$B2 \Rightarrow B19' \Rightarrow B2^T$ Martensitic Transformation as a Mechanism of Plastic Deformation of NiTi

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Published online: 27 November 2019
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Abstract Deformation of superelastic NiTi wire with tailored microstructure was investigated in tensile loading–unloading tests up to the end of the stress plateau in wide temperature range from room temperature up to 200 °C. Lattice defects left in the microstructure of deformed wires were investigated by transmission electron microscopy. Tensile deformation is localized up to the highest test temperatures, even if practically no martensite phase exists in the wire at the end of the stress plateau. In tensile tests at elevated temperatures around 100 °C, at which the upper plateau stress approaches the yield stress for plastic deformation of martensite, upper plateau strains become unusually long, transformation strains become unrecoverable and deformation bands containing {114} austenite twins appear in the microstructure of deformed wires. These observations were rationalized by assuming activity

of $B2 \Rightarrow B19' \Rightarrow B2^T$ martensitic transformation into the austenite twins representing a new mechanism of plastic deformation of NiTi, additional to the dislocation slip in austenite and/or martensite. It is claimed that this transformation becomes activated in any thermomechanical load in which the oriented B19' martensite is exposed to high stress at high temperatures, as e.g., during shape setting or actuator cycling at high applied stress.

Keywords Materials · Stress-induced martensitic transformation · Superelasticity · Twinning

Introduction

It is widely established in the shape memory alloy (SMA) field that tensile deformation of superelastic NiTi wires due to the cubic to monoclinic martensitic transformation proceeds reversibly in thermomechanical load cycles at low temperatures [1], but becomes gradually unrecoverable presumably due to the dislocation slip activated in tensile tests at high temperatures instead of the stress induced martensitic transformation [2]. Nevertheless, it has not been very clear, whether the dislocation slip takes place in the austenite or in the martensite phase, whether it prevents recoverability of transformation strains and how it actually interacts with the martensitic transformation.

Recently, we have argued [3] that dislocation slip accompanies the stress induced $B2 \Rightarrow B19'$ martensitic transformation during the forward loading as well as during the reverse unloading under stress, since it compensates the strain incompatibilities arising at the moving habit planes as well as at the stationary grain boundaries in NiTi polycrystals. In other words, we claimed in [3] that below some characteristic temperature and stress, dislocation slip

This article is an invited submission to *Shape Memory and Superelasticity* selected from presentations at the Shape Memory and Superelastic Technology Conference and Exposition (SMST2019) held May 13–17, 2019 at The Bodensee Forum in Konstanz, Germany, and has been expanded from the original presentation.

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accompanies the martensitic transformation if the forward (reverse) transformation proceeds under external stress, not when the wire is loaded in the martensite phase and not when the reverse martensitic transformation proceeds in the absence of external stress, as e.g. during the shape memory cycle. This is the case for cyclic superelastic loads at low temperatures within the superelastic window and the underlying theory [3] explains why dislocation slip accompanies both the forward and reverse transformations. However, commercial medical grade NiTi wires quickly loose the superelastic property with temperature increasing above 100 °C, which cannot be explained by this scheme.

As this loss of strain recoverability with the increasing test temperature cannot be explained by the above outlined scheme, we have systematically investigated tensile deformation of NiTi wires having range of microstructures in thermomechanical loading tests reaching up to high stresses-high temperature conditions [4–6]. Based on the obtained results, we have proposed that the key mechanism bringing about unrecoverable strains at high temperatures is actually not dislocation slip at the moving habit plane interfaces [3] but a stress induced $B2 \Rightarrow B19' \Rightarrow B2^T$ martensitic transformation into twinned austenite coupled with dislocation slip [6]. The idea that the $B19'$ martensite may transform under external load to the austenite twins was suggested in the literature earlier [7–9], based on the frequent observation of austenite twins in the microstructure of heavily cold rolled [7, 10] or severe plastic deformation (SPD) processed [8, 9] NiTi and NiTiFe alloys. Surikova et al. [11] was the first one who linked the occurrence of austenite twins in the NiTi single crystal deformed in compression to the deformation twinning in stress induced $B19'$ martensite. Nishida et al. [12–14] presented TEM evidence for direct correlation between the deformation twinning in martensite and austenite twins observed in deformed NiTiFe alloys [13] and characterized the austenite twins observed in the microstructure of deformed wires [14]. Ezaz et al. [15, 16] analyzed the (20–1) deformation twinning in $B19'$ martensite [15] and {114} austenite twins [16] theoretically from atomistic point of view. Gao et al. [17–19] developed a general theoretical framework (Phase Transformation Graph (PTG) theory) capturing the intrinsic coupling between martensitic transformation and deformation twinning in NiTi using group theory operations on austenite and martensite crystal lattices [17]. The PTG scheme allows for prediction of deformation twinning systems in the $B19'$ martensite [17] bringing about unrecoverable strains claimed by Gao et al. to be associated with functional fatigue [18] and causing grain refinement [19] of NiTi transforming cyclically under high stress. Chen et al. [6, 20, 21] carried out a systematic investigation of tensile deformation of NiTi wires having a range of microstructures in wide

temperature range. Based on the results of the observations of {114} austenite twins in microstructures of deformed wires and synchrotron x-ray experiments informing the evolution of phase volume fractions upon loading, they claimed that the deformation twinning in oriented martensite plays an instrumental role in superelastic deformation at elevated temperatures [6] and plastic deformation of NiTi wires from – 100 to 200 °C.

