R-phase transition and related mechanical properties controlled by low-temperature aging treatment in a Ti–50.8 at.% Ni thin wire

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A cold-drawn Ti–50.8 at.% Ni wire was annealed at 600 °C for 30 min, followed by aging at 250 °C for different times. A microstructure with small grains and nanoscaled precipitates was obtained. The thermally induced martensite transformation is suppressed in the samples aged for 4 h or longer, leaving a one-stage R-phase transition between −150 and +150 °C. The transformation behavior, work output and recovery stress associated with the R-phase transition are presented.

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In near-equatomic NiTi alloys, the reversible thermoelastic transformation between the B2 structured austenite phase (A) and the rhombohedral R-phase shows a shape memory effect and pseudoelasticity [1,2]. The transformation strain associated with the A ↔ R transition is very small (≈1%) [2], but it shows attractive properties, such as narrow thermal hysteresis [3,4], fast response with respect to temperature changes [2,4–7], high stability during mechanical or thermal cycling [7–9] as well as excellent fatigue resistance [5,10]. Based on these unique properties, the R-phase transition is very promising for applications. The A → R transition can be induced by various thermomechanical treatments, e.g. post-deformation annealing [11], thermal cycling [8,12,13] or aging of Ni-rich NiTi alloys [14,15]. Up to now, the mechanism of the R-phase transition has been well established [4]. However, there has been little discussion on how to control the R-phase transition temperatures. Some researchers reported the evolution of R-phase transformation temperatures with respect to annealing temperatures [16], aging time [17] as well as aging temperatures [18]. However, the observed two- or multi-stage transformation may limit the practical application of the R-phase transition. Therefore, in order to fully exploit the application of the R-phase transition, it is essential to solve the following two problems: (i) controlling the R-phase transition temperatures, as well as (ii) suppressing the B19’ structured martensite (M) transformation.

In our previous work [19], Ti–50.8 at.% Ni samples with different grain sizes were subjected to low-temperature aging treatment (250 °C for 24 h). It was found that the grain size can affect the aging microstructure, leading to different transformation behavior in samples with different grain sizes. The following two important features were highlighted: (i) an abnormal two-stage R-phase transition was observed in samples with large grains (average grain size between 6.6 and 21.7 μm), while a sample with small grains (average grain size 5.6 μm) showed normal A ↔ R ↔ M transformation; (ii) a decrease in martensite transformation temperatures was observed in samples with decreasing grain size. Inspired by the above findings, in the present work a sample with much smaller grain size is subjected to low-temperature (250 °C) aging treatment. The evolution of phase transformation behavior and mechanical properties with respect to aging time is studied.
A Ti–50.8 at.\% Ni thin wire, 50 μm in diameter, produced by room-temperature wire drawing with a cold deformation of 25\%, was studied. The as-received wires were annealed at 600 °C for 30 min, followed by aging at 250 °C for different times from 2 to 500 h. The size and orientation distribution of the grains of the annealed sample were measured using electron backscatter diffraction (EBSD), which was performed using a TSL-EDAX system on an FEI Nova 600 NanoLab instrument. The surface for EBSD measurement, which is perpendicular to the wire axis, was prepared using a JEOL cross-section polisher. The transmission electron microscopy (TEM) study was conducted using a FEI Tecnai G2 instrument operating at an accelerating voltage of 200 kV. The TEM specimens, taken along the axis of the wire, were prepared by focused ion beam (FIB) in an FEI Helios 650 NanoLab SEM/FIB instrument via the lift-out procedure. The transformation behavior was characterized by differential scanning calorimetry (DSC) in a TA Q2000 calorimeter from −150 to +150 °C with a heating/cooling rate of 10 °C min\(^{-1}\). The thermomechanical cycling was performed in a TA Q800 dynamic mechanical analyzer with a heating/cooling rate of 5 °C min\(^{-1}\).

Fully recrystallized equiaxed grains with an average diameter of 1.7 μm are observed in the sample after annealing at 600 °C for 30 min, as illustrated by the EBSD map in Figure 1a. The inverse pole figure (IPF) shows the grain orientation distribution with reference to the wire axis (WA) and reveals a strong (111) texture. After annealing at 600 °C for 30 min, the samples were further aged at 250 °C for different times. As the aging temperature is very low, the grain size and texture remain constant during aging.

