



Influence of Ni_4Ti_3 precipitates on phase transformation of NiTi shape memory alloy

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Abstract: NiTi shape memory alloy samples were aged for 2 h at 573, 723 and 873 K, respectively. Two *R*-phase variants are observed in the NiTi samples aged at 573 and 723 K, where the orientation relationship between the two *R*-phase variants and the *B2* matrix is determined. In the NiTi samples aged at 573 and 723 K, fine and homogeneous Ni_4Ti_3 precipitates are coherent with the *B2* austenite matrix. The Ni_4Ti_3 particles precipitate in the grain interior and at the grain boundaries, where the heterogeneous Ni_4Ti_3 precipitates are coherent, semi-coherent and incoherent with the *B2* matrix in the NiTi sample aged at 873 K. As for the NiTi sample aged at 873 K, one-stage phase transformation from *B19'* martensite to *B2* austenite occurs on heating, but two-stage phase transformation of *B2*–*R*–*B19'* arises on cooling. The NiTi sample aged at 723 K shows two-stage phase transformation of *B2*–*R*–*B19'* on cooling as well, but exhibits two-stage phase transformation of *B19'*–*R*–*B2* on heating. The NiTi sample aged at 573 K exhibits three-stage transformation on cooling due to local stress inhomogeneity and local composition inhomogeneity around the Ni_4Ti_3 precipitates.

Key words: shape memory alloy; NiTi alloy; martensitic transformation; heat treatment; microstructure

1 Introduction

NiTi shape memory alloy has been widely used in the engineering field because of shape memory effect [1–3]. Ni_4Ti_3 precipitate is a metastable phase as well as an important phase, which usually precipitates in Ni-rich NiTi shape memory alloy below about 923 K. Ni_4Ti_3 phase belongs to *R3* space group and it possesses a rhombohedral unit cell structure, in which there are six Ti atoms and eight Ni atoms [4,5]. The habit plane of Ni_4Ti_3 phase is $\{111\}_{B2}$ plane in the *B2* austenite matrix and there exists a certain orientation relationship between the precipitate and the matrix. Furthermore, there are four $\{111\}_{B2}$ planes in the parent phase and every two variants possess the same habit plane, so the Ni_4Ti_3 phase has eight variants [6,7]. The size, the density, the distribution and the shape of the Ni_4Ti_3 precipitate phase are related closely to aging temperature, aging time and composition of NiTi alloy, which further have an effect on the phase transformation of NiTi shape memory

alloy [8–10]. In general, the size of the Ni_4Ti_3 precipitates increases with the increase of aging temperature and aging time, and the smaller Ni_4Ti_3 particle (for example, less than about 100 nm) is coherent with the *B2* austenite matrix [11–14]. The presence of the Ni_4Ti_3 precipitates can suppress the occurrence of martensitic transformation and thus facilitates the formation of *R* phase. Therefore, the occurrence of two-stage phase transformation of *B2*–*R*–*B19'* is considered to be rational in the aged Ni-rich NiTi shape memory alloy. However, the abnormal three-stage phase transformation often occurs in the aged Ni-rich NiTi shape memory alloy [15–21].

In the present study, Ni-rich binary NiTi shape memory alloy with a nominal composition of 50.9% Ni (mole fraction) was subjected to solution treatment and subsequent aging at low temperature (573 K), intermediate temperature (723 K) and high temperature (873 K), respectively. In the case of three different aging temperatures, the influence of Ni_4Ti_3 precipitates on microstructural evolution and phase transformation

behavior of NiTi shape memory alloy was systematically investigated.

2 Experimental

The binary NiTi alloy with a nominal composition of 50.9% Ni is used in the present study and it belongs to the drawn cylindrical bar with a length of 1.5 m and a diameter of 12 mm. The NiTi bar was heated at 1123 K for 2 h and was then quenched into ice water. The NiTi samples with a diameter of 6 mm and a height of 9 mm were cut from the solution-treated NiTi bar by means of electro-discharge machining (EDM). The solution-treated NiTi samples were aged for 2 h at 573, 723 and 873 K, respectively, and subsequently were cooled to room temperature in the atmosphere. During all the aforementioned heat treatment, the specimens were placed into a silica tube, which was flushed with high purity argon gas three times and was then evacuated to a pressure of about 0.1 Pa.

Microstructural evolution of the NiTi samples subjected to solution treatment and aging was investigated by means of transmission electron microscopy (TEM). Foils for TEM observation were mechanically ground to 70 μm and then thinned by twin-jet polishing in an electrolyte consisting of 6% HClO_4 , 34% $\text{C}_4\text{H}_{10}\text{O}$ and 60% CH_3OH (volume fraction). TEM observations were conducted on an FEI TECNAI G2 F30 microscope with a side-entry and double-tilt specimen stage with angular range of $\pm 40^\circ$ at an accelerating voltage of 300 kV. Differential scanning calorimetry (DSC) test was performed at the heating and cooling rates of 10 K/min in order to obtain the phase transformation temperatures of all the NiTi samples.

3 Results

3.1 Microstructures

Figure 1 shows TEM image and the corresponding selected area electron diffraction (SAED) pattern of the microstructure of the solution-treated NiTi samples. It can be seen from Fig. 1 that there is an extremely small amount of TiC phase in the NiTi matrix, in which no Ni_4Ti_3 precipitates arise.

