Stress-induced phase transformation and detwinning in NiTi polycrystalline shape memory alloy tubes

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Abstract

Deformation behavior associated with initial austenite (A), rhombohedral (R) and martensite (M) phase structures was studied in polycrystalline NiTi shape memory alloy tubes by tensile testing at different temperatures. The nominal stress–strain curves of the tubes from room temperature (23 °C to 70 °C) were recorded. The deformation of NiTi tubes with initial structure of R-phase proceeded via R → M martensitic transformation, while the deformation of NiTi tubes with initial structure of M-phase proceeded via martensitic detwinning. It was found that the R → M martensitic type transformation was realized, at the macroscopic level, by nucleation and growth of an inclined cylindrical band, while the detwinning process of the tube was macroscopically homogeneous. Further, two-stage yielding, which is associated with austenite to rhombohedral (A → R) and R → M phase transformations, was observed in the stress–strain curves of NiTi tubes in a certain testing temperature range. With a further increase in temperature, the shape of the nucleated band remained cylindrical until 60 °C (> A₁) when the shape of the initial band suddenly became helical which was well observed in the superelastic microtubing.

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Keywords: NiTi polycrystalline; Shape memory alloy; Martensitic transformation; Detwinning; Martensitic band; R-phase

1. Introduction

NiTi polycrystalline shape memory alloy (SMA) microtubes are increasingly used in medical surgery and human implants (see Pelton and Duerig, 2003).

The applications make use of the NiTi SMAs' biocompatibility, large recoverable deformation, good fatigue life and outstanding superelastic and shape memory properties around body temperature or over other temperature ranges. They have been successfully used to manufacture medical devices in recent years. One of the most interesting applications for NiTi tubing is in extremely fine instruments. For instance, the 1 mm diameter grasper is
composed of a very thin-walled NiTi tube with a NiTi wire inside (Duerig et al., 1997). This combination not only enables it to bend around radii of less than 3 cm without kinking, but also allows opening and closing of the distal grasper jaws without increasing resistance. Stainless steel or other metallic instruments would kink and be destroyed by even very slight mishandling, while this NiTi device will continue to operate smoothly even after being bent around tortuous paths. Systematic investigations are crucial for understanding and further modeling the thermo-mechanical behavior of the material in the device design. In the past decade some fundamental mechanics studies on bulk NiTi wires and strips have been performed and reported (for example, see Leo et al., 1993; Shaw and Kyriakides, 1995, 1997, 1998; Tse and Sun, 2000). Due to the difficulties in testing the long and thin microtubes and the cost of the testing facility, only limited experimental research has been conducted by several groups (Li and Sun, 2000, 2002; Sun and Li, 2002; Berg, 1997; Helm and Haupt, 2001; McNaney et al., 2003). Even for tubes the experimental investigations were so far limited to superelastic NiTi tubes which experienced reversible phase transformation between austenite and martensite (\( A \rightarrow M \) and \( M \rightarrow A \)) under loading. Due to the special geometric shape of the tubes, significant differences in the transformation band morphology between the tube and those in the wire and strip can be expected. For superelastic NiTi tubing, a helical shaped martensitic transformation band was observed during phase transformation. The discovery brought up several important issues in the fundamental understanding and modeling of the phase transition in polycrystalline NiTi and therefore it is worth further investigation. One of the issues is about the competition between the interfacial energy of the \( A/M \) transformation front and the strain energy of the tube in determining the final morphology of the macroscopic martensite band during the deformation process. Such macroscopic \( A/M \) interfacial energy manifested itself in the deformation process and may play a very important role in the morphology evolution of the band. This is different from that in a strip where a straight inclined band forms through the whole cross-section. The observation of tube deformation which involves other deformation processes such as phase transformation associated with the rhombohedral (\( R \)) to martensite phase (\( R \rightarrow M \)) and martensitic detwinning (i.e., \( M \rightarrow M \)) process is still not available in the literature.

The objective of this paper is to examine and report the deformation behavior of the polycrystalline NiTi tubes during \( A \rightarrow M \), \( R \rightarrow M \), \( A \rightarrow R \rightarrow M \) and \( M \rightarrow M \) processes under uniaxial tension. It focuses on the stress–strain response of the material and the corresponding surface morphology during the above processes. The main purpose of this preliminary study is, through investigation, to provide a quantitative base in developing a constitutive model for this type of material.

