Thermomechanical behavior and microstructural evolution of a Ni-rich Ni_{24.3}Ti_{49.7}Pd₂₆ high temperature shape memory alloy

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Abstract – The effect of thermomechanical cycling on a slightly Ni-rich Ni_{24.3}Ti_{49.7}Pd₂₆ (near stoichiometric Ni-Ti basis with Pd replacing Ni) high temperature shape memory alloy was investigated. Aged tensile specimens (400 °C/24 hr/furnace cooled) were subjected to load-biased thermal cycling in conjunction with microstructural assessment via *in situ* neutron diffraction and transmission electron microscopy (TEM), before and after testing. It was shown that in spite of the slightly Ni-rich composition and heat treatment used to precipitation harden the alloy, the material exhibited dimensional instabilities with residual strain accumulation reaching 1.5% over 10 thermomechanical cycles. This was attributed to insufficient strengthening of the material (insufficient volume fraction of precipitate phase) to prevent plasticity from occurring concomitant with the martensitic transformation. *In situ* neutron diffraction revealed the presence of retained martensite while cycling under 300 MPa stress, which was also confirmed by transmission electron microscopy of post-cycled samples. Neutron diffraction analysis of the post-thermally-cycled samples under no-load revealed residual lattice strains in the martensite and austenite phases, remnant texture in the martensite phase, and peak broadening of the austenite phase. Texture developed in the martensite phase was composed

mainly of those martensitic tensile variants observed during thermomechanical cycling. Presence of a high density of dislocations, deformation twins, and retained martensite was revealed in the austenite state via in-situ TEM in the post-cycled material, providing an explanation for the observed peak broadening in the neutron diffraction spectra. Despite the dimensional instabilities, this alloy exhibited a biased transformation strain on the order of 3% and a two-way shape memory effect (TWSME) strain of ~2%, at relatively high actuation temperatures.

Keywords: High temperature shape memory alloy; Neutron diffraction; NiTiPd; Actuation; Two-way shape memory effect.

1. Introduction

Development of high temperature shape memory alloys (HTSMAs), materials with properties similar to NiTi but with transformation temperatures above 100 °C, will enable entirely new applications where such functional materials can be exploited. The great potential for shape memory alloys arises from the distinctive behaviors associated with the shape memory effect and superelasticity leading to multifunctional capabilities such as solid-state actuation [1], sensing [2], damping [3], and impact resistant mechanical components [4] amongst others. Alloys exhibiting martensitic transformations at temperatures above 100 °C and thus having potential as HTSMAs can be found in a variety of alloy systems spanning NiAl-based [5], Ti-based [6, 7], Cu-based [8], Zr-based [9], Ta-based [10], Co-based [11], Mn-based [12] and most commonly to NiTi-based alloys. A review of these and other possible HTSMAs can be found elsewhere [13-15]. HTSMAs are primarily sought for use as compact, high temperature actuators typically targeted for the automotive, aerospace, and oil exploration industries. NiTi-based alloys, in particular, have been shown to be applicable to these industries and have been consistently pursued for further development and maturation.

NiTi-based HTSMAs consist of alloying binary NiTi with one or more elements such as Pd [16, 17], Pt [18, 19], Au [20, 21], Hf [22-24], Zr [25, 26], Pd-Sc [27] and Pd-Cu [28]. Each of these alloy systems comes with certain advantages along with shortcomings. NiTiPd alloys are one of the more promising systems with processability similar to binary NiTi alloys and good work output at elevated temperatures. For compositions containing greater than about 10 at.% Pd, NiTiPd alloys (where Pd substitutes for Ni) exhibit a martensitic phase transformation between a high symmetry parent austenite phase (cubic B2) and a lower symmetry martensite phase (orthorhombic B19). The shape memory effect [16, 29-33], superelasticity [34], two-way

shape memory effect (TWSME) [27, 35], and combined creep and actuation behavior [36, 37] have been examined for alloys containing between 20–30 at.% Pd in just the last few years. Overall, these studies have indicated that the accumulation of residual strain is an issue during thermomechanical cycling of NiTiPd alloys. Consequently, precipitation strengthening [38-40], quaternary alloying [17, 27, 28, 41-43], and grain size refinements [31, 44] have been investigated in order to improve the alloys' response. Modeling of NiTiPd has also been attempted to understand various fundamental properties using atomistic [45-47], semi-empirical [48] and constitutive [49] approaches.

