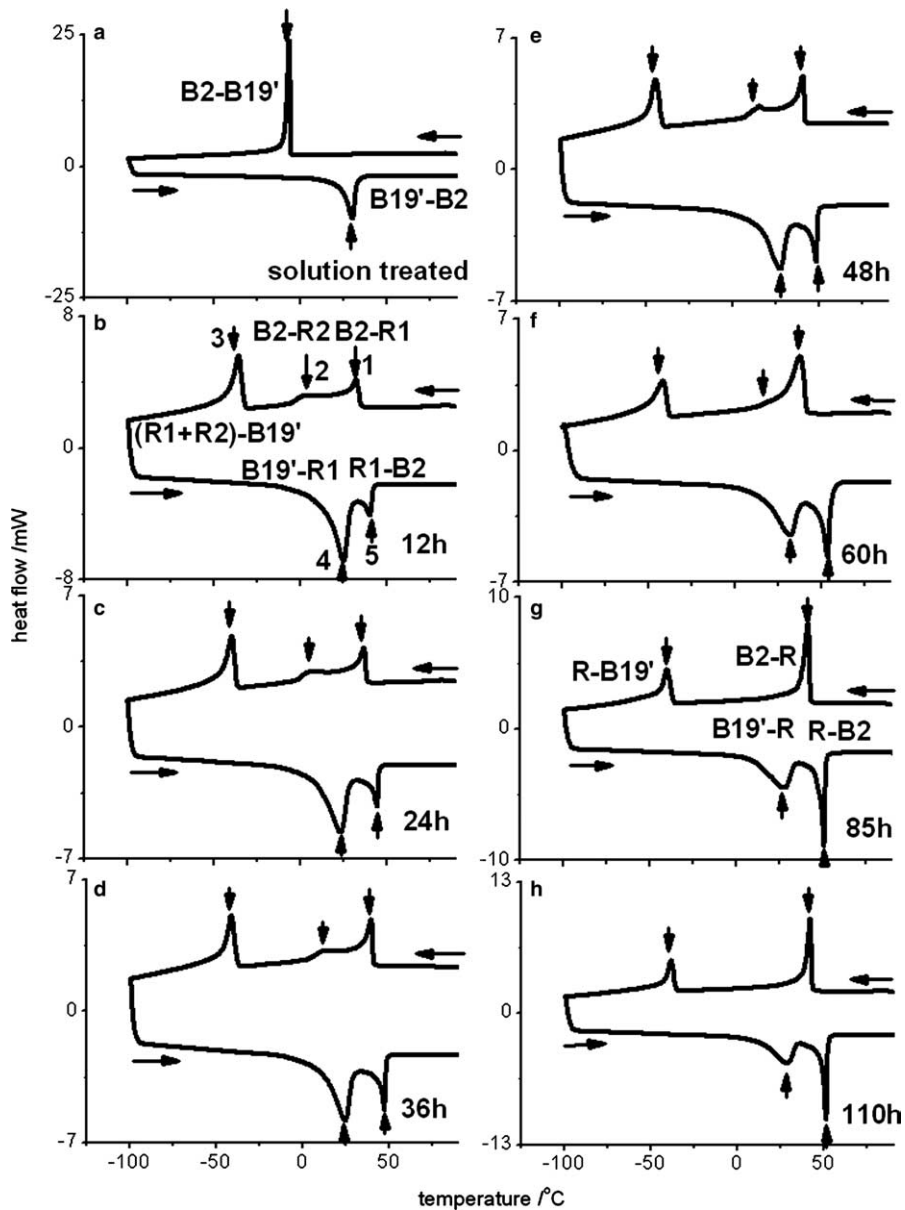


Fig. 2. DSC curves of Ti-50.6at.%Ni polycrystals: (a) annealed at 1000 °C for 1 h and water quenched; (b–h) aged at 250 °C for 12, 24, 36, 48, 60, 85, 110 h, respectively, after solution treatment.

window and thus there is no corresponding peak on DSC curves for all 250 °C-aged 51Ni polycrystals. Therefore, 51Ni polycrystals undergo two stages of R-phase transformation after short time aging and one stage of R-phase transformation when aged for a long time. Most importantly, 51Ni polycrystals show the abnormal 2-R transformation, which is similar to 50.6Ni polycrystals. This important result further implies that the existence of grain boundary is indeed responsible for the occurrence of 2-R transformation.

In contrast to the transformation behaviors of 50.6Ni and 51Ni polycrystals, 52Ni polycrystals exhibit only 1-stage transformation, irrespective of aging time (Fig. 5). From the small hysteresis, it can be identified that the peaks on cooling and heating are associated with B2–R and R–B2,

respectively. It is noticed that the peak is very broad after short time aging, but becomes sharper with further aging. The absence of R–B19' transformation is for the same reason as in the case of 51Ni polycrystals, that is, because of high-Ni content, the following R–B19' transformation temperature is out of our DSC measurement window, so there is no corresponding peak on the DSC curves. Therefore, all 52Ni polycrystals undergo normal 1-R transformation, which indicates that Ni content has an important effect on the occurrence of 2-R transformation.

