Austenite grain refinement during load-biased thermal cycling of a Ni_{49.9}Ti_{50.1} shape memory alloy

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Abstract

A near-equiatomic NiTi shape memory alloy was subjected to a variety of thermomechanical treatments including pure thermal cycling and load-biased thermal cycling to investigate microstructural evolution of the material under actuating conditions. In situ and post mortem scanning transmission electron microscopy (STEM) was used to study the effects of stress on the development of defect substructures during cycling through the martensitic transformation. High temperature observations of the austenite phase show rapid accumulation of dislocations and moderate deformation twinning upon thermomechanical cycling. Additionally, TEM-based orientation mapping suggests the emergence of fine crystallites from the original coarse austenite grain structure. A possible mechanism is proposed for the observed grain refinement based on the crystallographic theory of martensite transformation.

Keywords: SMA, microstructural evolution, actuation, orientation mapping, defect analysis

1. Introduction

Shape memory alloys (SMAs) such as NiTi are currently used in a wide array of applications, such as stents and other surgical devices, solid-state actuators, and MEMS devices [1-3]. The extensive potential of SMAs is attributed to their unique properties, namely the shape memory effect (SME) and pseudoelasticity. These shape-recovery behaviors are enabled by a thermoelastic martensitic transformation, which is either

thermally-induced (SME) or stress-induced (pseudoelasticity) and can be reversed upon heating or removal of the external load. In NiTi, this transformation is between a high temperature B2 austenite phase and a low temperature B19' martensite. Despite their potential, SMAs suffer from cyclic instabilities such as the accumulation of permanent strain, changes in transformation temperatures, and modified hysteretic behavior. It is well documented in the literature that the phase transformation in SMAs, even in the best commercial alloys, is accompanied by the generation of defects [4-6]; however, the evolution of these defects and the role they play in subsequent transformation cycles is still a subject of research. In a study by Miyazaki et al., pre-existing dislocations were found to impede the thermally-induced martensite transformation, as evidenced by a decrease in the martensite start temperature (M_s) during thermal cycling of a solutionized NiTi polycrystal [7]. It was later shown by Yawny et al. [8] that stress-induced martensite formation is promoted by the presence of dislocations, based on a gradual decrease in the critical stress upon mechanical cycling. Due to this complex interaction, there have been many attempts to characterize the nature of the coupling between plasticity and the martensitic transformation during stress or temperature cycling of SMAs [4,6,9-11].

Thermomechanical testing, such as load-biased thermal cycling, is a critical test mode that has been explored due to its relevance to many potential applications in the field of actuation and the fact that it incorporates the effects of both temperature and applied load. Grossmann et al. [12] showed that the M_s temperature increases during thermal cycling of NiTi spring actuators with a constant external load, which corresponds to an increase in the dislocation density. A study by Hamilton et al. [4] demonstrated that for “low” Ni alloys (50.1 at.% and 50.4 at.%), the thermal hysteresis grows with increasing bias stress. This was supported by TEM observations of dislocations emitting from the martensite-austenite interface and a hypothesis that the plastic strain accommodates and stabilizes the martensite, making the reverse transformation more difficult. It was also shown that for “high” Ni alloys (50.8 at.% and 51.5 at.%) the hysteresis shrinks with increasing bias stress. Since the higher Ni concentration leads to a more homogeneous precipitate distribution and thus stronger parent phase, it is suggested that the energy dissipation via plastic deformation is reduced, leading to a higher driving force for the reverse

transformation. It is clear from these observations that the cyclic response of SMAs under load-biased thermal cycling is dictated by a number of factors. However, to the authors' knowledge, there does not exist a systematic TEM-based study of the microstructural evolution of NiTi under load-biased thermal cycling conditions. An investigation of this nature is vital to understanding the underlying mechanism(s) responsible for the cyclic accumulation of residual strain typically observed during thermomechanical cycling of shape memory alloys.