In this work, we present experimental results on superelastic deformation of the 16 ms NiTi wire (see below) in tensile tests at elevated temperatures supported with the results of TEM analysis of lattice defects observed in the microstructure of deformed wires. We claim that the stress induced $B2 \Rightarrow B19' \Rightarrow B2^T$ martensitic transformation taking place at elevated temperatures is responsible for the gradual loss of NiTi superelasticity with increasing test temperature. We describe this two step transformation and discuss its implications for NiTi responses in general thermomechanical loads involving high temperatures and high stresses.

Material and Methods

Commercial superelastic NiTi wire produced by Fort Wayne Metals in cold work state (FWM #1, Ti-50.9 at.% Ni, 42.1% CW, diameter 0.1 mm) was heat treated by electropulse method to prepare NiTi wire samples with desired microstructure and properties [20]. 30 mm long wire segments were crimped by two steel capillaries, pre-stressed to ~ 300 MPa, constrained at current length and subjected to the short pulse of controlled electric power (power density 160 W/mm³, pulse time 16 ms). For given cold worked wire and power density used in the heat treatment, the pulse time scales with the maximum temperature reached during the electropulse heating which largely controls the microstructure and properties of the heat treated wire. Hence, the wire used in this work is called “16 ms NiTi wire”. It has fully recrystallized microstructure with grain size ~ 500 nm and transformation temperatures $M_s = -40$ °C and $A_f = -10$ °C in [20].

Thermomechanical loading tests in tension were carried out using self-made tensile testers for thin wires. These testers consist of a miniature load frame, environmental chamber, electrical conductive grips, a load cell, a linear actuator and a position sensor. The environmental chamber (Peltier elements, resistive elements and liquid nitrogen vapors) enables to maintain homogeneous temperature around the thin wire from – 100 to 500 °C. The temperature, stress or strain are controlled and recorded by the close-loop LabVIEW controlled system. The wire sample was gripped into the tester, strain was set to zero in the austenitic state at room temperature and the wire was

heated/cooled to the desired test temperature under 20 MPa stress and tensile thermomechanical test was performed according to preset program. Stress–strain–temperature–electric resistance of the wire was recorded during the whole test. In some experiments, evolution of local axial strain along the length of the wire was evaluated by one dimensional Digital Image Correlation (1D-DIC) method.

Lattice defects created by tensile deformation in the austenitic microstructure of the wires were observed by Transmission Electron Microscopy (TEM). Samples for TEM studies were prepared from deformed wires by Focused Ion Beam (FIB) method using FEI Quanta 3D FIB-SEM electron microscope. TEM lamellas were extracted from the subsurface layers of the deformed wires ($\sim 10 \mu\text{m}$ below the surface) in such a way that the wire axis always lies in the plane of the TEM lamella. In fact, the deformed and unloaded wires were always heated/cooled to $\sim 150^\circ\text{C}$ under small stress 20 MPa to complete the strain recovery by reverse transforming any potentially remaining residual martensite prior the TEM lamellas were made. TEM observations were carried out using FEI Tecnai TF20 X-twin field emission gun microscope operated at 200 kV with a double tilt specimen holder.

Localized Tensile Deformation of Superelastic NiTi Wire at Various Temperatures

Stress–strain responses recorded in tensile tests on the 16 ms NiTi wire in wide temperature range from -100 to 200°C are shown in Fig. 1a. As the upper plateau stress increases with increasing temperature and the yield stress for plastic deformation of martensite simultaneously

decreases, they become equal at test temperature of $\sim 60^\circ\text{C}$ (Fig. 1b). This essentially means that the martensite phase, stress induced within the macroscopic band fronts propagating in tensile tests at $T > 60^\circ\text{C}$, is exposed to stress levels at which it may deform plastically. The upper plateau strain increases linearly with increasing test temperature from -60°C to 60°C , shows a sharp peak in the temperature range 60 – 120°C and remains constant afterwards (Fig. 1b). Maximum upper plateau strain 16% was observed in tensile test at 90°C . Since we knew from the closely related work [21] that plastic deformation of the stress induced martensite proceeds via deformation twinning in martensite, we suspected that the B19' martensite newly appearing when the austenite transforms within the propagating martensite band front may deform further via deformation twinning—i.e. that the deformation twinning in B19' martensite takes place already during the forward loading till the end of the stress plateau [6].