Even though a wide range of NiTiPd alloys have been developed and studied over the years, they have not been fully exploited in engineering applications, but they have been considered for a few aerospace-related components [50-54]. Besides the high cost of Pd, the unsuccessful commercialization of this system is largely due to unresolved issues with dimensional/thermal stability, and lack of data concerning fatigue and durability, which are of prime importance to actuator applications at elevated temperatures (above 100 °C). Most NiTiPd alloys studied to date were near stoichiometric or Ni(Pd)-lean in composition (containing 50 at.% or less Ni+Pd), which like most Ni-lean NiTi-based shape memory alloys tend to exhibit unstable thermal response (i.e., shifts in transformation temperatures) and poor dimensional stability (i.e., accumulation of residual strains) when cycled under load.

Compared to their Ti-rich counterparts, Ni-rich NiTiPd has potential to exhibit superior thermomechanical response, though the volume fraction of precipitate phase has still to be optimized [39] through compositional and aging control [55, 56]. Stoichiometric and Ti-rich compositions also exhibit much larger transformation strains [39]. However, design of Ni-rich NiTi-based alloys typically requires precise composition, ageing, and processing control to yield

the desired properties. Furthermore, the size, coherency, and distribution of precipitates within the matrix dictate the internal stress, which in turn affects the alloy's performance.

Thus in order to develop a family of precipitation strengthened NiTiPd alloys, it is useful to examine the microstructural and micromechanical features of Ni(Pd)-rich alloys under applied stresses and temperatures. This can be accomplished using advanced tools such as *in situ* neutron diffraction, which provides microstructural details related to changes in lattice strains, textures and phase fractions, while simultaneously performing thermomechanical cycles on the material. *In situ* neutron diffraction provides the advantage of an unmatched high penetration of neutrons to examine the bulk behavior of the material in a nondestructive setting. Coupled with electron microscopy, the information can be used to analyze structure-property relationships leading to better optimized compositions and aging treatments for specific applications that may require high actuation strains, improved stability, extended durability, high TWSME, or a combination thereof.

In the present work, combined mechanical and microstructural experiments were carried out to investigate the thermomechanical behavior of a slightly Ni-rich $\text{Ni}_{24.3}\text{Ti}_{49.7}\text{Pd}_{26}$ alloy (near stoichiometric Ni-Ti basis with Pd replacing Ni). Initial microstructure and phase information were determined and related to the macroscopic stress-strain-temperature response. The role of deformation during initial cycling on post cycling behaviors (i.e., development of TWSME) was also examined in context of the microscopic mechanisms observed through neutron diffraction and TEM analysis.

2. Material and methods

2.1. *Material*

An ingot of nominal composition $\text{Ni}_{24.3}\text{Ti}_{49.7}\text{Pd}_{26}$ (at.%) and weighing ~500 g was prepared by vacuum induction melting of high purity elements (99.98 Ni, 99.995 Pd, 99.95 Ti) in a graphite crucible under a protective argon atmosphere. The melt was cast into a cylindrical copper mold (25.4 mm diameter $\times$ 102 mm long) with a built-in conical hot-top to accommodate shrinkage during solidification. The resulting ingot was vacuum homogenized for 72 hours at 1050°C and furnace cooled. The ingot was subsequently sealed in a mild steel can (after removing the hot top) and extruded at 900 °C through an area reduction ratio of 7:1. Test specimens were machined from the extruded rod (Ext. 159) with the tensile axis parallel to the extrusion direction and subjected to an aging treatment of 24 h at 400 °C followed by furnace cooling. This will be referred to as the “aged” condition in subsequent sections.