The current study investigates the microstructural evolution in NiTi under thermal cycling conditions both with and without a biasing stress. A near-equiatomic NiTi alloy, which is fully martensitic at room temperature, was deformed by several variations of pure and load-biased thermal cycling in an effort to clarify and explain the observations made in previous works. The thermomechanical testing is combined with *in situ* TEM heating experiments to directly compare mechanical response and austenite defect substructure development. It is found that special grain boundaries (Σ boundaries) can be generated accompanying the B2 to B19' martensitic transformation during thermal cycling. The experimental results are analyzed using the crystallographic theory of martensite transformation. This investigation reveals for the first time a possible mechanism of austenite grain refinement through phase transformations in SMAs.

2. Materials and methods

2.1. Experimental

A 49.9Ni-50.1Ti (at.%) polycrystalline alloy, supplied by Special Metals, New Hartford, New York (now SAES Smart Materials), was obtained in the hot-rolled and hot-straightened condition as a 10mm diameter rod. This same heat of material has been extensively studied in the past [13-17]. In this investigation, cylindrical tensile specimens were CNC machined with a diameter of 3.85 mm and a gage length of 25.4 mm. Two no-load thermal cycles from 30°C to 200°C were first performed on all as-machined samples prior to any mechanical testing, as shown in the first row in Table 1. The purpose of this initial cycling was to relieve any internal stress caused by machining. Table 1 also lists

the subsequent thermomechanical treatments on all samples. Sample A had no additional thermomechanical treatment after this initial cycling and was used as the baseline condition. A constant uniaxial tensile stress of 150 MPa was applied during two additional thermal cycles on sample B, and 100 cycles on sample C with a temperature range of 30°C to 165°C. To compare the structural changes induced by the bias stress, sample D was given 100 no-load thermal cycles in the same temperature range. These samples were augmented with an additional sample tested isobarically for 20 cycles at 100 MPa. For all cycled specimens, the heating and cooling rates were 20 K/min. Strain during thermal cycling was measured with an extensometer, which was attached to the gage section of the sample by alumina extension rods with v-chisel tips. A type-K thermocouple was spot-welded to the gage section for temperature measurement during thermal cycling. Additional details describing the mechanical test setup and procedures can be found in [15].

Sample	Number of Cycles				
	A	B	C	D	E
Initial (no-load) thermal cycles (30-200° C)	2	2	2	2	2
No-load thermal cycles (30-165° C)	-	100	-	-	-
Load-biased thermal cycles (30-165° C) (150 MPa)	-	-	2	100	-
Load-biased thermal cycles (30-165° C) (100 MPa)	-	-	-	-	20

Table 1. Thermomechanical history for all samples.

TEM foils were prepared by focused ion beam (FIB) milling parallel to the loading direction in a FEI Helios NanoLab 600 dual-beam system with an Omniprobe in-situ manipulator. Microstructural investigation was done using scanning transmission electron microscopy (STEM) diffraction contrast imaging on an FEI Tecnai F20 200kV microscope. Bright field and dark field micrographs were captured using a probe convergence angle of 5.9 mrad. In situ heating experiments were performed using a Gatan in situ water-cooled resistive heating stage. All FIB foils were heated from room temperature until no remaining martensite was visible. The final temperature varied from 130-170°C. The samples were then held at high temperature for one to two hours for additional imaging before cooling back to ambient temperature. Subsequent orientation mapping based on automated selected-area diffraction was carried out using a

Nanomegas ASTAR system. The ASTAR experiments were performed at ambient temperature on austenite TEM foils that had not transformed back to martensite after STEM analysis. It is believed that the lack of a reverse transformation in this case is due to an effect of the thin foil geometry, as *in situ* neutron diffraction studies of this material in bulk form always showed complete (100%) reverse transformation of the alloy under similar conditions [13-15].