Figures 2–4 indicate TEM images of the NiTi specimens aged at 573, 723 and 873 K, respectively. It can be seen from Figs. 2 and 3 that the fine Ni_4Ti_3 precipitate phases are homogeneously dispersed in the grain boundary and grain interior, but the size of the Ni_4Ti_3 precipitates in the NiTi specimen aged at 723 K is obviously greater than that in the NiTi specimen aged at 573 K. However, it can be found from Fig. 4 that the Ni_4Ti_3 precipitates exhibit the inhomogeneous distribution in the matrix of NiTi sample aged at 873 K,

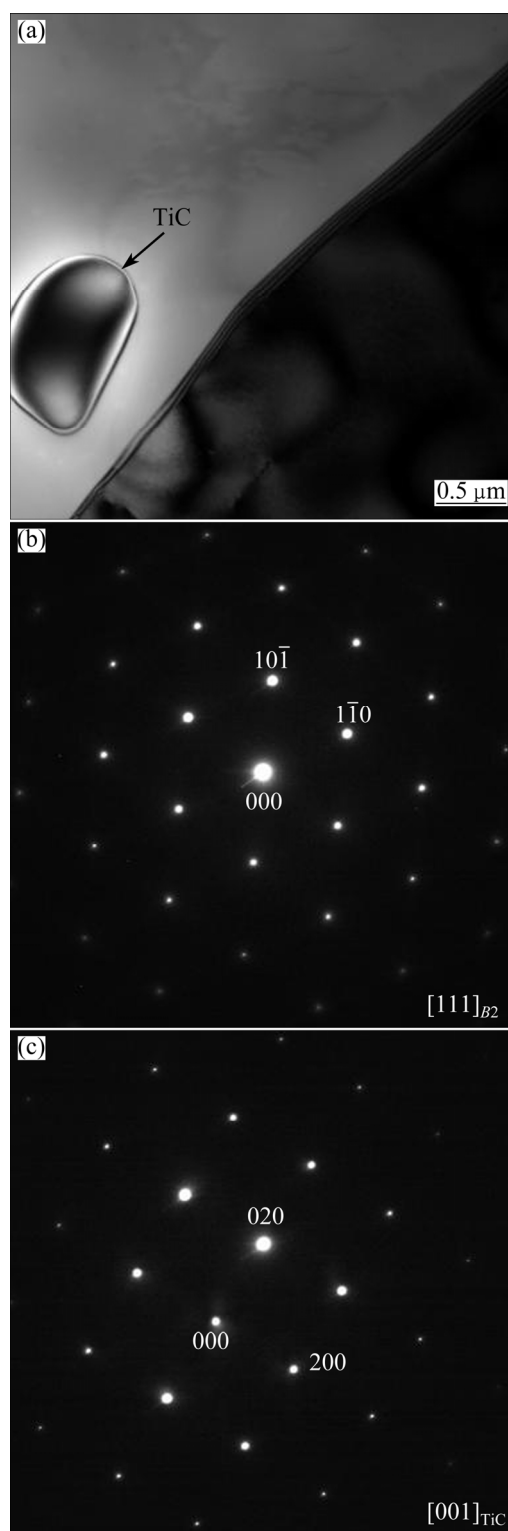


Fig. 1 TEM image (a) and corresponding SAED patterns (b,c) of solution-treated NiTi specimen: (a) Bright field image showing TiC phase in NiTi matrix; (b) SAED pattern of NiTi matrix showing B2 austenite; (c) SAED pattern of TiC

where the Ni_4Ti_3 precipitates are characterized by the typical lenticular shape and they are relatively much coarser than those aged at 573 and 723 K. It can be concluded that the size of the Ni_4Ti_3 precipitates

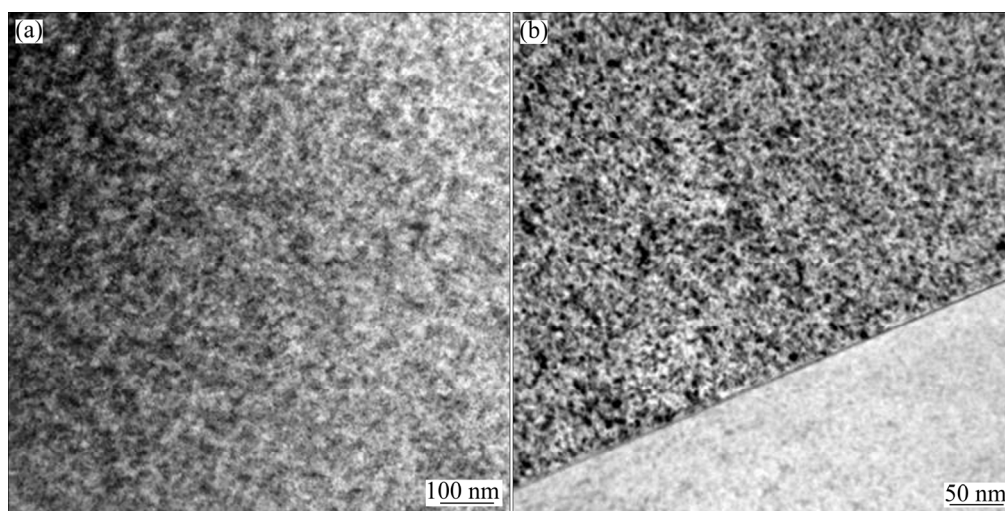


Fig. 2 TEM images of NiTi alloy aged at 573 K: (a) Precipitation of Ni_4Ti_3 in grain interior; (b) Precipitation of Ni_4Ti_3 at grain boundary

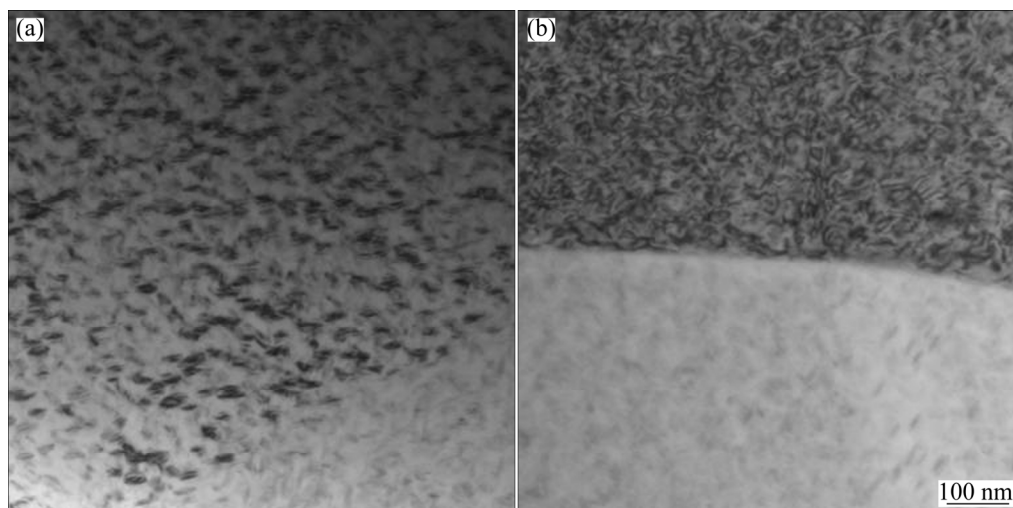


Fig. 3 TEM images of NiTi alloy aged at 723 K: (a) Precipitation of Ni_4Ti_3 in grain interior; (b) Precipitation of Ni_4Ti_3 at grain boundary