Summarizing the above systematic investigation, after aging at 250 °C, 50.6Ni single crystals undergo normal 1-R transformation and never show 2-R transformation, which this proves that the local heterogeneity of composition and stress is not responsible for the occurrence of

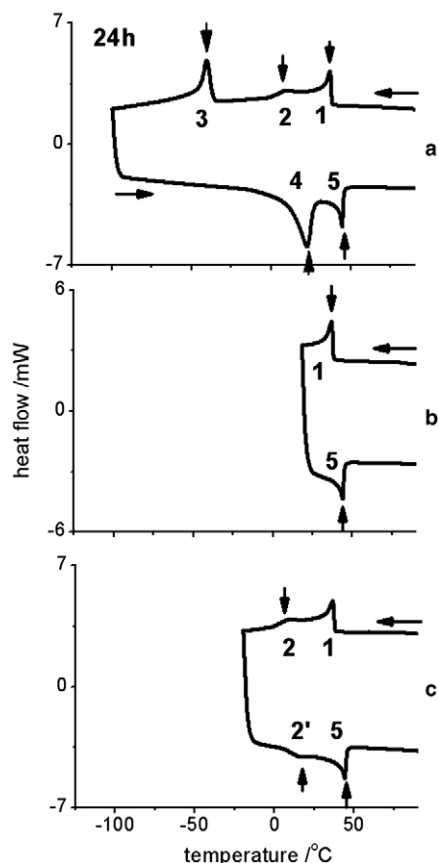


Fig. 3. Partial DSC cycles and full cycle for Ti-50.6at.%Ni polycrystal aged at 250 °C for 24 h after solution treatment.

2-R transformation. On the contrary, 50.6Ni polycrystals exhibit 2-R transformation. This contrasting behavior implies the possibility that the occurrence of 2-R transformation is due to the existence of grain boundaries. Further study with 51Ni polycrystals confirms the above possibility, because they also show 2-R transformation. However, 52Ni polycrystals again undergo normal 1-R transformation and this suggests that the existence of grain boundaries is not a sufficient condition for the occurrence of 2-R transformation: Ni content is also an important factor.

3.4. TEM observations of samples undergoing 2-stage R-phase transformation

TEM observations were carried out with a 50.6Ni polycrystal sample aged at 250 °C for 36 h to investigate the microstructural features of the samples showing 2-R transformation. Fig. 6(a) shows the distribution of Ti_3Ni_4 precipitates from grain boundary region to grain interior in a grain that is in a fully parent state (such grains can be occasionally found in very thin areas of our TEM samples, where the internal stress has been released and thus leads to a suppression of R formation). As the precipitate size is extremely small, they are better imaged under TEM when in the B2 state where no additional contrast due to twin boundaries exists; this is why we chose these B2 grains to

identify the distribution of precipitates. In this figure it can be seen that the density of Ti_3Ni_4 precipitates is largest in the vicinity of a grain boundary, and it becomes smaller away from a grain boundary. As will be discussed later, Ni atoms cannot undergo a long-range migration at such low-temperatures (250 °C), so the high density of Ti_3Ni_4 particles at grain boundary does not result from the diffusion of Ni from the grain interior to the grain boundary, compensating for the matrix Ni-depletion during aging. Thus, a higher density of Ni-rich Ti_3Ni_4 precipitates in the grain boundary region corresponds to a lower Ni concentration in the B2 matrix in this region. By the same reasoning, the B2 matrix in the grain interior (where Ti_3Ni_4 density is lower) has a higher Ni concentration. As a result, there is a large-scale heterogeneity in Ni concentration between the grain boundary region and the grain interior, which is on a much larger scale than the local heterogeneity of composition and stress between Ti_3Ni_4 particles.

We performed TEM observations to obtain direct evidence for where the two stages of R-phase transformation occur. We electrolytically polished another 50.6Ni sample at room temperature (~ 25 °C). By referring to its corresponding DSC curve (Fig. 2(d)), we know that the sample at room temperature (at which TEM observation is carried out) is in a state between the two R peaks, i.e., B2–R1 is already finished, but B2–R2 is not yet triggered. Fig. 6(b) show the images and corresponding diffraction patterns of the grain boundary region and the grain interior. It is found that the grain boundary region and grain interior show very different microstructures. Along grain boundary there is a ring of R-phase, as proved by its characteristic $1/3$ superlattice spots. But the grain interior is still in the B2 state, as proved by the B2 diffraction pattern of $[111]$ zone-axis. Our TEM observations unambiguously proved that B2–R1 occurs in the grain boundary region. And accordingly, B2–R2 occurs in the grain interior. This transformation sequence is consistent with the fact that Ni concentration of B2 matrix in the grain boundary region is lower than that in the grain interior. Therefore, it is the large-scale heterogeneity of Ni concentration between the grain boundary region and the grain interior that leads to 2-R transformation.

4. Discussion

4.1. Origin of the abnormal 2-stage R-phase transformation behavior

As shown in Fig. 1, all 50.6Ni single crystals undergo normal 1-R transformation, being independent of aging time. This important result suggests that the occurrence of 2-R transformation is not due to the local heterogeneity of composition and stress between particles, because such small-scale heterogeneity definitely exists in aged single crystals.