3. Results

3.1. Load-biased thermal cycling

Figure 1 shows the evolution of strain with pure thermal cycling and load-biased thermal cycling. For the sample with two pure thermal cycles in **Figure 1a**, both transformation and remnant strains were small. Even after 100 no-load cycles in **Figure 1c**, the residual strain was less than 0.25%. The load-biased specimens showed a dramatic strain accumulation upon cycling, to ~5.5% after two cycles (**Figure 1b**) and ~11% after 100 cycles (**Figure 1d**) (as measured in the martensite phase at room temperature), where both specimens had only a 0.34% elastic pre-strain due to the application of the biasing stress at room temperature prior to thermal cycling. Although an increase in residual strain with cycling is apparent in the strain-temperature curves for both load-biased and no-load cases, it is far more dramatic in the presence of an external load. It is important to note that the load in this case, 150 MPa, is still far below the bulk yield strength of both the austenite and martensite phases for this particular alloy [13,16,17]. In addition, the load-biased case demonstrates a decrease in transformation strain (decreased work output) at higher cycle counts, evidenced by a reduction in the height of the hysteresis loop, whereas the transformation strain of the no-load 100-cycle sample is fairly consistent cycle to cycle. A more detailed summary of the strain accumulation measured in the austenite and martensite phases, and the transformation strain as a function of cycle count for the 150 MPa load-biased condition, is shown in **Figure 2 a** and **b**, respectively.

Another major difference between load-free and load-biased samples is the change in M_s temperature with cycling. Comparing the transformation temperatures for the two 100-

cycle samples in **Figure 3**, it is clear that the M_s temperature *decreases* after pure thermal cycling and *increases* after load-biased thermal cycling. These results confirm the findings of Miyazaki et al. [7] and Grossmann et al. [12] with respect to changes in M_s for pure thermal and load-biased thermal cycling, as discussed in the introduction. In the presence of a biasing stress, certain martensite variants are more favored to form, leading to a highly aligned martensite microstructure after several cycles (**Figure 4d**). It is likely that the dislocation configurations accumulated during these initial load-biased cycles create an internal stress field that makes it easier for the favored martensite variants to reform. This is supported by the fact that M_s increases sharply for the first several cycles while the substructure is established. M_s decreases during pure thermal cycling, where the formation of self-accommodated martensite is constrained by the stress field of previously existing dislocations. The effect in this case is notably more gradual. Although the current experimental observations of microstructural evolution and transformation behavior are consistent with this explanation, the effect of the transformation-induced defect substructures on M_s is still under investigation.

All other transformation temperatures (M_f , A_s , A_f) decrease with cycling for both the load-free and load-biased conditions, after the initial transient response during the initial heating cycle. This transient response is shown in Figure 1 (c and d) as a “bump” in strain that occurs on the first heating cycle around 100°C. This common feature, only observed when thermal cycling is initiated in the martensite phase, corresponds to the martensite-to-austenite transformation in the first thermal cycle. This transient response is associated with the first transformation cycle of predominantly random variant or self-accommodated twinned martensite to austenite under load [15]. All succeeding thermal cycles occur between a predominantly single variant martensite (formed during cooling under load) and austenite, resulting in the large transformation strains observed in Figure 1 c and d.

3.2. STEM observations

Figure 4 shows STEM micrographs taken at 18°C of the four samples after thermomechanical cycling. After two pure thermal cycles (**4a**), the martensite structure is

randomly distributed with a large average plate size. Similarly, the 100-cycle no-load specimen (**4c**) exhibits a random plate distribution, but with a much finer average plate size. The random alignment in these cases indicates self-accommodation of the martensite, where multiple habit plane variants (HPVs) are induced to reduce elastic strain energy during transformation [18-20]. In situ observations of cooling through the transformation to martensite also demonstrate that the large, randomly oriented plates form rapidly in large bursts (see Video 1 in supplementary). This suggests that progression of the transformation is largely mediated by an autocatalytic effect [21].