2. Experimental procedures

2.1. Material and sample preparation

The material used (from Shape Memory Application, Inc.) was a commercial binary polycrystalline NiTi alloy and was received in tube form with a dark oxidized surface layer. The nominal composition is 54.1 at.% Ni. The grain size is about 50–100 nm by TEM as shown in Fig. 1 (see Ng, 2002). The original inner and outer diameters of the tubes were 1.1 mm and 2.15 mm respectively. The tubes were cut into pieces of 110 mm long for the test. Two types of samples were prepared. The original dark oxidized surface layer which was then coated with ethanol and rosin was kept on type I sample. A brittle and transparent layer (about 20 \( \mu m \) in thickness) of rosin would be formed after the volatilization of the ethanol. Microcracks would be formed due to the significant increase of strain during martensitic transformation. The color of the rosin layer would change from transparent to white due to the change of reflectivity of the microcracked coating layer. Thus, the transformed and non-transformed regions could be observed very easily. Type II sample was chemically etched into “dog-bone” shape and mechanically polished by fine grained sandpapers (finished with 50 nm aluminum oxide sandpaper) after etching. The final inner and outer diameters (the etched section) of Type II sample
were 1.1 mm and 1.87 mm (with tolerance of 0.01 mm) respectively (Fig. 2).

X-ray fluorescence spectrometer (XRF) and Differential Scanning Calorimeter (DSC) were used to measure the composition and the phase transformation temperatures of the NiTi tube respectively (see Table 1). It is noticed that the initial phase structure of the sample at room temperature depends on the heating/cooling history of the sample as shown in Fig. 3. Therefore, by cooling down from a higher temperature and heating up from a lower temperature, specimens with initial stress-free room temperature R-phase and room temperature M-phase were prepared respectively for testing.

2.2. Experimental set-up

Uniaxial tensile tests were performed on both the Universal Test Machine (UTM) and a small loading frame from room temperature to 70 °C through two specially designed water chambers (Fig. 4) in order to study the mechanical behavior of these NiTi tubes at different temperatures. On the UTM machine the load and displacement were measured by a load cell and cross-head movement respectively. In the small loading frame, the load was measured by the load cell and displacement was controlled by a stepping motor through the gear system. Both were under displacement controlled loading condition. All tests were performed at a relatively low loading rate of 0.2 mm/min (nominal strain rate of $5.6 \times 10^{-5}/s$) in order to minimize the self-heating effect caused by the transformation latent heat (Leo et al., 1993; Shaw and Kyriakides, 1995). In addition, higher loading rates of 0.5 mm/min (nominal strain rate of $1.4 \times 10^{-4}/s$), 1.0 mm/min (nominal strain rate of $2.8 \times 10^{-2}/s$) and 2 mm/min (nominal strain rate of $5.6 \times 10^{-4}/s$) were also used to examine the loading rate effect on the test results.
In the test by the UTM machine, the specimens were clamped at two ends by two specially designed screw-clamping blocks which were connected to the loading grips of the test machine through two double-hinge connectors (Fig. 5(a) used in room temperature test only). This clamping system could transfer the concentration force from the grip into a uniformly distributed shear stress at the end of the tube, therefore producing a uniform tensile stress in the measurement section of the tube. The clamping length of the tube was 20 mm at each end, and the overall length of the specimen was 110 mm with an etched length of 60 mm. In the test by the small loading frame, the specimen clamping method is similar to that in the UTM machine and is shown in Fig. 5(b).

Surface morphology observations of the tube surface during loading were conducted by a CCD camera with well adjusted lighting (Fig. 6).

3. Results and discussion

We first give a general description of the main deformation features of the tube in Section 3.1, special aspects such as the band nucleation and temperature effect are given and discussed in Sections 3.2 and 3.3, respectively.

3.1. Main deformation features of NiTi tube with initial R and M phases

Fig. 7 shows the typical stress–strain curve of the “dog-bone” shaped specimen (Type II) with initial state of R-phase at room temperature under a loading rate of 0.2 mm/min. The stress–strain curve could be divided into three regions. Region I represents the macroscopic homogeneous elastic deformation of the R-phase. Once the stress reached the critical value (about 98.05 MPa), the deformation became inhomogeneous through the formation of a macroscopic deformation (or transformation) band at the middle portion of the tube, which was accompanied by a very small amount of stress decrease (from 98.05 MPa to 97 MPa). The band grew under further loading while the stress was maintained at almost a constant value until the band grew all over the sample and the whole material within the etched section was fully transformed into the martensitic phase (see discussion.