Figure 1b shows a dark-field (DF) TEM image and the corresponding [100]\(_{B2}\) selected-area electron diffraction (SAED) pattern of the sample after aging at 250 °C for 8 h. Apart from the basic and ordering reflections of the B2 matrix, the SAED shows rings of elongated diffuse spots. The latter can be explained by the existence of small Ni\(_4\)Ti\(_3\) precipitates, as seen from the simulated diffraction pattern including reflections of eight variants of Ni\(_4\)Ti\(_3\) precipitates (four orientation variants, each with two ordering variants) within the [100]\(_{B2}\) zone axis. The simulated diffraction pattern is developed using a method as described by Li et al. [20]. The elongation of the diffuse spots in the experimental pattern corresponds to the onset of the well-known lens shape of Ni\(_4\)Ti\(_3\) precipitates [21]. The DF image is obtained from a 101\(_{\text{bif}}\) reflection, as indicated by the red arrow in the SAED pattern and reveals nanoscaled Ni\(_4\)Ti\(_3\) particles homogeneously distributed in the B2 matrix.

To further characterize the fine Ni\(_4\)Ti\(_3\) precipitates, a high-resolution (HR) TEM study was performed. Figure 1c shows the HRTEM image of the same sample as Figure 1b viewed along the [100]\(_{B2}\) axis. The zoom in the squared region shows the locally deformed character of the lattice. The fast Fourier transform (FFT) pattern of Figure 1c, which is presented as an inset in the same figure, shows the same features as the SAED pattern of Figure 1b including rings of diffuse reflections. After discarding the spots from the B2 matrix in the FFT pattern, the corresponding Fourier-filtered image is shown in Figure 1d where the lattice deformations of the Ni\(_4\)Ti\(_3\) nanoparticles are visible, as indicated by the arrows. Due to the small size of these precipitates, the strained B2 matrix surrounding the precipitates [22,23] blurs the HRTEM image so that no clear image of the Ni\(_4\)Ti\(_3\) structure can be obtained.

The above findings, and corresponding results for the other aging times, show that after annealing at 600 °C for 30 min followed by aging at 250 °C for different times, a microstructure with small grains (average grain size 1.7 μm) and nanoscaled Ni\(_4\)Ti\(_3\) precipitates is obtained in the investigated wire.

The transformation behavior of the samples after aging at 250 °C for different times is shown in Figure 2. The as-annealed sample shows a normal A ↔ M transformation with the martensite transformation peak temperature (\(M_p\)) at −52 °C, as shown in Figure 2a. After aging at 250 °C for 2 h, only one A → R transformation peak is detected during cooling, while two reverse transformation peaks are observed during heating, indicating that the R → M transformation peak is too broad to be detected during cooling. The internal stress, which is caused by the coherent Ni\(_4\)Ti\(_3\) precipitates, is considered to be responsible for suppressing the R → M transformation. With the increase of aging time to 4 h, the thermally induced martensite transformation is completely suppressed, leaving only A ↔ R transformation peaks observed in the temperature range from −150 to +150 °C. For the samples aged between 4 and 500 h,
the same transformation behavior is observed, but the R-phase transition peak shifts to higher temperatures with the increase in aging time. Interestingly, Figure 2a also shows that the reverse transformation peak becomes sharper with increasing aging time, while the shape of the forward transformation peak is less affected. Further investigations are needed to explain this phenomenon.

Figure 2b shows that the R-phase transition start temperature (R_s) rapidly increases from 6 to 27 °C with the increase of aging time from 4 to 24 h, and further increases to 38 °C with the increase of aging time to 500 h. As the R-phase transition temperature of aged samples depends only on the Ni concentration of the matrix [4,24], the increasing R_s temperatures indicates an increase of Ni depletion with increasing aging time, which can be related to the increase in density or size of Ni_4Ti_3 precipitates with the increase of aging time. Figure 2b also shows that the latent heat associated with the A → R transformation (ΔH^{A→R}) of the 4 h aged sample is 4.3 J g⁻¹. (ΔH^{A→R}) varies from 5.4 to 6 J g⁻¹ with the increase in aging time from 8 to 500 h.