The STEM results for the two-cycle load-biased case (**Figure 4b**) show that favored plate types are beginning to emerge in the martensite structure, as indicated by a preferred directionality of individual plates, but the average plate size remains similar to the two-cycle no-load case. Finally, in the load-biased 100-cycle sample (**Figure 4d**), the martensite plates show strong directionality and are primarily oriented approximately 45° from the tensile axis for this grain. This indicates that particular martensite plates are strongly favored by the externally applied stress, and upon repeated cycling they become permanent. Additionally, the average plate size is reduced and now of the same order as the 100-cycle no-load case. In situ cooling for this condition demonstrates a more heterogeneous nucleation and gradual or constrained growth of martensite (see Video 2 in supplementary). In this condition, the high internal strain of the material impedes the continued formation of martensite, resulting in the need to continually cool the sample in order to complete the transformation.

Figure 5 quantitatively describes the previously noted changes in martensite plate morphology. A number of plate dimensions were measured from images of each condition and then averaged. All measured TEM foils had the same orientation relative to the original tensile specimens. It should also be noted that the martensite plate measurements were taken only for plates that were readily distinguishable for the given foil orientation. The area fraction of visible plates varied for each condition, as can be observed in **Figure 4**. In both the 100-cycle no-load (NL) and load-biased (150 MPa) cases, the average martensite plate size decreases dramatically. Both average plate width

and plate length show this trend, however there is an increase in the average plate length and a large variation in this dimension for the 100-cycle load-biased case. This is consistent with the elongated nature of the plates observed for this condition, where a certain favored plate type grows at the expense of others after many cycles under a biasing stress (see **Figure 4d**). This trend is also reflected in the aspect ratio, which shows little difference for the other conditions but an increase for the 100-cycle load-biased sample (D). To further clarify the effect of many thermal cycles under load, **Figure 6** shows several individual martensite plate lengths as a function of the angle each plate makes with the loading direction. This plot clearly shows that the long, high aspect ratio plates are oriented approximately 45° from the loading direction for this particular grain, while the smaller plates have a more random orientation.

The same specimens shown in **Figure 4** were heated *in situ* above the A_f temperature where the material was qualitatively observed to be fully austenitic. **Figure 7** shows the austenite microstructure, at temperatures near 140°C , for the four test conditions. After two thermal cycles, a high density of dislocations is observed in both no-load and load-biased cases, distributed homogeneously throughout the specimens. After 100 cycles, the defect substructure becomes less homogeneous and pockets of high dislocation density develop. The “partitioning” effect is more pronounced in the load-biased case, but is clearly observed after pure thermal cycling as well. The microstructure in **Figure 7d** demonstrates these regions of high dislocation density adjacent to low-contrast regions that initially appear to be defect free. However, upon tilting the specimen, it is found that these “defect-free” regions themselves contain a high density of dislocations that are not initially visible due to the diffraction condition. This phenomenon is illustrated in **Figure 8**, which shows the change in defect contrast with two micrographs taken before and after 5° of sample tilt. The relatively small tilts required to bring these dislocations into contrast (and nearby dislocations out of contrast) suggest this is not due simply to the co-existence of multiple dislocation types, but instead is a result of changes in local crystal orientation.