The appearance of unusually long upper stress plateaus in tensile tests at elevated temperatures is not, however, specific property of the 16 ms NiTi wire. Long upper stress plateaus were observed in tensile tests on NiTi wires possessing wide range of virgin microstructures [6, 20]. The temperature range, at which the long plateaus were observed vary significantly with the starting microstructure of the NiTi wire. The origin of the long plateaus and related gradual loss of the strain recoverability in superelastic tensile tests on NiTi wires was rationalized in [6] by gradual increase of the activity of the stress induced $B2 \Rightarrow B19' \Rightarrow B2T$ martensitic transformation within the macroscopic band fronts propagating in tensile tests at $T > 60^\circ\text{C}$.

It is essential to keep in mind that the localized Lüders-like deformation occurs in tensile tests from room

Fig. 1 Tensile tests on 16 ms NiTi wire at various test temperatures till rupture [20]: **a** stress–strain curves, **b** material parameters evaluated from tensile tests: upper plateau stress σ_p^{UP} , yield stress

σ_Y and upper plateau strain ϵ_p^{UP} are determined from the stress–strain curves in (a) (Color figure online)

Fig. 2 Localized deformation observed by 1D-DIC method during tensile tests on 16 ms NiTi wire at 20 °C: **a** stress–strain curve, **b** stress–time record of the tensile test, **c** strain color maps informing time evolution of the axial strain component in various locations along the wire (z-position), **d** lattice defects in the microstructure of the deformed wire (Color figure online)

temperature up to 200 °C. Figure 2 shows 1D-DIC record of localized tensile deformation of 16 ms NiTi wire at room temperature. The tensile deformation of the wire is localized within a martensite band nucleating at one of the

grips and propagating in a form of a single martensitic band front moving towards the other grip during the forward loading as well as reverse unloading. Macroscopic deformation 8% is fully recovered on unloading and leaves only isolated dislocation defects in the microstructure of the deformed wire (Figs. 2,3). It shall be noted, that the wire was completely martensitic at the maximum strain, as confirmed by in-situ synchrotron x-ray diffraction experiments reported in [6]. Due to the nature of the localized deformation in tensioned wire, the forward and reverse martensitic transformations take place within the cone shaped martensite band front–macroscopic interface [22] propagating along the wire.

Microstructure of the virgin 16 ms wire (Fig. 3a) contains roughly equiaxed grains ~ 500 nm in diameter, which are essentially free of dislocation defects. Examples of lattice defects left in the microstructure of the 16 ms wire after superelastic loading–unloading cycle at room temperature up to 10% maximum strain are shown in Fig. 3b–h. There are isolated dislocations and dislocation loops around nonmetallic inclusions (Fig. 3d, h) statistically present in the microstructure of the deformed wire but no defects that could be meaningfully linked to the martensitic phase transformation. We believe that this is a typical pattern for fully recoverable superelastic deformation of NiTi–macroscopic deformation localized in Luders band fronts and practically no lattice defects left in the microstructure after unloading.

In tensile tests at higher temperatures, however, the situation is very different. Figure 4 shows 1D-DIC records of localized tensile deformation at 50 °C, 100 °C and 150 °C temperatures at which the upper plateau strains become significantly longer and only partially recoverable (Fig. 1b). In the tensile test at 50 °C, localized deformation upon forward loading is essentially similar to that at room temperature (Fig. 2). The deformation on the reverse unloading, however, is very different. Although the unloading deformation is still partially localized, the propagating martensite band front contains only ~ 2% strain, the rest recovers either homogeneously (~ 4.5% strain) or remains unrecovered (~ 2.5% strain). Another difference is that the microstructure of the unloaded and heated wire (Fig. 4) contains high density of slip dislocations and isolated deformation bands. A question remains whether these defects were created upon forward loading or reverse unloading. If they were created upon the forward loading, which is more likely, then this cannot be recognized from the stress–strain curves or DIC patterns, since these are the same in Figs. 2 and 4.

In the tensile test at 100 °C, Luders band was nucleated in the mid part of the wire and two fronts propagated towards the grips with similar rates. When one of the fronts reached the sample end at the grip ($z = 0$), the second front

Fig. 3 Microstructure in the virgin 16 ms NiTi wire (a) and wire deformed at room temperature till 10% strain and unloaded (b–h) observed by TEM. Isolated dislocation segments are observed at

grain boundaries (b), dislocation loop around nonmetallic inclusions (d, g, h), isolated slip dislocation within grain (e) and BF image of a grain oriented in low index $<111>$ zone (f)

started to propagate twice as fast (prescribed rate of the crosshead movement is constant). In response to that, the plateau stress slightly increased, since strain rate increased. The strain gradient across the martensite band front equals to the plateau strain $\sim 15\%$. The deformation upon the reverse unloading was nonlinear homogeneous leaving behind about 12.5% unrecovered strain. The microstructure of the deformed wire contains large amount of deformation bands and high density of slip dislocations. In the tensile test at 150 °C, Lüders band was nucleated near one of the grip. Two fronts propagated with very different rates, strain gradient across the front equals to plateau strain 11% and the deformation on the reverse unloading was nearly linear elastic leaving behind about 9% unrecovered strain. The microstructure of the deformed wire contains less deformation bands and more slip dislocations compared to the wire deformed at 100 °C.