After excluding the possibility that the local heterogeneity between particles results in 2-R transformation, we

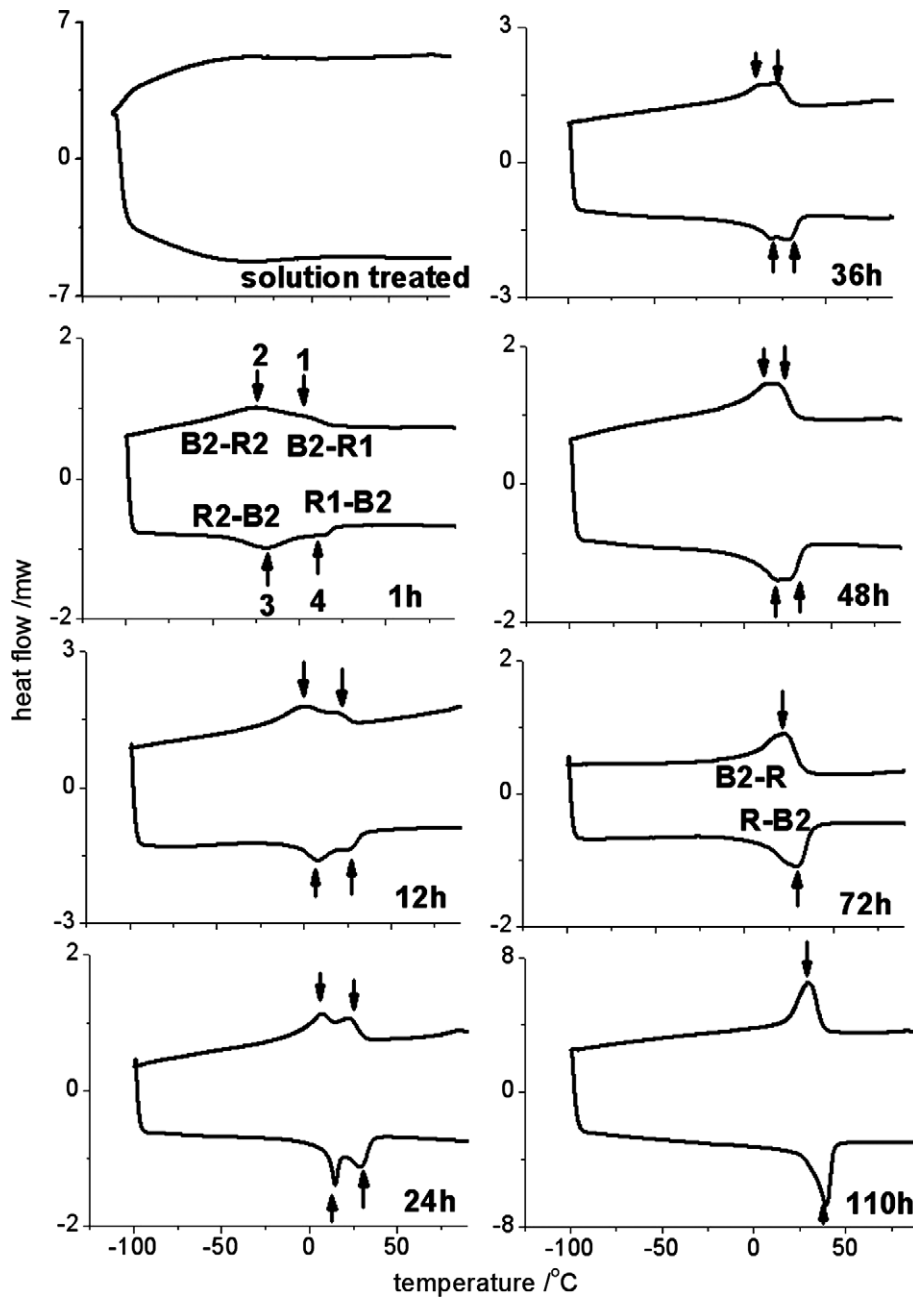


Fig. 4. DSC curves of Ti-51at.%Ni polycrystals: (a) annealed at 1000 °C for 1 h and water quenched; (b–h) aged at 250 °C for 1, 12, 24, 36, 48, 72, 110 h, respectively, after solution treatment.

consider that a large-scale heterogeneity may be responsible for 2-R transformation. The contrasting transformation behaviors of 50.6Ni single crystals and 50.6Ni, 51Ni polycrystals suggest that this large-scale heterogeneity must be due to the existence of grain boundaries. In the following, we explain how the grain boundary can result in such a large-scale heterogeneity by considering the precipitation kinetics in a supersaturated polycrystalline solid solution during low-temperature aging.

As the nucleation barrier is much reduced at the grain boundary compared with that at the grain interior, the nucleation rate at the grain boundary is larger than that

in the grain interior according to the theory of phase transformation kinetics [15]. Thus, during aging, precipitates are easier to nucleate in the grain boundary region than in the grain interior. Fig. 7 shows a schematic illustration for the relation between the nucleation rate and supersaturation degree in the grain boundary and the grain interior during low-temperature aging. The curves are calculated in a semi-quantitative way by nucleation kinetics theory [17]. It can be seen that the nucleation rate at the grain boundary (I_{GB}) is always larger than that in the grain interior (I_{GI}); the lower the supersaturation is, the greater is the relative difference. For 50.6Ni polycrystals, I_{GB} is many times