3.3. ASTAR observations

To investigate the origin of the defect “partitioning” observed in STEM, orientation mapping based on automated selected-area diffraction (using the ASTAR system) was performed on foils with a retained austenite microstructure after previous heating *in situ* in the TEM. This method was chosen due to its high spatial resolution (5nm step size for FEG-TEMs) and its ability to map highly deformed material. **Figure 9** shows inverse pole figure (IPF) maps from specimens with two no-load thermal cycles, 20 cycles with 100 MPa tensile stress, and 100 cycles with 150MPa to demonstrate the evolution of the microstructure with cycling. After two thermal cycles, the orientation within the field of view (**Figure 9a**) remains homogeneous with minor deviations near the periphery. After 20 cycles with a 100 MPa bias stress (**Figure 9b**), the emergence of new regions of varied crystal orientation begin to emerge. These regions, which exhibit irregular, tortuous boundaries, are shown in contrast to a discrete, planar grain boundary in the same map (marked with the large arrow in **9b**) that is representative of the initial B2 grain boundary character. Note that the average initial austenite grain size is approximately 20 microns [16], fully consistent with this interpretation. This distinct difference in boundary morphology is additional evidence that the misoriented regions with tortuous boundaries are not part of the virgin austenite microstructure prior to thermomechanical testing. After 100 load-biased thermal cycles (**Figure 9c**), the IPF map indicates further refinement of the grain structure. At this stage, the average domain size suggests that there may be multiple orientations present through the thickness of the foil, resulting in increased noise and reduced indexing confidence. Despite this, the observed domain size correlates well with features present in STEM (**Figure 7d**). Point-to-origin misorientation profiles are plotted for two regions of the 20-cycle specimen (**Figure 9e** and **f**). For each pixel along the profile's length (x), a misorientation relative to the first point (origin) is plotted. These plots confirm that the newly-formed grain boundaries are for the most part, sharp, high-angle boundaries. The tortuous nature of these boundaries observed after cycling is inconsistent with traditional recrystallization processes and suggest a different mechanism of grain refinement is responsible. Additionally, many of the observed boundaries were found to be “special” boundaries, where a well-defined disorientation (sigma value) is found based on coincident site lattice (CSL) theory. Table 2 highlights several specific boundaries observed in the same specimen from Figure 9b

(sample E). Other higher order sigma boundaries were also observed but are not listed here.

Sigma	Angle	Axis
3	60°	[17 18 14]
5	34.1°	[-1 30 -2]
9	40.3°	[20 0 -21]
9	40.6°	[1 0 -1]
9	39.7°	[21 1 -20]
15	46.8°	[-6 -13 0]

Table 2. Experimentally observed special boundaries in sample E.

4. Discussion

4.1. Comparison between STEM and ASTAR results

The defect structures observed in STEM demonstrate that even after modest thermomechanical cycling, a significant density of dislocations is accumulated. The large number of dislocations present precludes an accurate determination of a quantitative trend in dislocation density with thermal cycling. Nevertheless, qualitative observations suggest an increase in density with cycling, which agrees with the cyclic increase in irrecoverable strain shown in **Figure 1**. However, the total strain versus cycles plots (**Figure 2a**) suggest a reduced rate of defect accumulation with increased cycling. This plot indicates that residual strain per cycle, while significantly reduced after many cycles, has not saturated but instead has reached a pseudo-steady state where the residual strain level is constant (or nearly so) with each successive cycle. This behavior has been observed for a range of shape memory alloy systems, particularly when cycled at lower stresses [12, 22]. Benafan et al. [15] attributed this pseudo-steady state behavior to a dynamic equilibrium where dislocation generation and annihilation occur equally in each cycle, consistent with the generation of a nearly constant amount of residual strain per cycle [22].

In addition to the rapid accumulation of dislocations observed in STEM, a change in the morphology of this substructure is also apparent. The domain size of uniform defect contrast in bright field STEM is shown in **Figure 7** to decrease after many transformation

cycles in the load-free condition, and to an even greater extent in the load-biased condition. ASTAR orientation mapping suggests the “partitioning” of defects is due to a dramatic evolution in the austenite grain structure with thermomechanical cycling. The regions where dislocations are visible in STEM for a given sample tilt likely correspond to regions of uniform crystal orientation that are oriented favorably for diffraction contrast of defect content. This is evidenced by the correlation between domains observed in STEM and the sub-grain size measured from ASTAR. It should be noted, however, that the degree to which this phenomenon occurs varies on a grain-by-grain basis. This is likely due to the variation in stress state for individual grains.

4.2. Comparison with previous diffraction work

A number of diffraction studies have been carried out to quantitatively probe the microstructural evolution of NiTi during transformation cycling [14,15,17,23-29]. In particular, recent studies in the load-biased thermal cycling test mode provide important details for interpreting the current experimental results. Jones et al. [23] performed in situ synchrotron x-ray diffraction on a 49.8 at.% NiTi alloy thermally cycled under a range of different biasing stresses. It was shown that martensite texture evolves with cycling under load, indicating a preferred martensite variant selection to maximize transformation strain. This effect is magnified for greater applied stress and is progressive with the first few thermal cycles. Similar results were shown by Benafan et al. [15], who performed in situ neutron diffraction on this 49.9 at.% NiTi alloy. Results from both studies agree well with the current observations of variant selection for different thermomechanical histories, as shown in **Figure 4**.