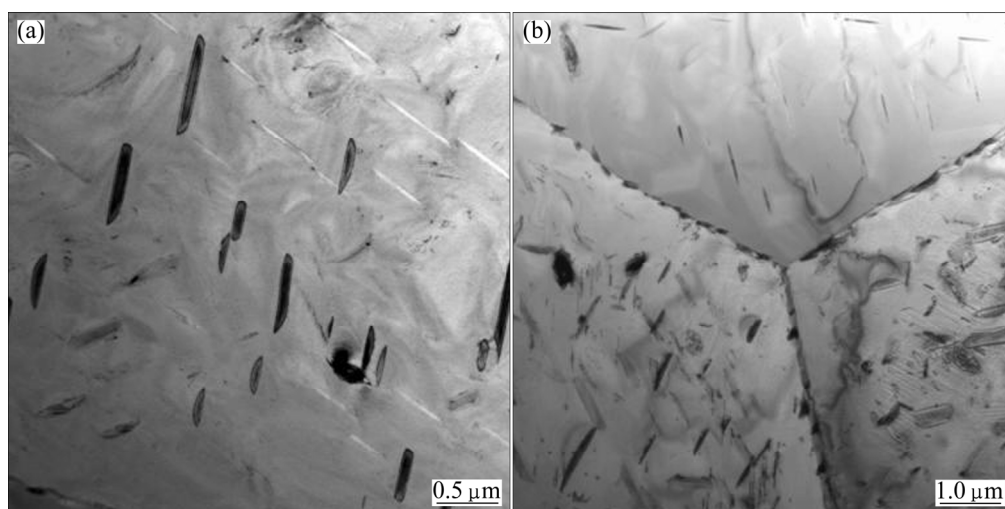


Fig. 4 TEM images of NiTi alloy aged at 873 K: (a) Precipitation of Ni_4Ti_3 in grain interior; (b) Precipitation of Ni_4Ti_3 at triple-junction grain boundaries

increases with the increase of the aging temperature. In addition, it can be observed from Fig. 4(b) that the Ni_4Ti_3 precipitates arise at the triple-junction grain boundaries and they are obviously coarser in the grain interior than those at the grain boundary. However, for the NiTi samples aged at 573 and 723 K, the distribution and the size of the Ni_4Ti_3 precipitates at the grain boundary show no difference from those in the grain interior, as shown in Figs. 2(b) and 3(b), respectively.

3.2 DSC analysis

Figure 5 indicates the DSC curves of NiTi samples which were solution-treated and subsequently aged at 573, 723 and 873 K, respectively. It can be found from Fig. 5 that the solution-treated NiTi sample shows one-stage phase transformation from $B2$ austenite to $B19'$ martensite on cooling and from $B19'$ martensite to $B2$ austenite on heating. As for the NiTi sample aged at 873 K, the one-stage phase transformation from $B19'$ martensite to $B2$ austenite on heating occurs, but the two-stage phase transformation of $B2-R-B19'$ on cooling arises. The NiTi sample aged at 723 K shows the two-stage phase transformation of $B2-R-B19'$ on cooling and the two-stage phase transformation of $B19'-R-B2$ on heating. However, for the NiTi sample aged at 573 K, the two-stage phase transformation of

$B19'-R-B2$ still takes place on heating, but the three-stage phase transformation can be observed on cooling, where the first and the second DSC peaks correspond to the transformation of $B2-R1$ and $B2-R2$, respectively, and the third DSC peak stands for the transformation of $R-B19'$.

4 Discussion

4.1 Precipitation kinetics of Ni_4Ti_3

It is generally accepted that the precipitation of Ni_4Ti_3 phase is a function of aging temperature and aging time in the aged Ni-rich NiTi alloy, where the size of the Ni_4Ti_3 precipitates increases with the increase of the aging temperature and the aging time. KIM and MIYAZAKI [11] found that in the NiTi sample aged at the low temperature of 373 K for 3000 h, the Ni_4Ti_3 precipitates cannot be detected by means of TEM, and even in the NiTi sample aged at the low temperature of 473 K, the Ni_4Ti_3 precipitates cannot be observed at the aging time less than 10 h. However, the Ni_4Ti_3 precipitates have only 2–3 nm in size even though the NiTi sample is subjected to aging at 473 K for 100 h [11]. In addition, the Ni_4Ti_3 precipitates with 3–4 nm in size can be detected in the NiTi sample aged at 573 K for 1.2 ks, and the size of the Ni_4Ti_3 precipitates increases