Microstructure of Wires Deformed at Elevated Temperatures

It appears that microstructure of wires deformed at temperatures $50\text{ °C} \leq T \leq 150\text{ °C}$ contain deformation bands and slip dislocations (Fig. 4). Maximum density of deformation bands was observed in wires deformed at temperature $\sim 90\text{ °C}$ (Figs. 5, 6, 7), at which longest upper plateaus were observed (Fig. 1b). Hence, when analyzing lattice defects by TEM, we were particularly interested in

those deformation bands, since they do not appear in conventional superelastic tests at low temperature (Figs. 2, 3) and can thus be linked to the deformation mechanism responsible to the long plateaus.

Before we discuss the results of the TEM analyses in Figs. 5, 6, 7, we shall briefly introduce the adopted method. We knew from the previous research on superelastic NiTi wires [4] that $\{114\}$ austenite twins form in the microstructure of NiTi wires transforming at high stresses and high temperatures. The problem was that the nanosized microstructure of NiTi wires used in [4] with lattice defects persisting from the previous cold work and multiple small grains overlapping through the thickness of the TEM lamella did not allow for meaningful analysis of very thin deformation bands [4]. This, however, became possible in the case of the 16 ms NiTi wire having large ($\sim 500\text{ nm}$) dislocation free recrystallized grains studied in this work. The microstructure of the deformed 16 ms wires contains large number of relatively wide deformation bands.

It was clear that the deformation bands contain austenite lattice differently oriented with respect to the matrix – most likely deformation twins. The goal was to find out which type of twins they are and describe the dislocation defects within the twins and matrix. If we tilt the lamella cut from a virgin NiTi wire into any of low index zone in the diffraction pattern from a particular grain, this grain becomes completely dark in the corresponding BF image (Fig. 3f). But if there are deformation bands in the grain,

Fig. 4 Localized deformation observed by 1D-DIC method during tensile loading–unloading of the 16 ms NiTi wire at 50 °C, 100 °C, 150 °C: **a** stress–strain curves, **b** stress–time record from the tensile tests, **c** strain color maps informing time evolution of the local axial

strain component in various locations along the wire (z-position), **d** lattice defects in the microstructure of the deformed wire (Color figure online)

Fig. 5 Lattice defects observed by TEM in the microstructure of the 16 ms NiTi wire deformed at 90 °C up to the end of the stress plateau, unloaded, heated to 150 °C and cooled to the room temperature

they typically remain bright, so they can be easily visualized while inspecting the microstructure.

To analyze microstructure with deformation bands containing $\{114\}$ austenite twins or B19' martensite, we need to tilt the lamella into one of the six equivalent $\langle 011 \rangle$ zones of the cubic structure, in which the electron beam is parallel to the twin axis. In this orientation, the deformation bands, which contain austenite twins or B19' martensite are oriented to the electron beam so that they diffract strongly and remain dark. The B19' martensite within the deformation band is oriented with $\langle 010 \rangle$ axis along the electron beam due to the B2/B19' lattice correspondence and martensite variant selection in this orientation [21, 23]. If we needed to visualize the austenite twins or B19' martensite, we just took DF image using diffraction

spot corresponding to one of these microstructure constituents. As the twin interfaces and austenite/martensite interfaces are oriented edge on, we could identify the interface plane and lattice misorientation. To analyze the microstructure within a selected grain of the deformed wire (austenite twins, interfaces, martensite variants and austenite/martensite interfaces), we thus had to tilt the TEM lamella into this particular $\langle 011 \rangle$ austenite zone axis in the grain selected for TEM analyses of deformed microstructure. See supplementary materials of Refs. [21, 23] for examples of TEM analysis of deformation bands.

Figure 5 shows selected examples of microstructures observed in the 16 ms NiTi wire deformed at high temperature 90 °C up to the end of the upper stress plateau.

