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## Low temperature deformation of the R-phase in a NiTiFe shape memory alloy

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Deformation in the  $P3$  phase (R-phase) of NiTiFe was investigated by *in situ* neutron diffraction during compressive loading at cryogenic temperatures. At 216 K, upon loading the R-phase detwinned and subsequently underwent a reversible stress-induced transformation to the  $B19'$  phase (martensite). At 92 K on the other hand, detwinning was suppressed and the stress-induced martensite formed did not transform back upon unloading. The experiments also directly observed a hitherto theoretically predicted  $B33$  phase. Rietveld refinement of the neutron diffraction spectra were used to determine lattice parameters of the  $B33$  and R-phases. Plane-specific elastic moduli were also determined for the R-phase. © 2010 American Institute of Physics.

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NiTiFe shape memory alloys are known to exhibit temperature and/or stress-induced phase transformations between cubic  $B2$ , trigonal  $P3$ , and monoclinic  $B19'$  phases (commonly designated as austenite, R-phase, and martensite, respectively). The R-phase and martensite have the ability to detwin and convert between their respective variants when deformed (phenomena commonly referred to as detwinning).<sup>1,2</sup> For example, cooling a NiTiFe alloy that is austenitic at room temperature can result in a phase transformation to the R-phase which can subsequently be deformed to detwin and/or form stress-induced martensite. The reverse transformation from detwinned R-phase can occur against external loads below room temperature making these alloys useful as actuators, e.g., in low temperature thermal switches. The R-phase transformation in NiTiFe is of particular interest owing to its stability and reduced hysteresis.<sup>3,4</sup> Macroscopic measurements cannot differentiate between elastic and inelastic strains associated with detwinning or stress-induced transformation. Therefore, knowledge on deformation in the R-phase is currently limited especially with respect to its elastic behavior and the competition between detwinning and the formation of stress-induced martensite. Furthermore, the reversibility of the R-phase transformation to martensite and the formation of any additional stress-induced phases have not been investigated.

With the objective of providing insight into the aforementioned issues, *in situ* neutron diffraction during cooling and mechanical loading was performed on a NiTiFe sample at the spallation neutron source at Los Alamos National Laboratory. This technique has previously provided valuable insight into the strain, texture, and phase fraction evolution in bulk shape memory alloy specimens (e.g., Refs. 5–7). However, the capability to perform *in situ* neutron diffraction during loading and cooling has only recently been implemented.<sup>8</sup> Here it was used to make *in situ* neutron diffraction experiments on a  $\text{Ni}_{46.8}\text{Ti}_{50}\text{Fe}_{3.2}$  alloy at a minimum temperature of 92 K and a maximum compressive stress of 700 MPa.

Cylindrical compression samples (10 mm in diameter and 24 mm length) were fabricated by electrical discharge machining from a vacuum-induction-melted and vacuum-arc-remelted billet. The samples were solutionized at 1023 K for 1 h in a vacuum furnace and subsequently oil quenched to room temperature. The R-phase start, R-phase finish, austenite start, and austenite finish, were determined by differential scanning calorimetry to be 236 K, 223 K, 227 K, and  $239 \pm 2$  K, respectively. The martensite start temperature was undetectable while cooling the sample to 20 K. Measurements were performed in “time-of-flight” mode using the capability for neutron diffraction during cooling and mechanical loading on the Spectrometer for Materials Research at Temperature and Stress (Ref. 9) at Los Alamos National Laboratory. Measurements were made on two samples. One sample was cooled to 216 K and mechanically loaded and unloaded to a maximum stress of 700 MPa while neutron spectra were recorded at selected stresses. A second identical sample was cooled to 92 K and mechanically loaded and unloaded to a maximum stress of 420 MPa while neutron spectra were again acquired at selected stresses.