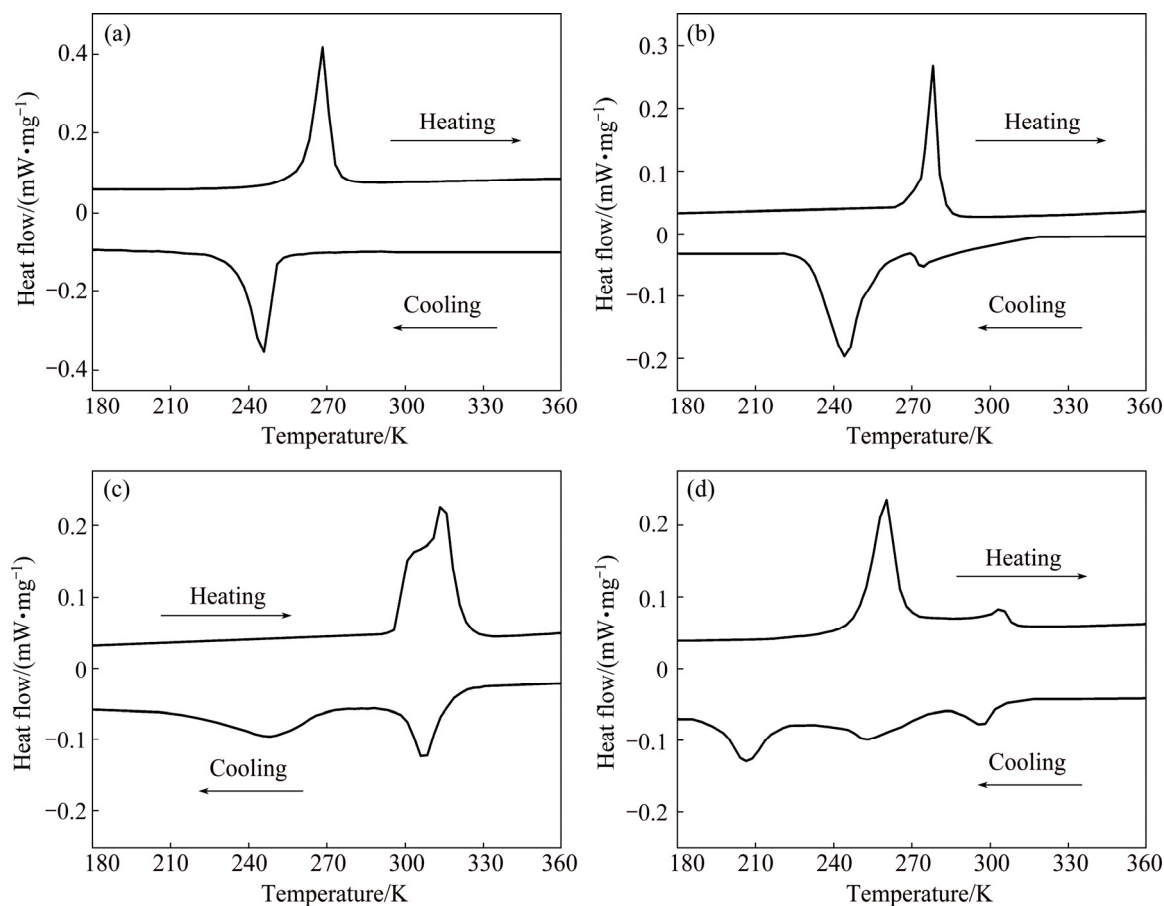


Fig. 5 DSC curves of NiTi alloys: (a) Solution-treated; (b) Aged at 873 K; (c) Aged at 723 K; (d) Aged at 573 K

from 10 to 40 nm when the aging time increases from 100 to 3000 h [11]. It can be concluded that the Ni_4Ti_3 precipitates do not occur until both the aging temperature and the aging time are greater than a critical value, which provides a sufficient driving force for nucleation of Ni_4Ti_3 phase. In the present study, the aging temperature was determined as the variable and the aging time was constant, where the aging temperatures were selected as 573 K (low temperature), 723 K (intermediate temperature) and 873 K (high temperature), respectively, and the aging time was determined as 2 h. The purpose of the three aging treatments was to generate the Ni_4Ti_3 precipitates with different sizes. The size of the Ni_4Ti_3 precipitates was estimated by means of TEM images, in which the diameter of the Ni_4Ti_3 precipitates can be obtained by combining digital micrograph software with equal perimeter method. In the NiTi sample aged at 573 K, the Ni_4Ti_3 precipitates show the uniform size, where the average size of the Ni_4Ti_3 precipitates is about 5 nm. In the NiTi sample aged at 723 K, the Ni_4Ti_3 precipitates also show the uniform size, where the average size of the Ni_4Ti_3 precipitates is about 50 nm. However, in the NiTi sample aged at 873 K, the Ni_4Ti_3 precipitates exhibit the very inhomogeneous size, where the average size of the Ni_4Ti_3 precipitates is about 200 nm, while the maximum precipitation size is about 1200 nm, and the minimum precipitation size is about 40 nm. In the NiTi sample aged at 573 K, the intensity of the diffraction patterns of the Ni_4Ti_3 precipitates is very weak due to small size and small volume fraction, while in the NiTi sample aged at 873 K, the electron diffraction patterns exhibit the basic characteristic of the Ni_4Ti_3 precipitate, where the diffraction spots are located at $1/7$ positions along $\langle 321 \rangle$ reciprocal vectors of $B2$ austenite matrix as shown in Fig. 6, which agrees with the results reported in Refs. [6,17,22]. Furthermore, it can be found from Fig. 6 that the orientation relationship between the Ni_4Ti_3 phase and the $B2$ matrix is determined as $[1\bar{2}1]_{B2} // [1\bar{1}02]_{\text{Ni}_4\text{Ti}_3}$ and $[11\bar{2}]_{B2} // [1\bar{1}02]_{\text{Ni}_4\text{Ti}_3}$, where it is convenient to describe the crystal structure of Ni_4Ti_3 phase by means of hexagonal system. It is of great importance to investigate the size of the Ni_4Ti_3 precipitates because whether the Ni_4Ti_3 phase is coherent with the $B2$ matrix depends on the size of the Ni_4Ti_3 precipitates. For the first time, ZOU et al [10] provided the experimental evidence by means of high resolution electron microscopy that the fine Ni_4Ti_3 precipitate is coherent with the $B2$ matrix in the Ni-rich NiTi sample aged at 723 K for 3 h, where the size of the Ni_4Ti_3 precipitate is approximately 60 nm. However, in the Ni-rich NiTi sample aged at 873 K for 20 h, large Ni_4Ti_3 precipitate possesses a semi-coherent interface with the $B2$ matrix, where the size of the Ni_4Ti_3 precipitate is not measured [12]. GALL et al [13,14] proposed that as the

Ni_4Ti_3 precipitates grow from nanometer to micrometer in size, they undergo a transition from coherent interface to incoherent interface with the $B2$ matrix. They further conclude that the Ni_4Ti_3 precipitates up to approximately 100 nm in size remain coherent with the $B2$ matrix, while the Ni_4Ti_3 precipitates with 500 nm lose coherency with the $B2$ matrix completely [13,14]. In our study, it can be inferred that the Ni_4Ti_3 precipitates keep the coherent interface with the $B2$ matrix in the NiTi samples aged at 573 and 723 K, while the Ni_4Ti_3 precipitates which are coherent, semi-coherent and incoherent with the $B2$ matrix coexist in the NiTi sample aged at 873 K.