Both diffraction studies referenced above noted little change in B2 texture with cycling despite the development of large residual strains. The x-ray data from Jones et al. [23] shows significant changes in relative peak intensities with cycling, however no preferred orientation emerges. Benafan et al. [15] attribute the lack of texture development to the dominance of $\langle 100 \rangle$ deformation, which can result in macroscopic strain without a change in texture [30]. An additional trend observed in both studies is a pronounced $\{110\}_{B2}$ peak broadening. The peak width is observed to increase with cycling until the

material has reached the pseudo-steady state discussed in the previous section. Diffraction peak width is directly influenced by the presence of defect content (dislocations) as well as crystallite size; however, Jones et al. [23] rule out grain refinement by estimating that for the observed increase in the full width half maximum (FWHM) of the $\{110\}_{B2}$ peak, a sub-micron grain size is necessary. In that study, light optical micrographs taken after etching continue to show grains on the order of 10 μm in diameter. However, the current ASTAR orientation data suggests that sub-micron grains can form during thermal cycling. It is also clear from **Figure 9b** that the original B2 grain boundaries from the coarse-grained microstructure persist after cycling, which could lead to an inaccurate grain size interpretation based on low magnification surface studies. Additionally, it should be noted that in the current study, dislocation generation is pronounced in addition to the observed grain refinement, so peak width determination based on only one of these mechanisms will likely be incorrect.

4.3. Proposed mechanism of austenite grain refinement

The above experimental observations have unambiguously shown that austenite grain refinement and generation of special grain boundaries (i.e., the Σ boundaries) is possible as a result of thermomechanical cycling of NiTi. The existence of special grain boundaries (Σ boundaries) revealed by the ASTAR suggest that symmetry breaking accompanying the martensitic transformation must have played a role in the grain refinement process. Below we show that even though the B2 to B19' transformation is fully reversible [31], there could exist a special symmetry-dictated *non-transformation* pathway (SDNTP) that generates special grain boundaries in B2 during the B2-B19'-B2 transformations induced by load-biased thermal cycling. This deformation pathway is distinctly different from the conventional plastic yielding observed during cycling.

To illustrate the existence of the SDNTP in NiTi and reveal its crystallographic origin, we first examine the crystal structure of the B19' martensite. This structure is geometrically similar to a base-centered orthorhombic (BCO) structure and has also been shown to be energetically similar by *ab initio* calculations [32]. Note that the symmetry relationship between B2 and B19' and that between B2 and BCO are fundamentally

different. There is a group-subgroup relationship in the former, but not in the latter [32, 33]. If a pathway from B2 to BCO is considered, which includes two steps, from B2 to B19' and then from B19' to BCO, the crystal symmetry first decreases from B2 to B19' and then increases from B19' to BCO.

As shown in **Figure 10a**, if the {011} cross-section of a B2 structure is considered, a simple rectangle structure in 2D can be found (**Figure 10b** where atoms of only one sublattice are shown for simplicity). The BCO structure, which can be taken as a centered rectangle structure in 2D, is formed through a shear along the [100] direction of the B2. A schematic drawing of the energy landscape connecting all the structural states is also shown in **Figure 10b**. Because the martensitic transformation is first-order, both B2 and B19' states are local minima on the energy landscape. The BCO state has a relatively high symmetry within its vicinity, so it has to be a stationary point (e.g., local minimum, local maximum, or saddle point) on the energy landscape, and there are two degenerate B19' states near the BCO state. Since we want to show the possible SDNTP between two B19' states, the BCO is taken as a local maximum in **Figure 10b** for simplicity without loss of generality.