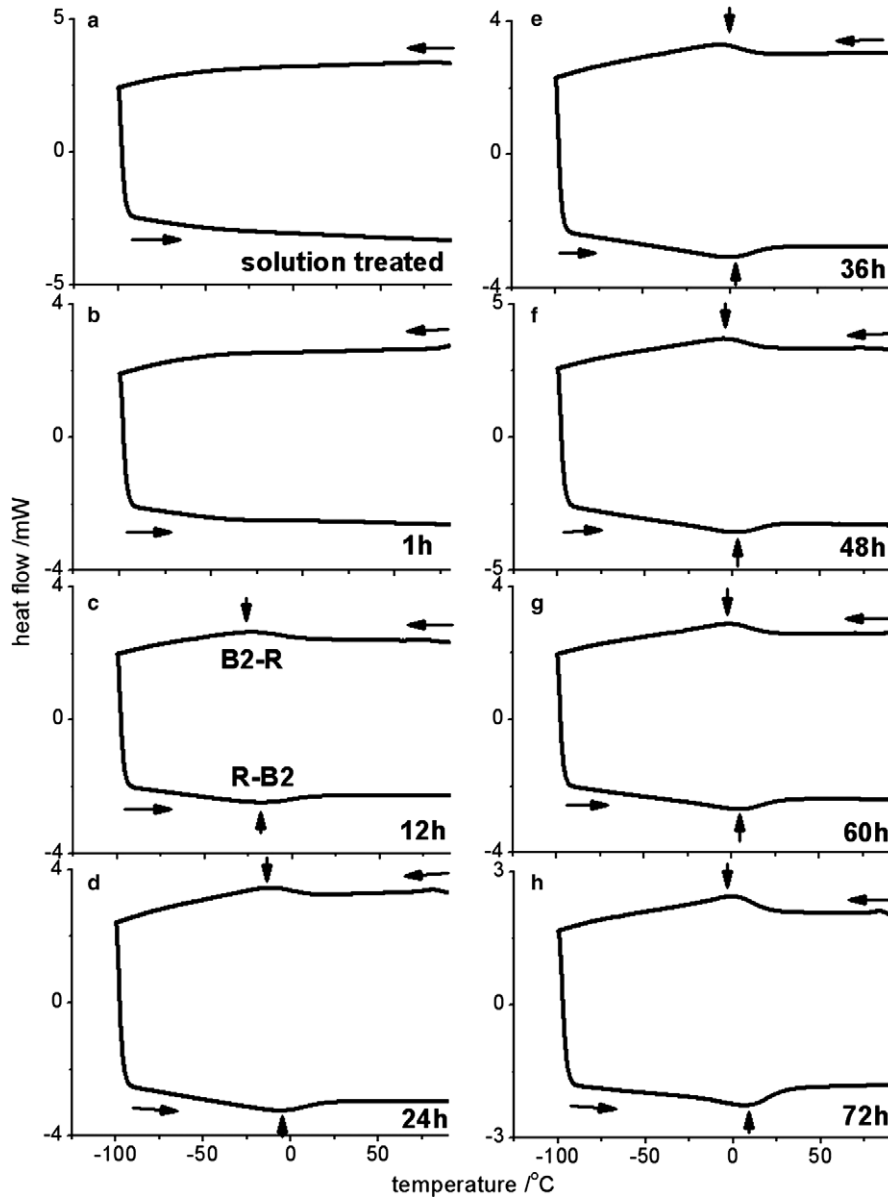


Fig. 5. DSC curves of Ti-52at.%Ni polycrystals: (a) annealed at 1000 °C for 1 h and water quenched; (b–h) aged at 250 °C for 1, 12, 24, 36, 48, 60, 72 h, respectively, after solution treatment.

larger than I_{GI} , and thus the precipitate density in the grain boundary region is larger than that in the grain interior, which is consistent with our TEM observation shown in Fig. 6(a). As a result, Ni concentration in the grain boundary region is lower compared with that in the grain interior. This is the large-scale heterogeneity caused by the grain boundary.

Fig. 8 shows the mechanism of 2-R transformation and its evolution with time, as well as its dependence on Ni concentration. Fig. 8(a) shows the illustration of precipitate distribution and corresponding Ni concentration profile from grain boundary region to grain interior for low-Ni content polycrystals after low-temperature aging. Following the discussion above, it can be deduced that there is a large change in Ni concentration between the grain bound-

ary region and the grain interior. This Ni concentration profile is the key to understanding the abnormal 2-R transformation.

Before explaining the mechanism for 2-R transformation, we address an important feature of R-phase transformation. Because of the small lattice distortion associated with a R-phase transformation, the presence of Ti_3Ni_4 particles has little effect on the formation of R-phase [7], thus R-phase transformation only depends on the Ni concentration. As a consequence, B2 in the low-Ni grain boundary region first transforms into R-phase on cooling, forming the DSC peak-1; at lower temperature B2 in high-Ni grain interior region transforms into R, forming the DSC peak-2. At intermediate temperatures between the peak-1 and peak-2, the R phase transformation of the intermediate