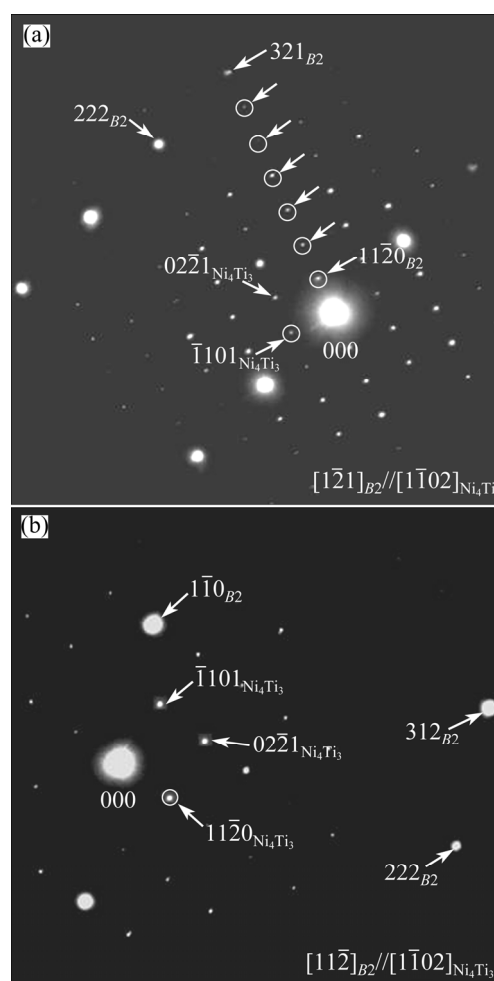


Fig. 6 Diffraction patterns of NiTi alloy aged at 873 K showing orientation relationship between Ni_4Ti_3 phase and $B2$ austenite: (a) $[1\bar{2}1]_{B2} // [1\bar{1}02]_{\text{Ni}_4\text{Ti}_3}$; (b) $[11\bar{2}]_{B2} // [1\bar{1}02]_{\text{Ni}_4\text{Ti}_3}$

It is well known that the distribution of the Ni_4Ti_3 precipitates in the microstructures plays an important role in the transformation behavior of the aged Ni-rich NiTi sample. The distribution characteristic of the Ni_4Ti_3 precipitates depends upon several factors, such as external stress, aging temperature, aging time and chemical composition [9,17,18,20,22,23]. For instance, as compared to stress-free aging, stress-assisted aging

results in the microstructures with a homogeneous distribution of Ni_4Ti_3 precipitates in terms of number density [17]. In the case of aging at the low temperature, the longer aging time contributes to obtaining the microstructures with a homogeneous distribution of Ni_4Ti_3 precipitates [20]. Furthermore, high Ni content leads to more homogeneous distribution of the Ni_4Ti_3 precipitates across the whole microstructure in the aged NiTi sample than low Ni content [18], where the grain boundary plays a predominant role. In general, according to the theory of phase transformation kinetics, the Ni_4Ti_3 precipitates preferentially nucleate and grow in the grain boundary region, where the nucleation rate is greater than that in the grain interior due to the decrease of nucleation barrier at the grain boundary. In addition, the grain boundary energy plays a significant role in promoting the nucleation of the Ni_4Ti_3 precipitates at the grain boundary. At the early stage of aging at 873 K, the Ni_4Ti_3 precipitates nucleate and grow at the grain boundary and thus Ni concentration in the grain boundary region is lower than that in the grain interior. Accordingly, Ni atoms in the grain interior diffuse towards the grain boundary region, but the Ni_4Ti_3 precipitates in the grain boundary region are unable to form the coherent interface with the $B2$ matrix, so the Ni_4Ti_3 precipitates in the grain boundary region are difficult to grow up towards the grain interior due to the impediment of the grain boundary. With the increase of the aging time, the Ni_4Ti_3 precipitates nucleate and grow in the grain interior along the coherent interface with the $B2$ matrix. Furthermore, the Ni_4Ti_3 precipitates in the grain interior grow larger and larger by absorbing Ni atoms from the $B2$ matrix around them and the larger Ni_4Ti_3 precipitates gradually merge the smaller Ni_4Ti_3 precipitates. As a result, the Ni_4Ti_3 precipitates lose coherency with the $B2$ matrix when they grow up to a certain value, and finally the microstructure with an inhomogeneous distribution of Ni_4Ti_3 precipitates is established. In the NiTi sample aged at 573 K, the Ni_4Ti_3 precipitates can also nucleate preferentially at the grain boundary at the beginning, but such a low temperature cannot provide a sufficient driving force for the long-range diffusion of Ni atoms from the grain interior to the grain boundary. Therefore, the supersaturation of Ni atoms in the $B2$ matrix promotes the homogeneous nucleation of the Ni_4Ti_3 precipitates in the grain interior due to no crystal defects in the solution-treated NiTi sample. In addition, it can be seen from Fig. 2 that the Ni_4Ti_3 precipitates uniformly distribute in the matrix of NiTi alloy, but the local inhomogeneous stress field and the local inhomogeneous chemical composition coexist due to the lower aging temperature and the shorter aging time. The high stress and the low Ni content occur near the Ni_4Ti_3 precipitates, while the low stress and the high

Ni content arise away from the Ni_4Ti_3 precipitates. In the NiTi sample aged at 723 K, the appropriate aging temperature and aging time lead to the homogeneous distribution of the Ni_4Ti_3 precipitates in the matrix of NiTi alloy, where the stress field and the chemical composition are relatively homogeneous.