2.2. *Microstructural characterization*

The microstructure of the extruded $\text{Ni}_{24.3}\text{Ti}_{49.7}\text{Pd}_{26}$ alloy was examined in the aged and post-thermomechanically cycled conditions using optical microscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM) techniques. Samples for optical and SEM were mounted, polished, and etched lightly using a solution of 85% H_2O , 12% HNO_3 and 3% HF (by volume) to reveal grain size. SEM samples were examined in a Hitachi 4700 microscope equipped with an IXRF energy-dispersive x-ray spectroscopy (EDS) detector for composition analysis. Samples for TEM were first electro-discharge machined (EDMed) into cylindrical specimens with a 3 mm diameter. Disks of ~500 μm thickness were sectioned from these 3 mm cylinders, mechanically ground to ~130 μm thickness, and electro-polished using a solution of 20% sulfuric acid and 80% methanol (by volume) cooled to -5 °C in a Struers Tenupol-5 twin-jet

electropolisher. TEM images and diffraction patterns were collected at room temperature in the martensite state using a double tilt holder, and at high temperature in the austenite state using a single tilt heating holder on a FEI CM200 microscope operating at 200 kV.

Bulk chemical composition was quantitatively determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES) for metallic elements, and the LECO[®] Nitrogen/Oxygen and Carbon/Sulfur determinators for nitrogen, oxygen, and carbon contents.

2.3. *Thermomechanical testing*

Thermomechanical testing was conducted using an MTS 810 servo-hydraulic load frame equipped with a NovaStar 7 kW induction heating system. Cylindrical dog-bone specimens (5.08 mm in diameter and 15.24 mm in gage length) were machined from the extruded rod and were subjected to two stress-free thermal cycles between 30 and 300 °C, while mounted in the test frame, to relieve any residual stresses resulting from the machining and sample handling. Temperature was measured using type-K thermocouples spot welded directly to the middle of the sample gage section. A Eurotherm temperature controller was used to control the heating rates at 30°C/min, while cooling was achieved through water-cooled grips. The transformation temperatures: martensite start (M_s), martensite finish (M_f), austenite start (A_s), and austenite finish (A_f) were determined from the stress-free, strain-temperature response of the aged material and were 134, 127, 150 and 163 ± 2 °C, respectively.

Constant stress thermal cycling was performed in tension between 30 and 300 °C. The experiment was comprised of (i) two thermal cycles at 0 MPa followed by (ii) ten thermomechanical cycles at 300 MPa and finally, (iii) four more thermal cycles at 0 MPa. The last four cycles in step (iii) were carried out to determine the strength of any two-way shape

memory effect (TWSME) that may arise due to the previous thermomechanical cycling. For clarity in data presentation, the sample at the end of cycling (steps *i+ii+iii*) will be referred to as the “post-cycled” condition. When applying stress, the material was loaded in the martensite phase using a loading rate of 40 MPa/min, while the strain was measured using a 12.7 mm gauge, high-temperature extensometer. The choice of the upper cycle temperature (i.e. 300 °C) and the stress level (i.e. 300 MPa) was made based on typical requirements for high temperature actuator applications where a $\text{Ni}_{24.3}\text{Ti}_{49.7}\text{Pd}_{26}$ alloy could be potentially used. Another reason for selecting the 300 °C upper cycle temperature was to ensure a complete phase transformation when the material was thermally cycled under stress.