Table 1
Composition (at.%) and transformation temperatures of the NiTi tube

<table>
<thead>
<tr>
<th>Ni</th>
<th>Ti</th>
<th>R_s</th>
<th>R_f</th>
<th>M_s</th>
<th>M_f</th>
<th>A_s</th>
<th>A_f</th>
</tr>
</thead>
<tbody>
<tr>
<td>54.1%</td>
<td>45.9%</td>
<td>52.1 °C</td>
<td>28.2 °C</td>
<td>5.5 °C</td>
<td>−32.7 °C</td>
<td>23.3 °C</td>
<td>57.1 °C</td>
</tr>
</tbody>
</table>

Fig. 3. Differential Scanning Calorimetry (DSC) thermogram of SME NiTi tube.
in a recent paper by Brinson et al., 2004). The onset of the stress drop has been generally recognized as a signal for band formation, and the stress plateau (Region II) demonstrates the growth of the nucleated macroscopic band via visible propagation of the band front (R–M front). After all the material was fully transformed, the stress increased monotonically corresponding to the elastic deformation and further detwinning of M-phase (Region III). The subsequent unloading response was almost linear elastic and the remaining transformation strain was about 4.2% which could be fully recovered by heating the specimen to $A_f$ (57.1 $^\circ$C).

Fig. 8 shows the typical stress–strain curve of the “dog-bone” shaped specimen (Type II) with initial state of twinned M-phase at room temperature under a loading rate of 0.2 mm/min. This stress–strain curve could be roughly divided into two regions. When compared with the regions I...
and II in $R \rightarrow M$ transition in Fig. 7 there is much less distinction in the detwinning process in Fig. 8. Region I in Fig. 8 demonstrates the elastic deformation of twinned martensite. With increasing stress (above 60 MPa), the stress–strain curve gradually bent and its slope gradually changed into that of region II where the martensitic detwinning process dominated the deformation. Further loading led to further detwinning and elastic deformation of the twinned martensite (Liu, 2002), this whole process occurs gradually instead of in one single step. Another contrast to the deformation of $R \rightarrow M$ process is that no macroscopic deformation band was found in the tube. Macroscopically, the stress–strain curve with considerable strain hardening shown in Fig. 8 gives a homogeneous deformation over the whole etched section. The response during unloading is almost linear elastic and the residual strain due to detwinning is about 3.4% which could be fully recovered by heating the specimen up to $A_f$ (57.1 °C).

The effect of the loading rate on the stress–strain curves and deformation of tubes are shown in Figs. 9 and 10. For the specimen which was initially in the R-phase, a flat stress plateau was observed at the loading rate of 0.2 mm/min. This is
because the required stress for the almost quasi-static and isothermal movement of the R/M interfaces was almost constant during $R \rightarrow M$ transformation. However, such stress plateau did not
exist in the cases of higher loading rates and the stress–strain curves maintained a positive slope during transformation. This means the required stress for the growth of band via interface migration in these cases kept increasing due to the latent heating effect. Surface morphology observation revealed that the higher the loading rate, the more bands formed sequentially with loading (see Fig. 11). On the other hand, for the specimen (type II specimen) which was in the M-phase initially, the stress–strain curves under different loading rates almost coincided. This reveals that the deformation due to martensitic detwinning was not affected in this loading range. We should notice that this may not be the case if the loading rate is very high (such as under an impact load) therefore further investigation at higher loading rates is crucial for studying the loading rate effect.

Fig. 8. Stress–strain curve of NiTi tube with initial state of M-phase. The “Heating” means heating to $A_f$ and the “Cooling” means cooling to $M_f$ then heating to room temperature.

Fig. 9. Stress–strain curves of NiTi tube with initial state of R-phase at different loading rates.

Fig. 10. Stress–strain curves of NiTi tube with initial state of M-phase at different loading rates.
3.2. Observation of macroscopic band formation and propagation at room temperature under a loading rate of 0.2 mm/min

The evolution of the R → M martensitic bands (Fig. 12) was recorded by observing the tube surface morphology. The starting structure of the specimen was R-phase and the specimen deformed homogeneously (Fig. 12(a)) before martensitic phase transformation (stress plateau). When the stress reached the critical level (peak stress) an inclined cylindrical martensitic band (Fig. 12(b)) appeared and a small nominal stress decrease was observed in the stress–strain curve. The band width of this initial martensitic band was about 1.2 mm and the inclination angle of the interface is about 55° to the loading axis.