Upon cooling from room temperature both samples underwent a phase transformation from austenite to R-phase. Figure 1 shows a section of neutron spectra obtained from the samples at 300, 216, and 92 K in the nominally unloaded condition (holding stress of 8 MPa). At 300 K, the  $\{110\}$  austenitic peak is seen which subsequently split with cooling to  $\{300\}$  and  $\{112\}$  R-phase peaks as a result of elongation along the  $\langle 111 \rangle$  crystallographic direction of the  $B2$  phase.<sup>10</sup> The splitting increased with cooling due to a change in the trigonal angle of the R-phase unit cell.<sup>11</sup> Similarly, splitting of the austenite  $\{210\}$  peak to R-phase  $\{303\}$  and  $\{411\}$  peaks were observed. The peaks were identified based on  $a = 3.0112 \pm 0.0002$  Å for the cubic austenite phase at 300 K and  $a = b = 7.3004$  c = 5.2878 ( $\pm 0.0002$  Å) for the trigonal R-phase at 92 K in the unloaded condition (as determined by Rietveld refinement of neutron spectra<sup>12</sup>).

Compressive loading of the R-phase at 216 and 92 K produced different results. On examining a section of neutron spectra corresponding to  $\{111\}$  R-phase and  $\{011\}$  mar-

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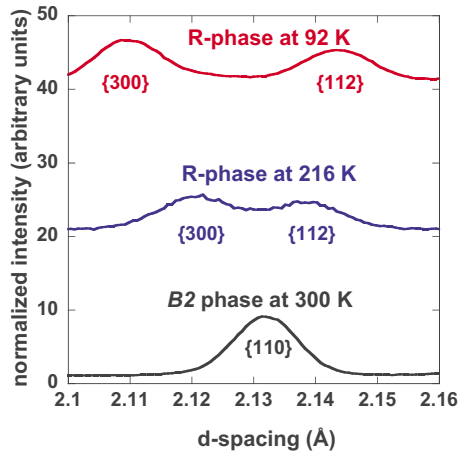


FIG. 1. (Color online) Section of normalized neutron diffraction spectra acquired at 300 K, 216 K, and 92 K, respectively, showing phase transformation from cubic austenite (*B2*) to trigonal R-phase in NiTiFe. The reflections are from lattice planes perpendicular to the length of the sample.

tensite peaks acquired during loading and unloading up to 700 MPa at 216 K in Fig. 2(a), a stress-induced R-phase to martensite phase transformation was observed during loading as the  $\{111\}$  R-phase peak decreased in intensity and the

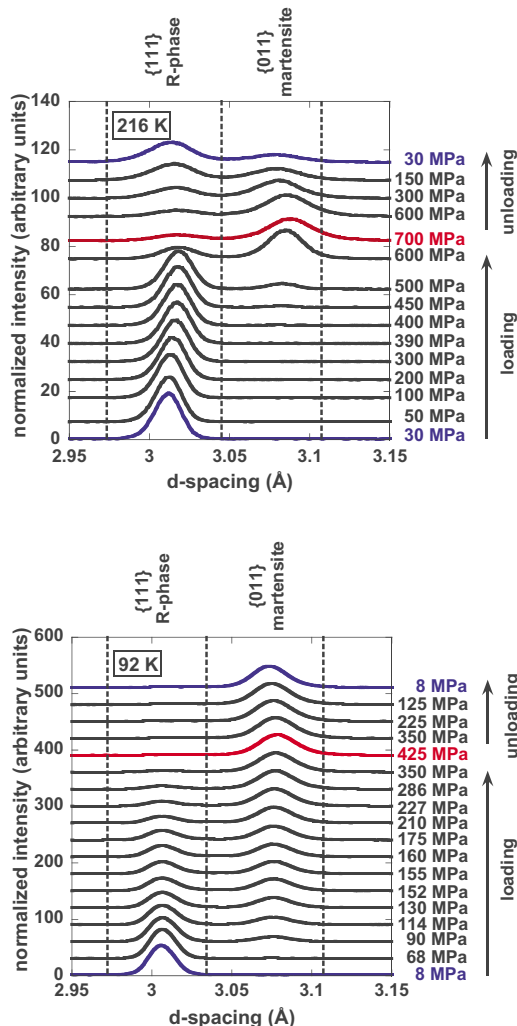


FIG. 2. (Color online) Section of normalized neutron diffraction spectra acquired during loading and unloading at (a) 216 and (b) 92 K in NiTiFe. At 216 K the R-phase reversed from martensite upon unloading but not at 92 K. The reflections are from lattice planes perpendicular to the length of the sample.