Fig. 6 Deformation bands containing $\{114\}$ austenite twins in the microstructure of the 16 ms NiTi wire deformed at 90 °C till the end of the stress plateau: **a** grain with multiple parallel bands in general orientation, **b** Diffraction pattern taken from the area denoted by the yellow circle in **(a)**, **c, d** indexing the diffraction pattern as austenite matrix (red) and two austenite twins (green, blue), **e** STEM image

showing the austenite twins as white bands, **f** DF image of the grain using austenite reflection (01–1), **g, h** DF images of the grain using austenite twin reflection (01–1) and (0–11), The green and blue lines in **(d, g, h)** denote the trace of the $\{114\}$ austenite twin interfaces. The white line in **g** (black in **d**) denotes the interface between both austenite twins (Color figure online)

Fig. 7 Deformation bands containing $\{114\}$ austenite twins in the microstructure of the 16 ms NiTi wire deformed at 90 °C till the end of the stress plateau: **a** grain with multiple deformation bands was selected for the analysis, **b** Diffraction pattern taken from the area denoted by the yellow circle in **(a)**, **c, d** indexing the diffraction pattern as austenite matrix (red) and two austenite twins (green, blue),

e STEM image showing the austenite twins as white bands, **f, g** DF images of the grain using austenite matrix reflections (-100) and (01–1), **h** DF image of the grain using (01–1) austenite twin reflection. The green and blue lines in **(d, g, h)** denote the trace of the $\{114\}$ austenite twin interfaces (Color figure online)

Compared to the microstructure of the wire deformed at room temperature (Fig. 3), there is high density of slip dislocations and deformation bands containing $\{114\}$ austenite twins and occasionally the oriented $B19'$ martensite. To characterize deformation bands in Fig. 5, the TEM lamella was tilted into one specific $\langle 011 \rangle$ orientation of the austenite matrix as introduced above. Selected results of detailed analysis of deformation bands are shown in Figs. 6, 7. Dark grain in Fig. 6a contains high density of parallel about ~ 50 nm thick deformation bands. The lamella was tilted into the desired $\langle 011 \rangle$ zone and diffraction pattern was taken from the SAED area denoted by the yellow circle. The diffraction pattern (Fig. 6b) was indexed as belonging to the three misoriented austenite lattices [matrix in red and two twins in green and blue (Fig. 6c, d)] mutually misoriented within the $\langle 011 \rangle$ zone. DF image taken with the austenite matrix spot (01–1) shows the austenite matrix in white (Fig. 6f). DF images taken using the (01–1) and (0–11) austenite twin spots (Fig. 6g, h) show the white $\{114\}$ austenite twin bands within the grain. The blue and green lines in Fig. 6d, g, h denote the traces of $\{114\}$ twin interfaces. A similar microstructure in another grain is shown in Fig. 7. There are again two sets of parallel deformation bands containing $\{114\}$ austenite twins. See dark bands in the DF image taken with (01–1) matrix reflection (Fig. 7g) or white bands in the DF image taken with (01–1) twin reflection (Fig. 7h). Green and blue lines denote the traces of the $\{114\}$ twin planes of the green and blue twins, respectively. It is essential that similar results were obtained when other grains in the microstructure were analyzed (not every grain can be analyzed in this way due to the limits in lamella tilting). The most important result of the TEM analyses of the wire deformed at 90°C is thus the fact that practically all grains, which were analyzed, contained $\{114\}$ austenite twins. Since the volume fraction of those $\{114\}$ austenite twins in the microstructure of deformed wire was frequently rather high, it is evident that the observed large unrecoverable strains are related to them.

Although most of the observed deformation bands contained mainly $\{114\}$ austenite twins, deformation bands containing $B19'$ martensite were occasionally observed as well (see Fig. 13 in [6]). However, since the number of those residual martensite bands was rather low, the residual martensite bands were not given special attention in this work. Martensite bands containing residual martensite were, however, regularly found in the microstructure of the 16 ms NiTi wire deformed beyond the yield point or in wires deformed by superelastic cycling at relatively low temperatures [23]. The residual martensite lattice is separated from the austenite matrix by $\{112\}_{B2}/(10-1)_{B19'}$ interface analyzed in detail in [23].

Mechanisms of the Stress Induced

$B2 \Rightarrow B19' \Rightarrow B2^T$ Martensitic Transformation

To explain the observation of long plateaus and loss of the strain recoverability in tensile tests at elevated temperatures around 100°C , we originally assumed, in accord with the state of the art view [3, 5], that plastic deformation of the austenite and/or stress induced martensite phases takes place via conventional dislocation slip proceeding alongside the stress induced martensitic transformation. This assumption, although it might potentially explain the long plateaus observed at elevated temperatures, cannot explain the loss of the recoverability of transformation strains as well as the occurrence of deformation bands containing $\{114\}$ austenite twins in the microstructure of NiTi wires deformed at elevated temperatures.