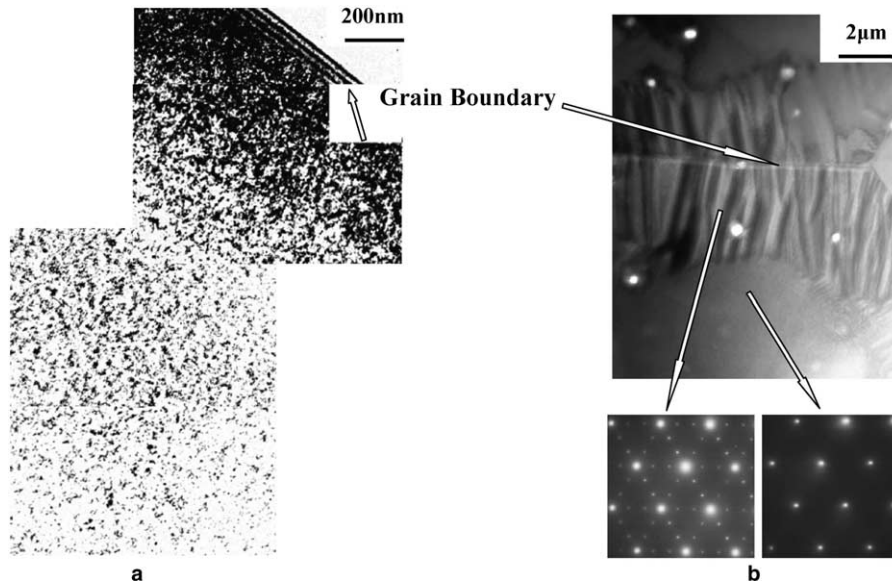


Fig. 6. TEM micrographs of Ti-50.6at.%Ni polycrystal aged at 250 °C for 36 h: (a) Ti_3Ni_4 precipitate distribution from grain boundary region to grain interior (the sample is in the parent state); (b) microstructures of grain boundary region and grain interior and corresponding diffraction patterns (the sample is in a state between peaks 1 and 2 in Fig. 2(d)). Diffraction patterns show that grain boundary is in R phase while the grain interior is in B2 state.

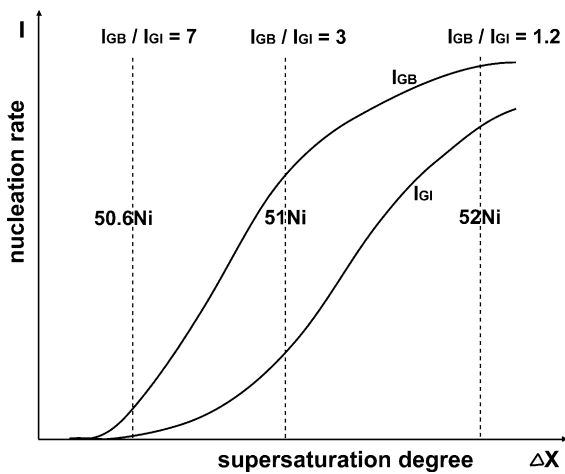


Fig. 7. Schematic illustration for the relation between nucleation rate during low-temperature aging and supersaturation degree in grain interior and grain boundary. The nucleation rates at grain boundary and at grain interior are indicated with I_{GB} and I_{GI} , respectively.

region (the one between the grain boundary region and the grain interior region) occurs. However, as the fraction of this region is small, this gradual formation of R does not produce a prominent peak, but contributes to the DSC background level at temperatures between peaks 1 and 2. This explains the fact that there is a high background level in DSC curves between peaks R1 and R2 (see Fig. 2(b)).

If only concentration heterogeneity between the grain boundary and grain interior is considered, it may be possible that B19' transformation also occurs in two stages like

R-phase transformation does (i.e., the grain boundary transforms first, followed by the grain interior). However, our experimental results showed only one B19' peak (Fig. 2b), in contrast to the case for R-transformation. Such a difference stems from the fact that B19' transformation is not only dependent on composition, but also dependent on precipitation density. The lattice deformation of B19' (compared with R phase) makes the formation of B19' more difficult with increasing density of Ti_3Ni_4 particles [7]. As a result, B19' transformation at grain boundary becomes more difficult than in the grain interior. Therefore, we can see that the precipitation heterogeneity effect is just opposite to the composition heterogeneity effect. Thus, these two opposite effects tend to cancel each other out and thus result in a 1-stage B19' transformation. Furthermore, since B19' involves a large transformation strain, it has a large nucleation barrier; thus B19' transformation proceeds in a burst-like way through the whole grain and gives rise to one transformation peak. Therefore, both R1 in grain boundary and R2 in grain interior transform into B19' in one stage directly and thus there is only one B19' peak shown in DSC curves.

Therefore, it is the preferential precipitation in the grain boundary region that results in a large-scale heterogeneity of Ni concentration between the grain boundary region and the grain interior, which directly gives rise to 2-R transformation. In addition, it is proved that this effect of the grain boundary on precipitate distribution is intrinsic for all supersaturated polycrystals by considering the kinetics of precipitation. However, the fact that all 52Ni polycrystals show normal 1-R transformation evidently implies that the existence of grain boundaries is not a suf-