The growth process of this martensitic band is shown in a series of photos of the tube (without surface coating) in Fig. 12(f) where the initial inclined cylindrical band gradually evolved into a cylindrical tube with the two fronts perpendicular to the loading axis. Fig. 12(b)–(e) shows the photos of the surface image of the tube with brittle coating where the inclined M band can be clearly seen and is in agreement with the surface morphology in Fig. 12(f). Also the second band formed during loading is shown in Fig. 12(d). The martensitic band maintained a cylindrical shape in the subsequent growth process under continued loading. During the heating process the reverse transition made the band gradually shrink back into an inclined band and finally disappeared.

Fig. 11. Variation of macroscopic band nucleation sites with loading rate: (a) 0.2 mm/min, (b) 0.5 mm/min, (c) 1.0 mm/min and (d) 2.0 mm/min.
3.3. Mechanical response of NiTi tubes at different temperatures

Uniaxial tensile tests were performed at 10 different temperatures from 23 to 70 °C using the water chamber to study the effect of temperature on material's response. The measured nominal stress–strain curves are summarized in Fig. 13 and are classified into three groups according to the initial phase structures. Each stress–strain curve is divided into three regions (similar to Fig. 7) for convenient discussion. The main results of the observation are summarized as follows.

In the temperature range of $M_s (5.5°C) < T < R_f (28.2°C)$, R-phase could be obtained as the...
initial phase of the specimen by cooling from a higher temperature. The stress–strain curves at 23 °C and 28 °C (Fig. 13) are in this range. Firstly, region I represents the elastic deformation of R-phase. When the stress reached the critical level, a small stress decrease was observed and this was the starting point of the stress-induced R → M transformation. A stress plateau (Region II) was formed during the growth of the martensitic bands. Two cylindrical martensitic bands were nucleated (loading rate 0.2 mm/min) within this temperature range. Region III was the elastic deformation and further detwinning of M-phase when the whole specimen was fully transformed from R to M phase.

In the temperature range of $R_f$ (28.2 °C) < $T$ < $R_s$ (52.1 °C), the initial structure consisted of a mixture of A-phase and R-phase as shown in Fig. 3. The stress–strain curves at 34 °C, 40 °C, 46 °C and 51 °C (Fig. 14) are in this range. Except for the elastic deformation of A-phase and R-phase, the stress-induced A → R and then R → M two-stage transformations occurred within this temperature range and therefore are observed in Fig. 14. The A → R transition is a gradual, stable process with a much smaller transformation strain (about 0.2–0.4%, Miyazaki and Otsuka, 1986) and the tube deformation was mainly dominated by the R → M (Region II) transition accompanied by a large stress plateau. Tube surface morphology observation shows that the deformation during the A → R transition was homogeneous (no band), having a strong contrast with the R → M process which was realized by band formation and growth. The surface morphology observation confirmed that the band shape is an inclined cylinder at room temperature and no obvious change in band shape is observed in this temperature range ($T = 34$ °C, 40 °C, 46 °C and 51 °C). Moreover, the transformation stresses for both A → R and R → M transitions increased with temperature as shown in Fig. 15. It should be noticed that so far the mechanism for the two-stage yielding here as well as in the literature is mainly based on the interpretation from the observed features of the measured stress–strain curves, and future direct verification (for example by XRD) of R-phase and more exact calculation are necessary.

At the temperatures $T > R_s$ (52.1 °C), the initial structure of the specimen was A-phase. The stress–strain curves at 56 °C, 61 °C, 65 °C and 70 °C (Fig. 13) are within this temperature range. The specimen exhibited SME at 56 °C ($<A_t = 57.1$ °C) and therefore the transformation strain did not recover upon unloading (Fig. 16(a)). The starting structure of the specimen was in A-phase, and the two-stage yielding still occurred at this testing temperature. The first stage with obvious

![Fig. 13. Stress–strain curves of NiTi tube at different temperatures.](image-url)
deviation from linearity represented the A → R phase transition and the second stage R → M phase transition started with a load drop. However, this two-stage yielding phenomenon gradually merged into one-stage A → M phase transition when the testing temperature was further increased to 61 °C, 65 °C and 70 °C (>\(A_f = 57.1 \, ^\circ\text{C}\)) at which the specimen exhibited superelasticity (refer to the phase diagram in Fig. 15). As shown in Fig. 16(b), region I consists of linear elastic deformation of A-phase only (no obvious deviation from linearity). The stress-
Fig. 15. Temperature dependence of transformation stress (phase diagram).