4.2 Influence of Ni_4Ti_3 on phase transformation

It is well known that the Ni_4Ti_3 precipitates have an important influence on the phase transformation behavior of NiTi shape memory alloy. In general, the Ni_4Ti_3 precipitates contribute to the occurrence of the R phase transformation. The R phase belongs to $P3$ space group and possesses a rhombohedral unit cell structure [24,25]. It can be found from Fig. 7 that in the NiTi samples aged at 573 and 723 K, the R -phase is indexed by means of the electron diffraction patterns, where the superlattice reflections are located at $1/3$ positions along $\langle 110 \rangle$ and $\langle 111 \rangle$ directions of the $B2$ austenite matrix in the reciprocal space. In addition, the two R -phase variants are observed in the NiTi samples aged at 573 and

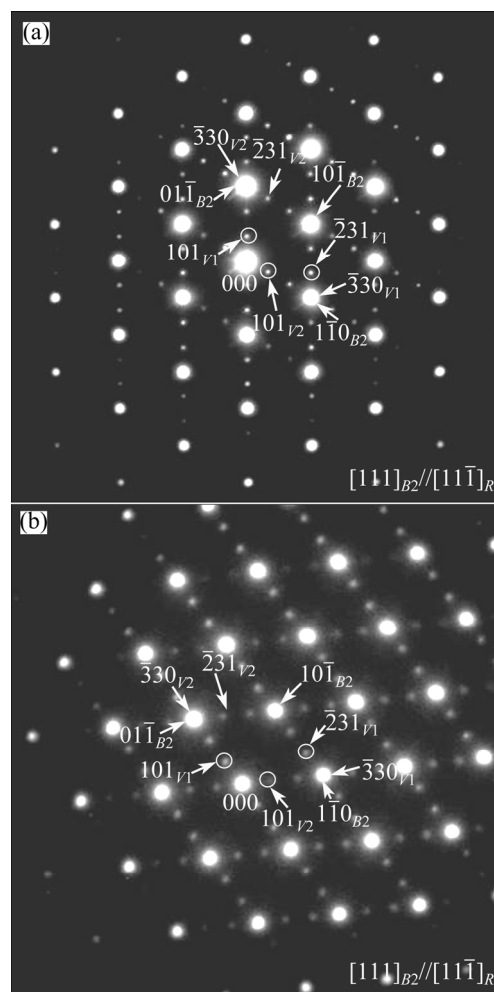


Fig. 7 Diffraction patterns of aged NiTi alloy showing orientation relationship between R phase and $B2$ austenite: (a) Aged at 573 K; (b) Aged at 723 K

723 K. In the NiTi samples aged at 573 and 723 K, the orientation relationship between the two *R*-phase variants and the *B2* austenite matrix is determined as $[111]_{B2} // [1\bar{1}\bar{1}]_R$, $(01\bar{1})_{B2} // (101)_{V1}$, $(1\bar{1}0)_{B2} // (\bar{3}30)_{V1}$ and $[111]_{B2} // [11\bar{1}]_R$, $(01\bar{1})_{B2} // (\bar{3}30)_{V2}$, $(1\bar{1}0)_{B2} // (101)_{V2}$, respectively.

It can be seen from Fig. 5 that the two-stage phase transformation of *B2*–*R*–*B19'* on cooling occurs in the NiTi samples aged at 723 and 873 K, while the NiTi samples aged at 573 K exhibit the three-stage phase transformation, which is in accordance with the results reported by KIM et al [19] and ZHOU et al [20,21]. So far, the mechanism of the two-stage phase transformation of *B2*–*R*–*B19'* has been uncontroversial in the aged Ni-rich NiTi shape memory alloy, where the presence of the Ni_4Ti_3 precipitates can impede the occurrence of martensitic phase transformation, which thus contributes to the formation of *R* phase. In general, the *R*-phase nucleates at the interface between the Ni_4Ti_3 precipitates and the *B2* austenite matrix, and subsequently *B19'* martensite nucleates at the interface between the Ni_4Ti_3 precipitates and the *R*-phase [22,23]. The mechanism of the three-stage phase transformation on cooling has attracted great attention over the last decade, but it has been controversial as well. For the NiTi samples aged at high temperatures, three different explanations can be generalized, according to the corresponding experimental observations. One explanation is that the three-stage phase transformation is attributed to the local stress heterogeneity around the Ni_4Ti_3 precipitates, where the transformation of *B2*–*R* first occurs, while the second transformation of *R*–*B19'* arises in the high stress region near the Ni_4Ti_3 precipitates, and the third transformation of *R*–*B19'* arises in the low stress region away from the Ni_4Ti_3 precipitates [15]. Another explanation is that the local composition heterogeneity around the Ni_4Ti_3 precipitates is responsible for the three-stage phase transformation, where the transformation of *B2*–*R* first occurs as well, while the second transformation of *R*–*B19'* arises in the low Ni region near the Ni_4Ti_3 precipitates, and the third transformation of *R*–*B19'* arises in the high Ni region away from the Ni_4Ti_3 precipitates [16]. The last explanation is that the grain boundary effect leads to the large-scale heterogeneity of the Ni_4Ti_3 precipitates between the grain boundary region and the grain interior, which is responsible for the three-stage phase transformation [17,18], where KHALIL-ALLAFI et al [17] and FAN et al [18] gave the different transformation sequences. The transformation sequence obtained by KHALIL-ALLAFI et al [17] is the transformation of *B2*–*R* in the grain boundary region with the Ni_4Ti_3 precipitates, the transformation of *R*–*B19'* in the same grain boundary region, and the transformation of *B2*–*B19'* in the precipitate-free grain