2.4. Neutron diffraction

In situ neutron diffraction measurements were performed on the Spectrometer for Materials Research at Temperature and Stress (SMARTS) at the Manuel Lujan Jr. Neutron Scattering Center, LANSCE, at Los Alamos National Laboratory (LANL). Details of this SMARTS engineering diffractometer are published elsewhere [57]. Samples were oriented 45° relative to the incident beam (white neutron beam) with two opposing $\pm 90^\circ$ ^3He tube detectors that record neutron data simultaneously with diffraction vectors parallel and perpendicular to the loading direction. The samples were loaded in uniaxial tension using the same conditions as described in section 2.3 (i.e., two thermal cycles at 0 MPa, ten thermomechanical cycles at 300 MPa, and four thermal cycles at 0 MPa). Diffraction data was collected for 30 minutes at room temperature and at 300 °C during each cycle for adequate statistical quality.

For a measure of initial texture, *ex situ* neutron diffraction experiments were conducted on the High-Pressure Preferred Orientation neutron diffractometer (HIPPO) [58, 59], also at LANL.

This instrument is equipped with a ^3He multi-detector system positioned in panels on rings of 150°, 90°, 40°, 20° and 10° diffraction angles around the incident beam. Specimens were mounted on an automated sample changer [60] for accurate measurements of the texture in the bulk.

2.5. Data analysis

Neutron diffraction data was analyzed using the Rietveld method implemented in the codes General Structure Analysis System (GSAS) [61] and Materials Analysis Using Diffraction (MAUD) [62]. Texture data obtained from the SMARTS diffractometer is represented using inverse pole figures (IPFs) constructed from the individual parallel and perpendicular diffraction vectors. These IPFs describe the distribution of specific macroscopic directions, e.g., the loading axis, in the coordinate systems of the individual crystallites comprising the polycrystalline sample. In contrast, the initial textures obtained from HIPPO data are represented using pole figures (PF) accounting for all the data collected from all detectors. Each PF represents the statistical distribution of the normal to the given (hkl) plane over all sample orientations.

A single peak fitting method was also used to compute (hkl) lattice strains from the individual reflections. The lattice strains were obtained from the change in interplanar spacing ($\Delta d_{hkl}/d_{hkl}$) where the initial d_{hkl} is taken as the interplanar d-spacing at 0 MPa at the respective temperature before deformation.

3. Results and discussion

3.1 Composition and initial microstructure

As confirmation, the bulk chemical composition of the alloy was determined for duplicate samples (Table 1) with each sample analyzed two times for metallic elements by inductively

coupled plasma atomic emission spectroscopy (ICP-AES) and analyzed once for interstitials. Note that the ICP run1-A and run2-A are the same sample run twice in the ICP, and run1-B and run2-B was a second sample from the same extrusion (Ext. 159) also run twice to determine the variability in compositional measurements. The measured metallic compositions reported in Table 1 were consistent with the aim composition of $\text{Ni}_{24.3}\text{Ti}_{49.7}\text{Pd}_{26}$ considering the measurement uncertainty for the technique of $\pm\sim 1\%$ of the absolute value. The detected carbon contamination was introduced from the graphite crucible used during melting of the alloy.

A representative scanning electron microscopy (SEM) micrograph of the alloy in the aged condition at room temperature, presented in Fig. 1a, shows the martensite grains and some second phase micron-size particles (black). These particles were identified via energy-dispersive x-ray spectroscopy (EDS) as TiC, as shown in Fig. 1b, and are observed in similarly processed alloys[16]. The basic microstructure consisted of equiaxed grains with an average grain size of $\sim 12\ \mu\text{m}$ in the aged condition, determined from optical and SEM micrographs. Based on transmission electron microscopy (TEM) analysis, the general microstructure at room temperature consisted of long martensite plates, each containing an array of parallel internal twins (Fig.1c). The orientation of these twins varied between adjacent plates, but remained the same in alternate plates. Analysis of selected area diffraction patterns (SADPs) from different zone axes suggested an orthorhombic (B19) structure with lattice parameters $a=2.8$, $b=4.7$, $c=4.4\ \text{\AA}$, $\alpha=\beta=\gamma=90^\circ$. A representative SADP from one of the twin arrays (region marked by a circle in Fig. 1c) is shown in Fig. 1d. The pattern consists of two sets of B19 reflections, marked “M” for “Martensite” and “T” for its “Twin”, with a common $[011]_{\text{M,T}}$ zone axis (ZA). The corresponding planes in the two sets are related to each other by mirror symmetry with respect to the common $(11\bar{1})_{\text{M,T}}$ plane. The trace of this plane is marked in Fig. 1c. Similar results with an