Figure 3a shows the representative cyclic strain–temperature curves under different constant stresses for the samples aged for 500 h. The samples were first loaded to the pre-set stresses (200, 300 and 400 MPa) at 80 °C, followed by thermal cycling between 80 and 0 °C. Compared with the first cycle, the second and third cycles show the same strain–temperature response. Therefore, the recoverable strain (ε) of the third cycle is used to calculate the specific work output (W) associated with the A → R transformation via the following equation:

\[ W = \frac{\epsilon \times \sigma_{\text{constant}}}{\rho}, \]

where \( \sigma_{\text{constant}} \) stands for the pre-set constant stress and \( \rho = 6.45 \text{ g cm}^{-3} \) is the density of NiTi alloy. As shown in Figure 3b, the sample subject to a higher constant stress gives rise to a higher work output. However, the work output is hardly affected by aging time when the exerted constant stress is the same. Figure 3c shows the evolution of the R-phase transition start temperatures under different constant stress (R_s) with respect to aging time. Under the same constant stress, the R_s increases with the increase of aging time, indicating a controllable working temperature of the R-phase transition under constant stress.

As shown in Figure 2a, after aging treatment, the thermally induced martensite can be fully suppressed in the temperature range between −150 to +150 °C. However, the stress-induced martensite (SIM) transformation is inevitable. Therefore, it is necessary to determine the working window, which is defined as the temperature interval between stress-induced R-phase and SIM transformation at a fixed stress. As shown in the inset of Figure 3c, the sample was loaded to 400 MPa at 100 °C, followed by cooling to −100 °C. The R-phase and martensite transformation start at 54 °C (R_{s400}) and −25 °C (M_{s400}), respectively. Therefore, the working window is defined as \( T_{\text{window}} = R_{s400} - M_{s400} \). As shown in Figure 3c, under a constant stress of 400 MPa, the working window varies from 57 to 82 °C. With decreasing the applied stress, the SIM transformation will shift to lower temperatures faster than the stress-induced R-phase transition, because the dσ/dT value, as described by the Clausius–Clapeyron-type relation [4,25], is higher for a stress-induced R-phase transformation than for SIM transformation [4,5]. Therefore, the working window will increase with the decrease of the applied stress. The large working windows enable the sample to work safely in the A ↔ R state, avoiding interference from the R → M transformation.

The R-phase transition can be beneficially used to produce recovery stresses with a higher rate of recovery than that of the martensite transformation. In order to measure the recovery stress associated with the R-phase transition, the samples were first deformed to a strain of 1.2% at a temperature of 20 °C below the R-phase transition finish temperature (R_f). The samples were then unloaded, leaving some strain due to the reorientation of the R-phase [5]. The strain decreases from 0.6% to 0.2% in the samples aged from 4 to 500 h. This is probably due to the decrease in the R-phase reorientation strain with increasing deformation temperature [2]. The samples were subsequently heated with constrained strain to 100 °C and the stress response was recorded, as shown in Figure 4a. The maximum recovery stress gradually increases from 252 to 374 MPa with the increase in aging time from 4 to 500 h, as shown in Figure 4b. Although the observed stress recovery rate is lower than the previously reported value (17 MPa °C⁻¹) [5], it is interesting to note that the observed stress recovery rate increases from 8.3 to 12.4 MPa °C⁻¹ with the increase in aging time. The above results indicate that the maximum recovery stress and recovery stress rate, due to a constrained R → A transition, can indeed be influenced by the microstructure (e.g. size or density of precipitates). However, further research is needed to explain how the aging microstructure affects the recovery stress and recovery stress rate of the R-phase transition.
Figure 4c shows the reverse transformation (R → A) temperatures during constrained heating ($A_r'$ and $A_f'$) with respect to the aging time. Both $A_r'$ and $A_f'$ increase with the increase in aging time, indicating that the working temperature range, in which the R-phase transition can produce high recovery force, can be controlled by the aging time.

In this study, a microstructure with small grains (average diameter 1.7 µm) and nanoscaled precipitates was produced in a Ti–50.8 at.% Ni thin wire. The thermally induced martensite transformation is successfully suppressed, leaving only the $A_M$ transformation between +150 and −150 °C. A high work output and recovery stress associated with the $A_M$ transition are observed. Moreover, the transformation temperatures of the R-phase transition both under constant stress ($R_s'$) and constrained strain ($A_r'$ and $A_f'$) conditions can be controlled by the aging time. This behavior yields interesting properties for future applications.

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