interior, while the transformation sequence observed by FAN et al [18] is the transformation of *B2*–*R* in the grain boundary region with a high density of Ni_4Ti_3 precipitates, the transformation of *B2*–*B19'* in the almost precipitate-free grain interior region, and the transformation of *R*–*B19'* in the previous grain boundary region. For the NiTi samples aged at low temperature, ZHOU et al [20,21] proposed that the grain boundary effect also plays a critical role in the three-stage phase transformation, where the grain boundary region with low Ni content first undergoes the transformation of *B2*–*R*, and then the grain boundary region with high Ni content undergoes the transformation of *B2*–*R*, which finally is followed by the transformation of *R*–*B19'*. In the present study, we do not obtain the experiment evidence that the presence of the grain boundary has a predominant influence on the three-stage phase transformation. We suggested that the three-stage phase transformation is attributed to the combination of the local stress heterogeneity and the local composition heterogeneity in the NiTi matrix. In the NiTi samples aged at 573 K for 2 h, the shorter aging time and the lower aging temperature are insufficient to establish an equilibrium Ni concentration between the region near the Ni_4Ti_3 precipitates and the region away from the Ni_4Ti_3 precipitates. Therefore, there is a low Ni content near the Ni_4Ti_3 precipitates, while there is a high Ni content away from the Ni_4Ti_3 precipitates. In addition, the fine Ni_4Ti_3 precipitate is coherent with the *B2* matrix, so there is a coherent stress field at the interface between the Ni_4Ti_3 precipitate and the *B2* matrix. As a consequence, there is a high stress region near the Ni_4Ti_3 precipitate, while there is a low stress region away from the Ni_4Ti_3 precipitate. In the case of cooling, the *R*-phase first nucleates at the interface between the Ni_4Ti_3 precipitate and the *B2* matrix so as to relax the coherent stress [10], and with the progression of cooling, the transformation of *B2*–*R* occurs away from the Ni_4Ti_3 precipitate. Finally, all the *R* phases are transformed into the *B19'* martensite. The mechanism of the influence of the inhomogeneous composition on the three-stage phase transformation will be investigated in the future.

5 Conclusions

1) In the NiTi samples aged at 573 and 723 K, the two *R*-phase variants are observed, and the orientation relationship between the two *R*-phase variants and the *B2* austenite matrix is determined as $[111]_{B2} // [1\bar{1}\bar{1}]_R$, $(01\bar{1})_{B2} // (101)_{V1}$, $(1\bar{1}0)_{B2} // (\bar{3}30)_{V1}$ and $[111]_{B2} // [11\bar{1}]_R$, $(01\bar{1})_{B2} // (\bar{3}30)_{V2}$, $(1\bar{1}0)_{B2} // (101)_{V2}$, respectively.

2) The Ni_4Ti_3 precipitates preferentially nucleate and grow at the grain boundary. In the NiTi sample aged

at 873 K, the Ni_4Ti_3 precipitates in the grain boundary region are unable to form the coherent interface with the $B2$ matrix, and thus they are difficult to grow up towards the grain interior due to the impediment of the grain boundary. In the NiTi sample aged at 573 K, the low temperature cannot provide a sufficient driving force for the long-range diffusion of Ni atoms from the grain interior to the grain boundary. In the NiTi sample aged at 723 K, the appropriate aging temperature and aging time lead to the homogeneous distribution of the Ni_4Ti_3 precipitates in the matrix of NiTi alloy.

3) In the NiTi samples aged at 573 and 723 K, the size of the Ni_4Ti_3 precipitates is uniform, where the former is about 5 nm, and the latter is about 50 nm. However, in the NiTi sample aged at 873 K, the Ni_4Ti_3 precipitates exhibit very inhomogeneous size, where the average size of the Ni_4Ti_3 precipitates is about 200 nm, while the maximum precipitation size is about 1200 nm, and the minimum precipitation size is about 40 nm. In the NiTi samples aged at 573 and 723 K, the Ni_4Ti_3 precipitates are coherent with the $B2$ matrix, while the Ni_4Ti_3 precipitates which are coherent, semi-coherent and incoherent with the $B2$ matrix coexist in the NiTi sample aged at 873 K.

4) The two-stage phase transformation of $B2 \rightarrow R \rightarrow B19'$ on cooling occurs in the NiTi samples aged at 723 and 873 K, while the NiTi samples aged at 573 K exhibit the three-stage phase transformation on cooling. The three-stage phase transformation is attributed to the combination of the local stress heterogeneity and the local composition heterogeneity in the NiTi matrix, where the two-stage phase transformation of $B2 \rightarrow R$ occurs in the low Ni and high stress region near the Ni_4Ti_3 precipitates and in the high Ni and low stress region away from the Ni_4Ti_3 precipitates, respectively, which is followed by one-stage transformation of $R \rightarrow B19'$.