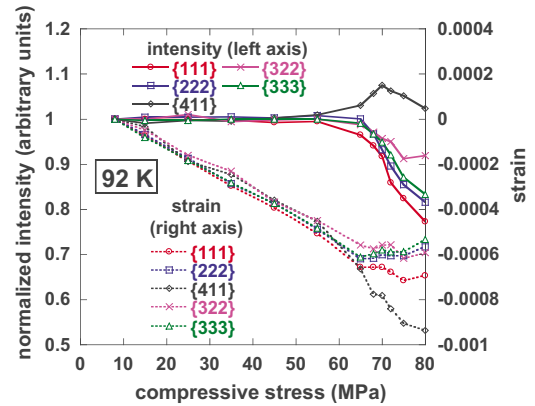
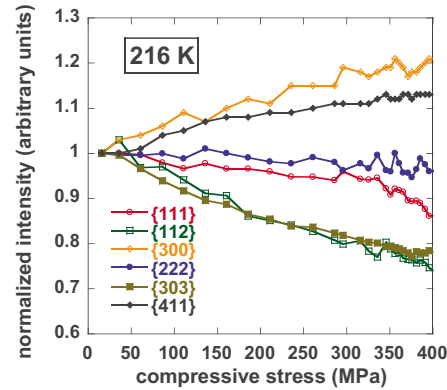


FIG. 3. (Color online) The solid lines are the normalized R-phase peak intensity ratios (relative to the unloaded state) with loading at (a) 216 and (b) 92 K. The dashed lines in (b) are the strains determined from changes in d-spacing of various R-phase reflections at 92 K. The reflections in (a) are from lattice planes parallel and in (b) perpendicular to the length of the sample and are, respectively, selected for clarity and in order to determine plane-specific moduli.

$\{011\}$  martensite peak increased in intensity. Upon unloading, the martensite reverted to the R-phase as seen in the reverse trend in the  $\{111\}$  R-phase and  $\{011\}$  martensite peaks. In contrast, for the sample cooled to 92 K, the stress-induced martensite formed from R-phase upon loading remained in the nominally unloaded condition [Fig. 2(b)]. This difference in behavior between testing at 216 and 92 K is attributed to the thermodynamic hysteresis typically associated with martensitic transformations wherein the reverse transformation to R-phase from martensite occurs at higher temperatures (higher than 92 K in this case).<sup>13</sup> Furthermore, as expected thermodynamically, martensite is favored at lower temperatures resulting in stress-induced martensite forming at around 65 MPa at 92 K and at around 450 MPa at 216 K.

The solid lines in Figs. 3(a) and 3(b) are presented to investigate detwinning in the R-phase and correspond to the ratio of normalized intensities of individual R-phase diffraction peaks with respect to the unloaded state. The information is presented for peaks selected for the statistical quality of their fits as previously established during the analysis of neutron diffraction spectra acquired *in situ* during loading in NiTi.<sup>12</sup> The observation that certain reflections increase in normalized intensity with loading and certain reflections decrease in normalized intensity with loading up to 400 MPa at 216 K [Fig. 3(a)] is indicative of texture evolution associated with detwinning in the R-phase at 216 K. In contrast, Fig. 3(b) which represents deformation in the R-phase at 92 K does not show this trend and the intensities remained around

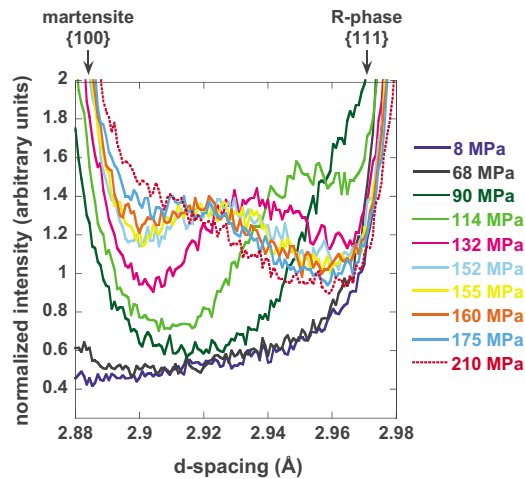


FIG. 4. (Color online) Section of normalized neutron diffraction spectra acquired at 92 K during loading, showing stress-induced phase transformation from R-phase to  $B19'$  martensite. The  $\{012\}$  peak of an hitherto theoretically predicted  $B33$  martensite is observed.