During thermal cycling, the transformation pathway (TP) between B2 and B19' is activated by the driving force for the transformation (i.e. undercooling). During this process, the SDNTP between two B19' states could also be activated by internal and external stresses, especially when an external load is applied. To connect the SDNTP to the austenite grain refinement observed in our experiment, we analyze the possible defect structures generated along this pathway using the framework of phenomenological theory of martensitic crystallography (PTMC) [31,35-37] and compare them with the experimental observations. Note that PTMC was developed for analyzing the transformation pathways and domain structures of martensite. Now we show that a similar mathematical approach can be applied to analyze the SDNTPs and other defect structures as well. As shown in **Figure 10b**, the deformation pathway between the two B2 structural states (initial and new) includes three segments: two TPs between B2 and B19' and one SDNTP between two B19' structural states. The deformation gradient

matrix can be found by choosing two sets of corresponding lattice vectors in the two B2 structural states. For simplicity, the initial B2 state is chosen as the reference and the deformation gradient of the new B2 state can be expressed as,

$$\mathbf{T} = \begin{bmatrix} 1 & 0.5 & 0.5 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Assuming a boundary is formed between two neighboring B2 domains, one being the initial B2 state and the other being the new B2 state, the defect structure formed at the boundary can be determined by applying an invariant plane strain condition (or geometrical compatibility condition) [31,35-37],

$$\mathbf{Q}\mathbf{T} - \mathbf{I} = \mathbf{a} \otimes \mathbf{n} \quad (1)$$

Where $\mathbf{Q}$ is a rigid body rotation, and $\mathbf{a}$ and $\mathbf{n}$ are the shear vector and boundary plane normal, respectively. Two solutions exist for the above equation, each corresponding to a unique defect structure:

$$\left\{ \begin{array}{l} \mathbf{a}_1 = \frac{1}{2} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \\ \mathbf{n}_1 = \begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix} \end{array} \right. \text{ and } \left\{ \begin{array}{l} \mathbf{a}_2 = \frac{1}{18} \begin{pmatrix} -1 \\ 2 \\ 2 \end{pmatrix} \\ \mathbf{n}_2 = \begin{pmatrix} 4 \\ 1 \\ 1 \end{pmatrix} \end{array} \right.$$

The first solution describes a $[100](011)$ dislocation, which is the typical type of dislocation observed in B2 NiTi. The second solution suggests a relatively high index boundary plane (411) . By calculating the rotation $\mathbf{Q}$ corresponding to the second solution, it is found that $\mathbf{Q}$ is a 38.94° rotation around $[0\bar{1}1]$, which are the characteristic rotation axis and angle for a $\Sigma 9$ boundary in BCC structures.

The above calculations are for defect structures between two B2 states connected by the TPs and SDNTP shown in **Figure 10b**. However, during multiple thermal cycles, more and more defect types will be generated. A convenient way to analyze defect structures generated by multiple transformation cycles is to construct a pathway network as shown in **Figure 11**. After one transformation cycle, defects can be generated at the boundaries between a given B2 state (e.g., the one in the middle in **Figure 11**) and its two first-nearest neighbors (to the left and right in **Figure 11**), and at the boundaries between the two neighbors themselves (which are second-nearest neighbors). After two cycles, defects can be generated at boundaries between different B2 states that are first-, second-, third-, and fourth-nearest neighbors. In general, after N cycles, defects can be generated at the boundaries between different B2 states up to its $2N^{\text{th}}$ -nearest neighbors. As a result, it is found that $\Sigma 3$, $\Sigma 5$, $\Sigma 7$, $\Sigma 9$ and $\Sigma 13$ boundaries can be generated after one cycle, which can be determined directly from **Equation 1**. Higher order special grain boundaries such as $\Sigma 11$, $\Sigma 15$, $\Sigma 17$, ..., $\Sigma 37$, $\Sigma 39$,... can be generated after two cycles. As the number of cycles increases, the Σ value of grain boundaries that can be generated increases as well.