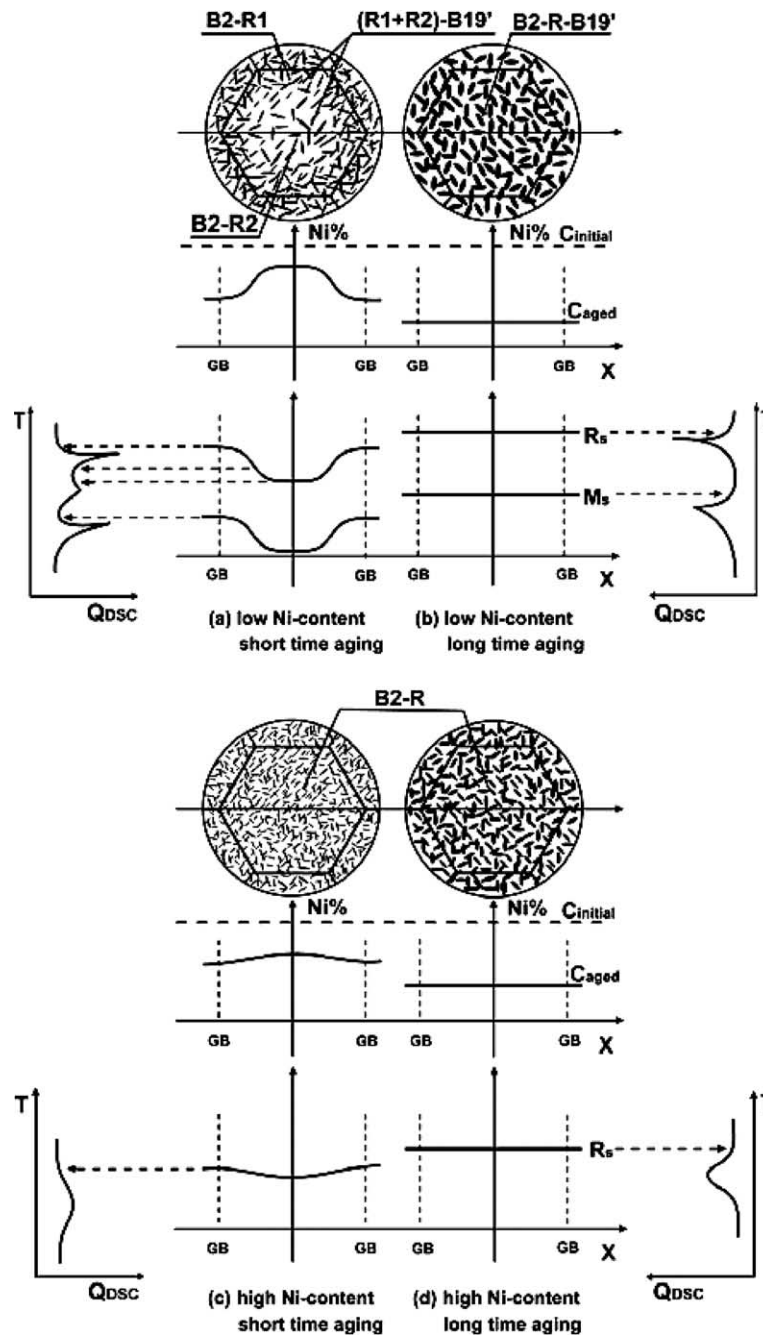


Fig. 8. Schematic illustration for the microstructure evolution at low-Ni content (a,b) and high-Ni content (c,d). It can explain both the 2-stage and 1-stage R-phase transformation behaviors of supersaturated Ti–Ni solid solution. In the figure, C_{initial} and C_{aged} curves represent the Ni concentration profile of initial (as-quenched) state and that after aging, respectively. GB denotes grain boundary. R_s and M_s represent the start transformation temperature of R-phase transformation and B19' transformation, respectively.

cient condition for the occurrence of 2-R transformation, and Ni content is also an important factor.

By referring to Fig. 7, we can understand the Ni content dependence of 2-R transformation. Although both I_{GB} and I_{GI} increase with increasing Ni content, the ratio of $I_{\text{GB}}/I_{\text{GI}}$ decreases, e.g., $I_{\text{GB}}/I_{\text{GI}}$ is 7 for 50.6Ni polycrystal; 3 for 51Ni polycrystal and 1.2 for 52Ni polycrystal. This sharp decrease of $I_{\text{GB}}/I_{\text{GI}}$ with increasing Ni content indicates

that the preferential precipitation in the grain boundary region becomes less effective, so high-Ni content favors the tendency for homogeneous precipitation across the whole sample. For 51Ni polycrystal, $I_{\text{GB}}/I_{\text{GI}}$ is 3, so the difference of precipitate density between grain boundary region and grain interior is not as large as that of 50.6Ni polycrystals and naturally the heterogeneity of Ni concentration is smaller. Thus, for 51Ni polycrystals, the two peaks repre-

senting 2-R transformation on the DSC curves are much closer to each other than those for 50.6Ni polycrystals. Following the same reasoning, it is understandable that 52Ni polycrystals show only one broad stage of R-phase transformation. Since I_{GB} and I_{GI} are almost the same, which results in nearly homogeneous precipitate distribution and Ni concentration across the whole grain, as shown in Fig. 8(c), so the R-phase transformation can proceed continuously from the low-Ni grain boundary to high-Ni grain interior, and thus there is one corresponding broad peak on the DSC curve.

In a word, whether the R-phase transformation occurs in two stages or one stage depends on whether the precipitate distribution is heterogeneous or homogeneous. For single crystals, the precipitates are homogeneously distributed across the whole sample, so R-phase transformation occurs in only one stage. For polycrystals, how precipitates are distributed is dependent on the competition between two opposite tendencies: (1) a tendency for preferential distribution in grain boundary region; (2) a tendency for homogeneous distribution across the whole grain with high-Ni content. With low Ni content (50.6Ni, 50Ni), the preferential precipitation in grain boundary region is dominant and this results in a large-scale heterogeneity of Ni concentration between the grain boundary region and the grain interior; as a result, 2-R transformation occurs. On the other hand, with high-Ni content (52Ni), the tendency for homogeneous precipitation across the whole grain is dominant and thus only one stage R-phase transformation occurs. Therefore, the composition dependence of the transformation behavior can be well understood by this explanation.