It was already mentioned that deformation twinning in oriented $B19'$ martensite was found to be responsible for the onset of plastic deformation of NiTi wires at low temperatures [21]. Deformation twinning in the $B19'$ martensite [13, 15] differs from the conventional transformation twinning in martensite [24], particularly in that the deformation twins do not transform back to the original parent austenite phase on unloading and heating. Instead, they give rise to the austenite twins accommodating large residual strains [13]. Sittner et al. [6, 21] described the role of deformation twinning in tensile deformation of NiTi with the help of potential energy landscape (Fig. 8). The scheme shown in Fig. 8A corresponds to the low temperatures, at which martensite is the stable phase. The austenite energy minima (austenite configurations **I** and **R**) lie above the martensite minima (martensite configurations **F_J** and **F_NR**) in mirror symmetry on the left and right side with respect to the center. The martensite configurations **F_J** and **F_NR** form upon cooling from the austenite configurations **I** and **R** by overcoming the energy barrier between them. In the language of continuum mechanics of SMAs [25], the scheme in Fig. 8A describes a set of material states reachable by martensitic transition from two different reference austenite configurations **I** and **R**.

This energy landscape changes with increasing temperature and stress as Fig. 8C suggest. Taking into account the effect of uniaxial applied stress on the energy landscape, the mirror symmetry is broken (the rotated austenite configuration **R** becomes of lower energy than **I**, since rearranging the atoms into the configuration **R** would provide external strain in the direction of the applied stress). The scheme is used to treat system response on mechanical loading as follows. At room temperature (Fig. 8C), the austenite is the stable phase and the $B19'$ martensite can be induced by overcoming the energy barrier between austenite and martensite by increasing stress.

Fig. 8 Potential energy landscape for martensitic transformation and deformation twinning in NiTi (A) [6]. The high symmetry austenite phase appears in the original reference configuration **I** and a rotated configuration **R** at the same energy level in mirror symmetry with respect to the center. The low symmetry martensite phase **F_J** (**F_NR**) forms from the austenite phase **I** (**R**) via martensitic transformation upon cooling by overcoming the energy barrier between **I** and **F_J** (**R** and **F_NR**). The martensite variant **F_J** belonging to the Ericksen–Pitteri neighborhood of **I** (b) may form the martensite variant **F_NR** belonging to the E–P neighborhood of **R** (d) by deformation twinning involving combination of plastic shearing and shuffling (c). Parent phase with reference configuration **R** (e) may be obtained from the **F_NR** by reverse martensitic transformation on

heating, unloading and/or further tensile loading. The {20–1} twin interfaces in the martensite phase (f) are converted into {114} twin interfaces in the austenite phase (g) after the reverse martensitic transformation. The atomic configurations appearing successively upon tensile loading at various temperatures **B** the initial austenite lattice (a); the oriented B19' martensite phase (b); the deformation twinned B19' martensite phase (d); twinned austenite (e) yield increasing respectively effective strain (right). Sketches of polycrystal grains outlines the microstructure in the wire at the peak stress at three different temperatures. Figures at the bottom **C** show schematically the effects of temperature and applied stress on the energy landscape (Color figure online)

If tensile loading at room temperature continues further above the upper plateau stress, the martensite would undergo deformation twinning [21], which never occurs in conventional superelastic tests till the end of the upper stress plateau because of the energy barrier at the center. The stress induced martensitic transformation in superelastic tensile loading–unloading cycle at room temperature thus proceeds reversibly between the B2 austenite and B19' martensite, as suggested in Fig. 8B(a ↔ b). The volume of the wire transforms completely to the martensite [6] and there is no massive dislocation slip accompanying the forward and reverse stress induced martensitic

transformation in the first cycle. See also the schematic sketch of a polycrystal grain in the microstructure at the peak stress at 20 °C containing the yellow oriented B19' phase only.

The situation is different in tensile tests at 100 °C (Fig. 8C), since the barrier for deformation twinning at the center is lower and consequently, the NiTi lattice may pass through the sequence of atomic configurations down to the deformation twin (d) or even austenite twin (e), as suggested in Fig. 8B(a → d(e)). Considering this, we assume that the stress induced transformation at 100 °C proceeds in one step as B2 ⇒ B19' ⇒ B2^T (Fig. 8B(a → e)) within

the deformation bands (Figs. 5–7) and simultaneously conventionally as $B2 \Rightarrow B19'$ (8B (a $\leftrightarrow$ b)) elsewhere in the austenite matrix. In other words, stress induced martensitic transformation proceeds into the $B19'$ everywhere in the volume of the wire and only somewhere the distortion proceeds further into the deformation twinned martensite and $B2^T$ austenite. The schematic sketch of the microstructure at the peak stress at 100 °C thus contains the yellow oriented $B19'$ phase and austenite twins. As a result of the $B2 \Rightarrow B19' \Rightarrow B2^T$ transformation, the upper plateau strains become larger than the plateau strains due to the $B2 \Rightarrow B19'$ at room temperature, the plateau strains become partially unrecoverable and $\{114\}$ austenite twins are observed in the austenitic microstructure of the deformed wire. There is dislocation contrast in the austenite matrix as well as in the austenite twins. These dislocations are different from the $\{011\}/\langle 100 \rangle$ slip dislocations in austenite we observed earlier in the 16 ms NiTi wire after 10 superelastic cycles at room temperature [26] or which others reported [27, 28]. It is thus possible that the deformation twinning in martensite involves dislocation slip in martensite.