the normalized value of unity until about 65 MPa. At stresses higher than 65 MPa, the R-phase underwent a stress-induced transformation to martensite, and hence a decrease in the normalized intensities of the various reflections was observed. Thus at 216 K and at stresses below 500 MPa, the free energy of the R-phase is lower than that of the monoclinic phase and hence detwinning is favored as the deformation mode to accommodate stress. However, at stresses above 500 MPa the system lowers its energy by undergoing a stress-induced transformation to martensite, which reverts to the R-phase upon unloading [Fig. 2(a)]. At 92 K on the other hand, detwinning is suppressed and a direct stress-induced transformation to martensite is observed that does not revert due to the thermal hysteresis associated with martensitic transformations. The fact that detwinning is limited at stresses lower than 65 MPa at 92 K enabled the comparison of the macroscopic modulus determined from extensometry with the plane-specific elastic moduli determined from changes in d-spacing (relative to a stress free d-spacing) with stress.<sup>12</sup> The dashed lines in Fig. 3(b) represent these strains with increasing stress for various R-phase planes. The modulus from extensometry was determined to be 90.9 GPa and compared well with the values of 95.6 GPa, 113.8 GPa, and 105.2 GPa for the  $\{111\}$ ,  $\{322\}$ , and  $\{411\}$  planes, respectively. At stresses above 65 MPa, the onset of stress-induced transformation results in redistribution of strain among various grains resulting in a nonlinear and anisotropic response.<sup>7,12</sup>

Figure 4 shows a section of neutron spectra recorded from the sample at 92 K as it is loaded from the nominally unloaded condition (8 MPa) to 210 MPa. The spectra have been normalized and are overlaid. The maximum value of the  $x$ -axis corresponds to that of the d-spacing of the  $\{111\}$  R-phase peak on the right and the minimum value to that of the  $\{100\}$  martensite peak on the left. As the sample is loaded a peak appears in the middle and shifts with stress. The shift if hypothetically attributed to elastic straining due to applied stress results in an unrealistic modulus of 6.3 GPa. The position of this reflection is consistent with that of the  $\{012\}$  reflection in a base-centered orthorhombic  $B33$  NiTi structure (space group  $Cmcm$ ) predicted from density functional theory calculations.<sup>14</sup> This structure does not possess a

unique crystallographic relationship with the parent phase and is expected to only exist in the absence of shear and hydrostatic stresses (applied or residual). The experimentally observed shifting is thus attributed to a change in the monoclinic angle to  $\gamma \approx 98^\circ$  as the symmetry changes from  $B33$  to that of  $B19'$  with stress. Rietveld refinement of the acquired spectra resulted in the following lattice parameters for the  $B33$  phase:  $a=2.911$ ,  $b=9.393$ ,  $c=3.806$ , and ( $\pm 0.001$  Å)  $\alpha=\beta=\gamma=90^\circ$  which compared well with the aforementioned theoretical predictions.

In summary, by recourse to capability of neutron diffraction during loading at cryogenic temperatures at a spallation neutron source insight is provided into deformation in the trigonal R-phase in bulk shape memory NiTiFe. At 216 K, there is direct evidence of detwinning in the R-phase followed by a reversible stress-induced martensitic transformation as the R-phase transforms to martensite and transforms back upon unloading. At 92 K, however, detwinning is suppressed and the stress-induced martensite formed does not revert to the R-phase due to hysteresis in the transformation. The elastic modulus of the R-phase from atomic measurements was consistent with that from extensometry. A nascent peak was observed during loading of the R-phase at 92 K that shifted with loading and was attributed to that of the  $B33$  martensite, a phase that hitherto has only been predicted in theory. These findings have practical implications for using the R-phase in cryogenic actuator applications, wherein a limiting temperature exists below which detwinning is suppressed in the R-phase (as was seen here at 92 K), thereby not providing recoverable strains necessary for the alloy to exhibit shape memory behavior.

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