equivalent $\{111\}$ twin variant were obtained from the analysis performed on the twins in the adjacent plate portraying the self-accommodated nature of martensite in the aged condition. Thus, the predominant twin system in the alloy is $\{111\}$ type I twin, which is also the lattice invariant shear (LIS) for the martensitic phase transformation from B2 to B19 structures. The same twin system has been reported previously in several NiTiPd and TiPd alloys [63, 64]. In addition to twins, anti-phase boundary (APB) type structures, some of which are marked with red arrows in Figs. 1e-f, were observed between the twin plates. These APBs are likely the displacive transformation-induced boundaries resulting from the impingement of martensite domains during the austenite to martensite transformation, as previously observed in Ti-Pd alloys by Matsuda et al. [65].

A fine precipitate phase was also present in the martensite, as shown in Fig. 1f. The aged sample was heated *in situ* in the TEM to 300 °C to observe the transformation from B19 martensite to B2 austenite. The same region in the foil is shown at room temperature (Fig. 2a) in the fully martensitic condition (as confirmed in Fig. 2c) and at 300 °C in the fully austenitic condition (Fig. 2b) confirmed in Fig. 2d. Although the entire region had transformed to austenite, as evidenced by the selected area diffraction patterns SADPs (Fig. 2d), imprints of the prior martensite phase were still present in the austenite as seen in Fig. 2b. This residual contrast has been previously observed in Cu-Zn-Al alloys by Perkins and Bobowiec [66, 67], in a $\text{Zn}_{45}\text{Au}_{30}\text{Cu}_{25}$ alloy by Song et al. [68], and in $\text{Ni}_{10}\text{Ti}_{50}\text{Pd}_{40}$ alloy by Kumar and Lagoudas [37], and is believed to be a result of dislocation structure remnant from the phase transformation. The microstructure at 300 °C was nearly dislocation free except for the presence of occasional subgrain boundaries, which were formed during hot extrusion of the alloy. Due to the twin-free austenite microstructure, the fine precipitate phase was clearly visible as shown by the

corresponding bright field (BF) and dark field (DF) images in Fig. 2e-f respectively. Selected area diffraction patterns suggested that it is likely a “P” phase, originally identified in the NiTiPt system by Kovarik et al. [69] and later confirmed in the NiTiPd system [39, 70]. The size of the precipitate was estimated to be $\leq 10\text{nm}$.

Neutron diffraction spectra collected at room temperature (RT) and at 300 °C were refined using the *Pmcm* orthorhombic space group for B19 martensite and *Pm $\bar{3}m$* cubic space group for B2 austenite, respectively. The Rietveld best fit lattice parameters were $a=2.7846$, $b=4.7057$, $c=4.4554$ Å, $\alpha=\beta=\gamma=90^\circ$, for orthorhombic martensite, and $a=3.1006$ Å for cubic austenite. It is cautioned that the absolute lattice parameters determined from the neutron diffractometer can be affected by penetration power of the neutrons and the setup geometry (center of mass), thus only an average value from multiple Rietveld refined patterns is reported here. The output of the refined B19 and B2 neutron spectra after two 0 MPa thermal cycles at RT and 300 °C, respectively are shown in Fig. 3. From both spectra (i.e., martensite and austenite phases), there were no detectable secondary peaks corresponding to the precipitate phase that was observed in Fig. 1e, suggesting a low volume fraction (possibly less than 5%). Furthermore, in the aged state under stress free conditions, no residual austenite was observed at room temperature (Fig. 3a), and no retained martensite was observed in the austenite phase at 300 °C (Fig. 3b), consistent with the TEM-SADP analysis discussed previously.