It is clear from this geometrical analysis that it is indeed possible for new grain boundaries to be introduced in the austenite upon load-biased thermal cycling in NiTi. Although the ASTAR measurements presently conducted are limited in terms of microstructure area sampled, there is indeed a significant occurrence of low Σ boundaries, as indicated in Figure 9 and Table 2. Grain refinement has also been observed in our experiments under stress-free thermal cycling. In this case, local stresses induced by the martensitic transformation (and the resulting B2 dislocation content) after multiple cycles could activate the SDNTP and thus create unique sub-grain orientations.

5. Conclusions

A bulk 49.9 at.% NiTi alloy was thermally cycled under stress-free and load-biased conditions and the evolution of the microstructure was probed via STEM diffraction

contrast imaging and TEM-based orientation mapping. The conclusions from this work are:

- a) Preferred martensite variant selection is observed during load-biased thermal cycling, where a martensite texture develops relative to the loading direction. This effect becomes more pronounced with greater cycles.
- b) Martensite formation becomes restricted after many cycles due to the accumulation of dislocation content. This leads to a more gradual transformation with a smaller average martensite plate size.
- c) A high density of austenite dislocations is observed even after a few cycles. The dislocation content continues to increase with additional cycles and a partitioning of defect content is noted in STEM. This apparent partitioning is found to be the result of local crystal rotation.
- d) ASTAR orientation maps demonstrate the development of sub-micron crystal domains within the original B2 microstructure. These are typically high angle boundaries with an irregular morphology. This grain refinement may contribute to the $\{110\}_{B2}$ peak broadening observed in many diffraction studies.
- e) Calculations based on crystallographic theory are used to propose a new mechanism of transformation-induced austenite grain refinement by means of a special symmetry-dictated, non-transformation pathway. The results of these calculations are supported by the grain boundary characters determined from current experiments, which often have low sigma values that are theoretically predicted.

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Figure 1: Strain vs. temperature curves for (a) two no-load thermal cycles; (b) 100 no-load thermal cycles; (c) two load-biased thermal cycles at 150 MPa; (d) 100 load-biased thermal cycles at 150 MPa. Note the differences in strain scales between the no-load and load-biased thermal cycle results.

Figure 2: (a) Total strain vs. cycles for austenite (red) and martensite (blue) phases, and (b) transformation strain vs. cycles for 150MPa load-biased condition.

Figure 3: Transformation temperatures vs. cycles for no load (left) and 150 MPa load-biased (right) conditions.

Figure 4: Bright field STEM micrographs taken at 18°C of the martensite microstructure of samples A, B, C, and D. Foils obtained in the longitudinal orientation relative to the applied stress direction (which is vertical in all cases).

Figure 5: Plots of average martensite plate dimensions and aspect ratio for the four specimens shown in Figure 4. Error bars show the mean standard deviation.

Figure 6: Plot showing martensite plate length as a function of angle relative to the loading direction for the specimen shown in Figure 4d.

Figure 7: Bright field STEM micrographs taken at 140°C of the austenite microstructure of samples A, B, C, and D. Foils obtained in the longitudinal orientation relative to the applied stress direction (which is vertical in all cases).

Figure 8: BF STEM micrographs taken 5° tilt apart illustrating the rapid contrast change observed for the defect structures. Arrows point to specific regions within the grain for comparison.

Figure 9: ASTAR inverse pole figure maps of samples (a) A, (b) D, and (c) E. (d) IPF triangle. (e) and (f) are point-to-origin misorientation profiles for the two lines shown in (b) ((e) corresponds to line 1 and (f) to line 2).

Figure 10: (a) crystal structure of B2 with $\{011\}$ plane indicated; (b) the $\{011\}$ cross-section of B2 and BCO structures and a schematic illustration of the energy landscape connecting all states.

Figure 11: Schematic illustration of first nearest-neighboring B2 states and second nearest-neighboring B2 states.

2nd nearest neighbor (NN)

1st nearest neighbor (NN)