4.2. Evolution of transformation behaviors with aging time

As mentioned in the above, for low-Ni content (50.6Ni, 51Ni) polycrystals, there are two R-phase transformation peaks after short time aging and the second peak on cooling gradually shifts into the first one until finally merging into the first one with prolonged aging. The evolution of transformation temperatures with increasing aging time for 50.6Ni polycrystal is illustrated in Fig. 9, and hereafter, we use Rs1, Rs2, and Ms for the start temperatures of B2–R1, B2–R2 and R–B19' transformations, respectively. We can see that both Rs1 and Rs2 increase with increasing aging time until becoming constant, while Ms first decreases and then increases with increasing aging time until finally becoming constant. The same is true for 51Ni polycrystal, except that no R–B19' transformation is shown within our measurement window. However, all high-Ni content (52Ni) polycrystal undergo normal 1-stage R-phase transformation, and the corresponding peak becomes sharper with increasing aging time.

The microstructural evolution shown in Fig. 8 can well explain the different transformation behaviors of both low- and high-Ni content low-temperature aged alloys after prolonged aging. For low-Ni content (50.6Ni, 51Ni) poly-

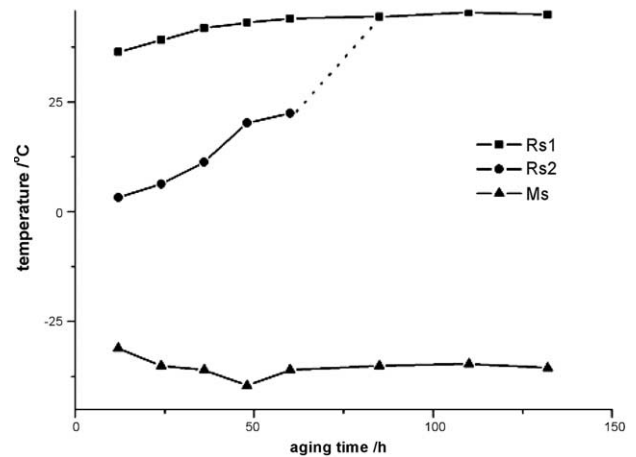


Fig. 9. Relations between Rs1, Rs2, Ms and aging time for Ti-50.6at.%Ni polycrystals aged at 250 °C. Here, the start temperatures of B2–R1, B2–R2 and R–B19' transformations are indicated by Rs1, Rs2 and Ms, respectively.

crystals aged for a short time, shown in Fig. 8(a), Ti_3Ni_4 particles of small size gradually nucleated both in grain boundary region and grain interior, by the driving force of supersaturated Ni in the matrix. However, since the nucleation rate in grain boundary region is much larger than that in grain interior, the precipitate density in the grain boundary region is much larger than that in the grain interior. As a result, the Ni concentration of the matrix in the grain boundary region is much lower than that in the grain interior and thus there is a large heterogeneity of Ni concentration between the grain boundary region and the grain interior. For this reasoning, B2 in the low-Ni grain boundary region transforms into R-phase for the first stage and then that in the high-Ni grain interior for the second stage, and thus 2-R transformation occurs. In addition, precipitation of Ti_3Ni_4 particles causes a decrease in Ni concentration of the B2 matrix both in the grain boundary region and the grain interior and this favors an increase in Rs1 and Rs2, because the formation of R-phase is not affected by Ti_3Ni_4 particle size and is only determined by the Ni concentration. However, the presence of small Ti_3Ni_4 particles produces a strong resistance to the large lattice deformation associated with the formation of B19' and thus it results in a decrease in Ms.

With increasing aging time, since Ni atoms cannot undergo long-range diffusion at such low-temperatures, i.e. from grain interior to grain boundary, Ti_3Ni_4 particles grow larger by absorbing Ni from their nearby B2 matrix and consequently, Ni concentration both in the grain boundary region and the grain interior are further lowered, so both Rs1 and Rs2 increase with increasing aging time. Meanwhile, Ti_3Ni_4 particles grow and the spacing becomes larger. These widely spaced particles then produce relatively small resistance to the formation of B19', so Ms increases rapidly. Since there is an equilibrium Ni concentration between the B2 matrix and Ti_3Ni_4 particles

at each aging temperature [18], the growth of particles will saturate when Ni concentration in the surrounding matrix reaches the equilibrium value. As a result, with increasing aging time, the density of precipitates in grain boundary region and grain interior becomes more homogeneous, which is shown in Fig. 8(b). Accordingly, Ni concentration across the whole grain becomes more homogeneous and the heterogeneity between grain boundary region and grain interior becomes smaller; this favors the two R-phase transformation peaks becoming closer to each other until finally merging into one. After Ni concentration in B2 matrix reaches the equilibrium value, Rs will no longer change with aging time. However, Ti_3Ni_4 particles still grow larger by consuming other small particles and spacing becomes larger, so Ms gradually increases. When the particle size is large enough that has no resistance on the formation of B19', Ms becomes constant.