Fig. 16. The stress–strain curves with initial structure of A-phase: (a) Exhibiting the Shape Memory Effect (SME) at $T < A_f$. (b) Exhibiting the Superelasticity (SE) at $T > A_f$. 
induced $A \rightarrow M$ transition process (Region II) started with a sharp load drop signaling the formation of band and followed by the single band growth at almost constant stress plateau. During unloading, the $M$-phase was transformed back to $A$-phase by the reverse movement of the band front on a lower stress plateau. Special attention was paid to the band morphology variation with temperatures. Below $60^\circ C$ the nucleated macroscopic bands remained cylindrical in shape. As the temperature was raised to above $60^\circ C$ the band shape suddenly changed to helical as shown in Fig. 17(a) and (b) at $60^\circ C$ and $65^\circ C$ respectively. This type of helical band was well observed in previous researches on superelastic tubing (Sun and Li, 2002; Li and Sun, 2002). There also seems to be a correlation between the initial band volume and the amount of stress drop. The stress drop increased almost monotonically with temperature.

A phase diagram in temperature and stress space can be drawn by plotting the transformation stress versus temperature as shown in Fig. 15. The required stresses are represented by solid squares for the $A \rightarrow R$ transition, by solid circles for $R \rightarrow M$ and by open circles for the $A \rightarrow M$ transitions. They all increased with temperature and generally satisfy the Clausius–Clapeyron relationships for each type of phase transition (except when there was a small deviation at low temperatures, i.e., $T = 34^\circ C$ and $40^\circ C$ in this case). Moreover, the slope of the Clausius–Clapeyron relationship was steeper for the $A \rightarrow R$ transition than for the $R \rightarrow M$ and $A \rightarrow M$ transitions, which are responsible for the observed two-stage and one-stage yielding (transition) phenomena.

4. Conclusions

To investigate the stress-induced phase transformation and detwinning processes in polycrystalline NiTi tubes under tension, displacement controlled uniaxial tensile tests on the tubes with different initial phase structures were performed. Depending on the pre-testing heating/cooling history and the test temperature, different initial phases of the material were obtained and four different types of deformation process ($A \rightarrow M$, $R \rightarrow M$, $A \rightarrow R \rightarrow M$ and $M \rightarrow M$) were realized by the loading. The key experimental findings of this preliminary research are listed as follows:
Deformation due to the stress-induced R → M transition in NiTi tubes with initial R-phase structure is inhomogeneous, i.e., the R → M transformation process of the tube is realized through the formation and growth of macroscopic cylindrical shaped deformation bands under loading. Test results under different elongation rates show an obvious rate effect (due to the latent heat of R → M transition) on both stress–strain curves and surface morphology of the tube. The number of bands increased from two at loading rate of 0.2 mm/min to six at loading rate of 2 mm/min.

Deformation of the NiTi tubes with initial M-phase structure is homogeneous and proceeded by M → M martensitic detwinning. No macroscopic deformation band was observed on the tube surface during the deformation. There is also no loading rate effect observed for the tested loading rate (0.2–2 mm/min).

In the high temperature tests (34 °C < T < 51 °C) where the initial structure is a mixture of A and R phases, two-stage transition (yielding) was observed in the stress–strain curves of the tube. The first-stage yielding corresponds to A → R phase transition and the deformation is macroscopically homogeneous, while the second-stage yielding corresponds to R → M phase transition which is realized by macroscopic inclined cylindrical band formation and growth. The variation of the required stresses with temperature (phase diagrams) for both types of phase transition satisfies the Clausius–Clapeyron relationships. As a natural result of such a phase diagram, the two-stage (A → R and R → M) phase transitions merged into one-stage (A → M) transition with further increase in temperature.

At even higher temperatures (T = 56 °C, 61 °C, 65 °C and 70 °C), the initial structure of the material is A-phase. At 56 °C, two-stage transition (yielding) can still be observed in the stress–strain curve of the tube. At 61 °C, 65 °C and 70 °C, the tube only experience one-stage (A → M) transition. Close observation at the tube surface showed that the temperature (or the magnitude of the applied stress) has a strong effect on the band morphology. The band shape changed abruptly from an inclined cylinder (below 60 °C) to helical shape (above 60 °C). The later one was well observed in superelastic microtubing.

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