In tensile tests at 150 °C, the barrier for deformation twinning at the center (Fig. 8c) practically does not exist, which means that any $B19'$ martensite, which becomes stress induced, immediately undergoes deformation twinning and transforms to the $\{114\}$ austenite twin upon tensile loading. Because of that, martensitic transformation

does not occur everywhere in the volume of the wire and the austenite matrix surrounding the deformation bands deforms via conventional dislocation slip in austenite. The higher the temperature, the less volume of the wire undergoes the two step transformation within the bands. Although the stress induced transformation does occur and causes the macroscopic deformation to be localized within Luders band front propagating under constant load (Fig. 4), there is a very less volume of the martensite in the wire in any moment of the tensile test as was experimentally verified for the end of the plateau (see Fig. 9 in [6]). The schematic sketch of the microstructure at the peak stress at 150 °C contains the white austenite deformed by dislocation slip and austenite twins. As a result of this, the upper plateau strains become lower in tensile tests with temperature increasing from 100 °C up to 150 °C, less austenite twins are observed in the microstructure of deformed wire, the plateau strains become completely unrecoverable in tensile tests at 150 °C (Fig. 4) and $\{011\}/\langle 100 \rangle$ slip dislocations were observed in the microstructure of deformed wires [6].

Gradual activation of the $B2 \Rightarrow B19' \Rightarrow B2^T$ martensitic transformation and dislocation slip in austenite on the expense of the stress induced $B2 \Rightarrow B19'$ martensitic transformation with increasing temperature thus explains the observation of the long upper stress plateaus, loss of the strain recoverability, and appearance of $\{114\}$ austenite twins in tensile tests at elevated temperatures. The deformation pathway changes with increasing test temperature from 20 °C to 200 °C. The change is gradual, which gives rise to the upper plateau strain peak in temperature dependence (Fig. 9). These experimental results, particularly to the $\{114\}$ austenite twins in the microstructure of deformed wires, can be hardly explained considering the conventional dislocation slip based mechanisms of functional fatigue of NiTi proposed in the state of the art articles on this topic in the literature [3, 27–31].

B2 $\Rightarrow$ B19' $\Rightarrow$ B2^T Martensitic Transformation in Thermomechanical Loads

Since the $B2 \Rightarrow B19' \Rightarrow B2^T$ martensitic transformation occurs in NiTi only under high stress – high temperature conditions – i.e., out of the range where these alloys are normally used in engineering applications, one may wonder whether it is worth of investigation. In our opinion, there are several reasons why this transformation is of wide general interest for superelastic and shape memory technologies.

First reason is that the $B2 \Rightarrow B19' \Rightarrow B2^T$ transformation becomes activated in all NiTi wires, only the temperature and stress at which it happens vary significantly,

Fig. 9 Stress-Temperature diagram of the 16 ms NiTi wire constructed from experimental data (Fig. 1) with denoted critical [temperature, stress] (red point), at which the upper plateau stress σ_p^{UP} equals to the yield stress σ_Y ($[T^*, \sigma^*] = [700 \text{ MPa}, 60 \text{ °C}]$). Stress-temperature paths corresponding to three common thermomechanical loading paths on NiTi wires are denoted by color arrows. When the thermomechanically loaded wire is exposed stress—temperature conditions within the gray triangle area, the $B2 \Rightarrow B19' \Rightarrow B2^T$ takes place and brings about large unrecoverable strains and $\{114\}$ austenite twins are observed in the microstructure of deformed wires (Color figure online)

since they heavily depend on the virgin microstructure of the wire [6, 20]. While the long plateaus and deformation bands were observed at 60 °C/800 MPa on 20 ms NiTi wire, they appeared above 150 °C/1400 MPa in tensile tests on 12 ms NiTi wire, the properties of which are similar to commercial superelastic NiTi wires [20].

Second reason is that the deformation bands evidencing the activity of the two step transformation were systematically observed in the microstructure of superelastically cycled NiTi wires at relatively low test temperatures – after tens, hundreds or thousands of cycles depending on the wire microstructure [32]. This suggests that this transformation becomes activated later upon tensile cycling and accelerates functional fatigue of NiTi with increasing temperature [23, 32]. Number of cycles after which the bands appear in the microstructure depends on the wire microstructure and test temperature [20, 23]. The deformation bands observed after superelastic cycling frequently contain residual B19' martensite [23]. See [23] for detailed analysis of the austenite/martensite interfaces of deformation bands created by cyclic deformation.