For high-Ni content (52Ni) polycrystals, nucleation of Ti_3Ni_4 particles in the grain interior is almost the same as that in the grain boundary region, so precipitate distribution is nearly homogeneous across the whole grain shown in Fig. 8(c), and is almost unaffected by the existence of the grain boundary. Thus, the whole sample undergoes one broad stage of R-phase transformation. With further aging, Ti_3Ni_4 particles grow larger by absorbing Ni from their nearby matrix and the growth will saturate when the Ni concentration in the B2 matrix reaches the equilibrium value, so both precipitate density and Ni concentration across the whole grain becomes more homogeneous, shown in Fig. 8(d), and thus the corresponding peak becomes sharper with further aging.

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

In this part, we will show that transformation behaviors of both low-temperature and intermediate-temperature aged alloys can be understood by a unified explanation.

For low-Ni content polycrystals aged at intermediate temperatures (400–500 °C), the low supersaturation leads to a preferential precipitation along the grain boundary. This causes the grain boundary region to be of lower Ni concentration than that in the grain interior, and there is a tendency for Ni to migrate from the grain interior to the grain boundary region. As the temperature is high enough, such a long-range diffusion is possible [15]. As a result of the Ni diffusion from the grain interior to the grain boundary, the depletion of Ni in the grain interior makes the grain interior even more difficult to form precipitates, thus making it almost precipitate-free. Therefore, the grain boundary region undergoes 2-stage B2–R–B19' transformation and the grain interior undergoes a direct B2–B19' transformation, so the sample as a whole undergoes the abnormal 3-stage martensitic transformation.

When a low-Ni polycrystal is aged at the low-temperature (250 °C) for a short time, although the same preferen-

tial nucleation happens around the grain boundary and there is also a tendency for Ni to migrate from the grain interior to the grain boundary, such a long-range diffusion is prohibited due to the low-temperature. As a result, it is impossible to form a precipitate-free zone at the grain interior; thus both the grain boundary and grain interior form Ti_3Ni_4 precipitates, although there may be a difference in the precipitation density and Ni concentration between the grain boundary region and the grain interior. Therefore, the grain boundary region (low-Ni concentration) undergoes B2–R1 and the grain interior (high-Ni concentration) undergoes B2–R2 with further cooling, followed by one stage of R–B19' transformation, which has been discussed above by considering the large barrier for the formation of B19' and the effect of Ti_3Ni_4 particle size on B19' transformation. After long time aging, when Ni concentration of the matrix reaches the equilibrium value, density of precipitates and Ni concentration across the whole grain becomes more homogeneous. As a result, B2 transforms into R-phase in only one stage, and then B19' transformation occurs; this leads to the normal 2-stage (B2–R–B19') martensitic transformation.

For high-Ni alloys aged at both low and intermediate temperatures, a nearly homogeneous precipitation across the whole grain is obtained as a result of large supersaturation. So the whole sample undergoes normal B2–R–B19' transformation or only B2–R transformation if the Ni content is high enough, i.e., 52Ni alloys aged at 250 °C.

Summarizing the above, both the abnormal 3-stage martensitic transformation for intermediate-temperature aged polycrystals and 2-stage R-phase transformation for low-temperature aged polycrystals are due to the large-scale heterogeneous precipitation of Ti_3Ni_4 particles between the grain boundary region and the grain interior, which results from the preferential precipitation in the grain boundary region. The differences in transformation behavior between intermediate-temperature and low-temperature aged polycrystals lie in whether or not there exists a long-range diffusion of Ni from grain interior to grain boundary.

5. Conclusions

In order to find the origin of the abnormal 2-stage R-phase transformation in low-temperature aged Ni-rich Ti–Ni alloys, we investigated the transformation behaviors of 50.6Ni single crystal and 50.6Ni, 51Ni, 52Ni polycrystals, which were aged at 250 °C after solution treatment, with DSC and TEM techniques. We reached the following conclusions.

- (1) 50.6Ni single crystal undergoes normal 1-R transformation. This fact indicates that the local heterogeneity of composition and stress between Ti_3Ni_4 particles is not responsible for the occurrence of 2-R transformation because such small-scale heterogeneity apparently exists in aged single crystal.

- (2) Low Ni content (50.6Ni, 51Ni) polycrystals undergo 2-R transformation, but high-Ni content (52Ni) polycrystals again undergo normal 1-R transformation. This suggests that the existence of grain boundaries is a necessary but not sufficient condition for the occurrence of 2-R transformation; Ni content is also an important factor.
- (3) All these transformation behaviors can be understood by considering the competition between two opposite tendencies: (i) for preferential precipitation in the grain boundary region; (ii) for homogeneous precipitation across the whole grain with increasing Ni content as a result of the supersaturation of Ni. 2-R transformation is ascribed to a large-scale heterogeneity of Ni concentration between the grain boundary and grain interior, and B2–R1 occurs in the low-Ni grain boundary region and B2–R2 in the high-Ni grain interior. On the contrary, when Ni content is high, large nucleation driving force makes precipitate distribution homogeneous, so R-phase transformation occurs in only one stage.
- (4) We proposed a unified explanation for different transformation behaviors of both low-temperature and intermediate-temperature aged alloys, which are naturally determined by the kinetics of precipitation in supersaturated solid solutions.

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