References

- [1] JIANG Shu-yong, ZHANG Yan-qiu, ZHAO Ya-nan. Dynamic recovery and dynamic recrystallization of NiTi shape memory alloy under hot compression deformation [J]. Transactions of Nonferrous Metals Society of China, 2013, 23(1): 140–147.
- [2] JIANG Shu-yong, HU Li, ZHAO Ya-nan, ZHANG Yan-qiu, LIANG Yu-long. Plastic yielding of NiTi shape memory alloy under local canning compression [J]. Transactions of Nonferrous Metals Society of China, 2013, 23: 2905–2913.
- [3] JIANG Shu-yong, TANG Ming, ZHAO Ya-nan, HU Li, ZHANG Yan-qiu, LIANG Yu-long. Crystallization of amorphous NiTi shape memory alloy fabricated by severe plastic deformation [J]. Transactions of Nonferrous Metals Society of China, 2014, 24(6): 1758–1765.
- [4] SABURI T, NENNO S, FUKUDA T. Crystal structure and morphology of the metastable X phase in shape memory Ti–Ni alloys [J]. Journal of the Less-Common Metals, 1986, 125: 157–166.
- [5] TADAKI T, NAKATA Y, SHIMIZU K, OTSUKA K. Crystal structure, composition and morphology of a precipitate in an aged Ti–51at.%Ni shape memory alloy [J]. Transactions of Japan Institute of Metals, 1986, 27: 731–740.
- [6] NISHIDA M, WAYMAN C M, KAINUMA R, HONMA T. Further electron microscopy studies of the $\text{Ti}_{11}\text{Ni}_{14}$ phase in an aged Ti–52at.%Ni shape memory alloy [J]. Scripta Metallurgica, 1986, 20: 899–904.
- [7] NISHIDA M, WAYMAN C M. Electron microscopy studies of precipitation processes in near-equiatomic TiNi shape memory alloys [J]. Materials Science and Engineering A, 1987, 93: 191–203.
- [8] JIANG Shu-yong, ZHAO Ya-nan, ZHANG Yan-qiu, HU Li, LIANG Yu-long. Effect of solution treatment and aging on microstructural evolution and mechanical behavior of NiTi shape memory alloy [J]. Transactions of Nonferrous Metals Society of China, 2013, 23(12): 3658–3667.
- [9] HEINEN R, HOPPE U, HACKL K. Prediction of microstructural patterns in monocrystalline shape memory alloys using global energy minimization [J]. Materials Science and Engineering A, 2008, 481–482: 462–465.
- [10] ZHOU N, SHEN C, WAGNER M F X, EGGELER G, MILLS M J, WANG Y. Effect of Ni_4Ti_3 precipitation on martensitic transformation in Ti–Ni [J]. Acta Materialia, 2010, 58: 6685–6694.
- [11] KIM J I, MIYAZAKI S. Effect of nano-scaled precipitates on shape memory behavior of Ti–50.9at.%Ni alloy [J]. Acta Materialia, 2005, 53: 4545–4554.
- [12] ZOU W H, HART X D, WANG R, ZHANG Z, ZHANG W Z, LAI J K L. TEM and HREM study of the interphase interface structure of Ti_3Ni_4 precipitates and parent phase in an aged TiNi shape memory alloy [J]. Materials Science and Engineering A, 1996, 219: 142–147.
- [13] GALL K, JUNTUNEN K, MAIER H J, SEHITOGLU H, CHUMLYAKOV Y I. Instrumented micro-indentation of NiTi shape-memory alloys [J]. Acta Materialia, 2001, 49: 3205–3217.
- [14] GALL K, MAIER H J. Cyclic deformation mechanisms in precipitated NiTi shape memory alloys [J]. Acta Materialia, 2002, 50: 4643–4657.
- [15] BATAILLARD L, BIDAUX J E, GOTTHARDT R. Interaction between microstructure and multiple-step transformation in binary NiTi alloys using in-situ transmission electron microscopy observations [J]. Philosophical Magazine A, 1998, 78: 327–344.
- [16] ALLAFI K J, REN X, EGGELER G. The mechanism of multistage martensitic transformations in aged Ni-rich NiTi shape memory alloys [J]. Acta Materialia, 2002, 50: 793–803.
- [17] KHALIL-ALLAFI J, DLOUHÝ A, EGGELER G. Ni_4Ti_3 -precipitation during aging of NiTi shape memory alloys and its influence on martensitic phase transformations [J]. Acta Materialia, 2002, 50: 4255–4274.
- [18] FAN G, CHEN W, YANG S, ZHU J, REN X B, OTSUKA K. Origin of abnormal multi-stage martensitic transformation behavior in aged Ni-rich Ti–Ni shape memory alloys [J]. Acta Materialia, 2004, 52: 4351–4362.
- [19] KIM J I, LIU Y N, MIYAZAKI S. Ageing-induced two-stage R -phase transformation in Ti–50.9at.%Ni [J]. Acta Materialia, 2004, 52: 487–499.
- [20] ZHOU Y M, ZHANG J, FAN G L, DING X D, SUN J, REN X B, OTSUKA K. Origin of 2-stage R -phase transformation in low-temperature aged Ni-rich Ti–Ni alloys [J]. Acta Materialia, 2005, 53: 5365–5377.
- [21] ZHOU Y, FAN G, ZHANG J, DING X, REN X, SUN J, OTSUKA K. Understanding of multi-stage R -phase transformation in aged Ni-rich Ti–Ni shape memory alloys [J]. Materials Science and Engineering A, 2006, 438–440: 602–607.
- [22] MICHUTTA J, SOMSEN C, YAWNY A, DLOUHÝ A, EGGELER G. Elementary martensitic transformation processes in Ni-rich NiTi single crystals with Ni_4Ti_3 precipitates [J]. Acta Materialia, 2006, 54:

- 3525–3542.
- [23] DLOUHÝ A, BOJDA O, SOMSEN C, EGgeler G. Conventional and in-situ transmission electron microscopy investigations into multistage martensitic transformations in Ni-rich NiTi shape memory alloys [J]. Materials Science and Engineering A, 2008, 481–482: 409–413.
- [24] GORYCZKA T, MORAWIEC H J. Structure studies of the *R*-phase using X-ray diffraction methods [J]. Journal of Alloys and Compounds, 2004, 367: 137–141.
- [25] KHALIL-ALLAFI J, SCHMAHL W W, TOEBBENS D M. Space group and crystal structure of the *R*-phase in binary NiTi shape memory alloys [J]. Acta Materialia, 2006, 54: 3171–3175.

Ni₄Ti₃ 沉淀相对镍钛形状记忆合金相变的影响

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摘 要: 镍钛形状记忆合金样品分别在 573、723 和 873 K 时效 2 h。在 573 和 723 K 时效的镍钛样品中, 可以观察到 2 个 *R* 相变体, 而且这 2 个 *R* 相变体与 *B2* 基体之间的取向关系可以确定。在 573 和 723 K 时效的镍钛样品中, 细小均匀的 Ni₄Ti₃ 沉淀相与 *B2* 奥氏体基体之间保持共格关系。在 873 K 时效的镍钛样品中, 可以观察到 Ni₄Ti₃ 沉淀相在晶粒内部和晶界处析出, 不均匀的 Ni₄Ti₃ 沉淀相与 *B2* 基体之间保持共格、半共格和非共格关系。对于 873 K 时效的镍钛样品, 加热时发生 *B19'* 马氏体向 *B2* 奥氏体转变的一阶相变, 但在冷却时发生 *B2*–*R*–*B19'* 的二阶相变。723 K 时效的镍钛样品在冷却时也表现出 *B2*–*R*–*B19'* 的二阶相变, 但在加热时发出 *B19'*–*R*–*B2* 的二阶相变。对于 573 K 时效的镍钛样品, 由于 Ni₄Ti₃ 沉淀相周围的局部应力不均匀和局部成分不均匀, 则其发生三阶相变。

关键词: 形状记忆合金; 镍钛合金; 马氏体相变; 热处理; 显微组织

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