Third reason is that both superelastic and actuator NiTi wires can be accidentally exposed to high stress—high temperature conditions, at which the $B2 \Rightarrow B19' \Rightarrow B2^T$ transformation becomes activated and brings about unrecoverable strains. Hence, it is important to understand the risks and consequences of that. Figure 9 shows the temperature dependence of the upper plateau stress (σ_p^{UP}), martensite yield stress (σ_y) and upper plateau strain (ϵ_p^{UP}) experimentally determined from the tensile tests. The figure represents a stress-temperature diagram informing stress-temperature conditions at which various deformation mechanism become activated in NiTi wire subjected to thermomechanical loads. There is the critical temperature-stress [T^* , σ^*], at which upper plateau stress equals to the yield stress for plastic deformation of martensite. It is denoted by the red point. Stress-temperature paths corresponding to three common thermomechanical loading paths on NiTi wires are denoted by color arrows. The stress-temperature region, where the $B2 \Rightarrow B19' \Rightarrow B2^T$ transformation is expected to occur, is denoted by the gray triangle. When the thermomechanically loaded NiTi wire is exposed to [temperatures, stress] within the gray triangle, the $B2 \Rightarrow B19' \Rightarrow B2^T$ martensitic transformation takes place, unrecoverable strains are generated and unusual TRIP like stress-strain-temperature responses are recorded in cyclic thermomechanical loading tests (see Figs. 9–12 in [4]). The critical [T^* , σ^*] depend significantly on the virgin microstructure of the NiTi wire (see Fig. 8 in [20]). The [T^* , σ^*] is [60 °C, 700 MPa] for the 16 ms NiTi wire. In case of medical grade superelastic NiTi wire, however, the critical [T^* , σ^*] is [150 °C, 1300 MPa] and can be slightly shifted upwards by suitable precipitation aging treatment.

We consider the critical [T^* , σ^*] condition to be a very important material characteristics of NiTi and recommend it to be regularly determined from temperature the dependence of upper plateau stress and yield stress for plastic deformation of martensite.

Based on the results of systematic experiments focusing on thermomechanical responses of superelastic NiTi wire in tensile tests reaching up to the stress-temperature region where the $B2 \Rightarrow B19' \Rightarrow B2^T$ becomes activated, a TRIP like deformation mechanism was incorporated [4] into our earlier mechanics model of NiTi [33].

Conclusions

Stress induced martensitic transformation in superelastic NiTi wire (grain size ~ 500 nm) deformed in tensile test at room temperature proceeds reversibly in localized manner without leaving any significant unrecovered strain or dislocation defects in the microstructure of the deformed wire.

However, as the temperature increases, the stress induced martensitic transformation takes place at elevated temperatures, at which the upper plateau stress approaches the yield stress for plastic deformation of martensite, the upper plateau strains become unusually long, transformation strains become only partially recoverable and deformation bands containing {114} austenite twins appear in the microstructure of deformed wires. Temperature dependence of upper plateau strains shows sharp peak with maximum at 90 °C. These observations were rationalized by assuming activity of the $B2 \Rightarrow B19' \Rightarrow B2^T$ martensitic transformation into austenite twins in the temperature range where the long plateaus are observed. It represents a new mechanism of plastic deformation of NiTi, additional to the dislocation slip in austenite and/or martensite.

The $B2 \Rightarrow B19' \Rightarrow B2^T$ martensitic transformation is not activated only in tensile tests at high temperatures studied in this work but also in any thermomechanical loading test, in which the oriented B19' martensite is exposed to high stress at high temperatures, as e.g. during shape setting or actuator cycling under large applied stress.

Temperature stress [T^* , σ^*] condition, at which upper plateau stress equals to the yield stress for plastic deformation of martensite, is proposed to be taken as important material parameter of NiTi characterizing temperatures and stresses, above which the $B2 \Rightarrow B19' \Rightarrow B2^T$ martensitic transformation becomes activated in thermomechanical loads.

Acknowledgements Ms. Y. Chen acknowledges the support of her Ph.D. work from Nanjing University of Aeronautics and Astronautics, China as well as from the Functional Materials Department, Institute

of Physics of the ASCR, Prague, Czech Republic. Support of the research from Czech Science Foundation (CSF) projects 18-03834S (P. Šittner), 17-00393 J (L. Heller) is acknowledged. MEYS of the Czech Republic is acknowledged for the support of infrastructure projects FUNBIO-SAFMAT (LM2015088), LNSM (LM2015087), SOLID 21 (CZ.02.1.01/0.0/0.0/16_019/0000760) and European Spallation Source—participation of the Czech Republic – OP (CZ.02.1.01/0.0/0.0/16_013/0001794). National Natural Science Foundation of China (No. 11872207) is acknowledged.

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