For a complete measure of initial texture of the martensite phase in the aged condition, pole figures were constructed from the room temperature no-load diffraction data collected using the HIPPO instrument (Fig. 4). The pole densities at $\theta \approx 0^\circ$ (center of the pole) correspond to the sample axis or the loading direction, while the pole densities in the $\theta \approx 90^\circ$ (outer rim) correspond to the transverse or Poisson’s direction. There was little preferential texture and the

material exhibited a random grain distribution in the as processed and aged condition, prior to any deformation/cycling.

3.2 Thermomechanical cycling

The macroscopic strain-temperature behavior of the $\text{Ni}_{24.3}\text{Ti}_{49.7}\text{Pd}_{26}$ alloy as a function of cycling is summarized in Fig. 5. Specifically, the initial two no-load thermal cycles are shown in Fig. 5a, the ten 300 MPa load-biased cycles are shown in Fig. 5b, and finally the four additional thermal cycles at 0 MPa showing the development of a two-way shape memory effect (TWSME) are shown in Fig. 5c. These curves were generated during the *in situ* neutron diffraction experiments (in stress control). The vertical strain increases/decreases at the temperature endpoints, RT and 300 °C (circled areas labeled “Hold” in Fig. 5b) occurred during the 30 min hold periods for diffraction data acquisition. The end-strains of the strain-temperature plots, which represent the strain in the martensite phase measured at 40 °C and the strain in the austenite phase measured at 300 °C, are plotted in Fig. 5d. These end strains were subsequently used to determine the actuation strains (Fig. 5e) by calculating the difference between the martensite and austenite true end-strains for each cycle. The residual (unrecovered) strains (Fig. 5f) were also determined from the difference in strain from one cycle to the next at both the lower (40 °C) and upper cycle (300 °C) temperatures. Details of the methods used to determine these parameters can be found elsewhere [71].

Within the ten cycles tested at load (Fig. 5b), an average actuation strain of 3.1% was obtained, which was essentially constant after the third cycle (Fig. 5e). But it is evident from Fig. 5d that the material was not dimensionally stable in the current aging condition (aged at 400 °C for 24 h). Both the martensite and austenite end strains evolved with cycling and did not reach a

stable condition after ten cycles (Fig 5d). This behavior is not unusual for the Ti-rich NiTiPd counterparts [16], but higher Ni-rich alloys such as $\text{Ni}_{27}\text{Ti}_{48}\text{Pd}_{25}$ [39] have shown better dimensional stability, though at the expense of lower transformation temperatures and significantly reduced transformation strains. The material used in this study was processed with only a slightly Ni-rich composition $((\text{Ni}+\text{Pd})_{50.3}\text{Ti}_{49.7})$ with the goal of retaining higher transformation temperatures and strains. A fine precipitate phase, on the order of 10-20 nm, has been proven to be an ideal size for strengthening NiTi [72-74], NiTiHf [22, 23, 75, 76], and NiTiZr [26, 77] alloys resulting in extremely stable shape memory and pseudoelastic behaviors. It was shown that a volume fraction of around 15-20% is generally necessary to provide strengthening against plastic deformation leading to the types of stability reported in the previous references [78]. However, the aging treatment (i.e., 400 °C for 24 h) used to produce the dispersion of nano-sized precipitates in this alloy was not sufficient to provide enough precipitate hardening. Even though a low aging temperature and relatively long time was used to maximize precipitate volume fraction, the lack of any peaks associated with the precipitate phase in the neutron diffraction (and unpublished x-ray) spectra suggest a precipitate volume fraction of less than about 5 vol.%. Thus, plastic deformation leading to observed dimensional instabilities, was present in the current alloy.

Sections of normalized neutron diffraction spectra taken at room temperature, corresponding to the thermal/thermomechanical cycles described above, are shown in Figs. 6a-d for diffracting lattice planes perpendicular to the loading axis and in Figs. 6e-h for diffracting planes parallel to the loading axis (equivalent to a Poisson's effect). Included in the plots are the initial stress-free thermal cycles before deformation, the ten thermomechanical cycles at 300 MPa, and finally the four unloaded thermal cycles at 0 MPa that exhibit the TWSME. These spectra correspond to the

B19 orthorhombic phase at room temperature and show the changes in selected martensitic diffraction peaks with cycling.

The initial cycles represent the starting texture of this material, which was shown to be a random distribution (Fig. 4). Once the material was loaded to 300 MPa, preferential selection of martensite variants along the tensile loading direction is shown by the increase in intensity of the $(011)_M$, $(020)_M$ and $(030)_M$ orientations (Figs. 6a-b, 6d), while the intensity at the $(100)_M$ and $(111)_M$ orientations decreased (Figs. 6a, 6c). The opposite trend can be observed for the planes parallel to the loading direction, which represents the Poisson's effect (Figs. 6e-h). The change was pronounced for the first cycle or two under load. Continued cycling under load had little further effect on the observed martensite peak intensities for the remaining cycles, which corroborates the constant transformation/actuation strains shown in Fig. 5e after the first two cycles under load.

For a complete representation of texture, the entire neutron spectrum, as opposed to a few distinct orientations as shown in Fig. 6, was used to generate the inverse pole figures (IPFs) shown in Fig. 7. These IPFs were plotted in a scale of multiples of random distribution (MRD) for both the loading direction (Fig. 7a) and the Poisson's direction (Fig. 7b). For clarity, a unique MRD scale was adopted for each data set (7a versus 7b) due to differences in the strengths of the textures for each set. Finally, the maximum and minimum values of MRD are recorded within each IPF for ease of comparison. Also included in Figs. 7a and 7b, before the "pre-cycle 0" IPF, is the irreducible orthorhombic stereograph plotted with select crystal orientations. As expected, based on the individual reflections plotted in Fig. 6, the intensity at the $(030)_M$ orientation (Fig. 7a) exhibited the highest change after loading and thermomechanical cycling. Therefore, the variant of martensite responsible for this reflection is primarily responsible for the 3.1%

actuation strain obtained in the material (Figs. 5b and 5e). Continued cycling beyond the second isobaric cycle did not result in a new texture or major variations of the maximum intensity in the $(030)_M$ orientation. This is consistent with the near constant transformation/actuation strains shown in Figs. 5b and 5e. Similarly, the IPFs representing the planes parallel to the loading direction showed an increase in the $(202)_M$ and $(102)_M$ orientations, which is similar to what was observed in compressive loading in a similar NiTiPd alloy [79].

In addition to the texture changes, the internal strain/stress state of the material in the martensite phase was also captured through the measured lattice strains and reported in Fig. 8a-b. Lattice strains developed as the material was loaded while cycled through the phase transformation. In general, the lattice strains increased or decreased sharply during the very initial cycles before approaching an asymptotic limit consistent with the nature of the macroscopic strains of Figs. 5d and 5f. In either data set, the material exhibited a large anisotropy in B19 lattice strains during cycling. Perpendicular planes that experienced the maximum lattice strain along the loading direction (Fig. 8a) were found to be $(011)_M$ and $(032)_M$, while those that exhibited the highest intensity change (e.g., the $(030)_M$ plane) exhibited a significantly lower lattice strain. This is also the case for planes parallel to the loading direction (Fig. 8b) where the planes of maximum intensity (e.g., the $(102)_M$) exhibited less strain compared to the $(002)_M$ and $(011)_M$ planes. In fact, some planes reverted to compressive strains such as the case of the $(020)_M$ planes (Fig. 8a). This behavior is related to the martensitic reorientation process that takes place during the initial load-biased thermomechanical cycle. The planes favored for detwinning/reorientation (e.g., the $(030)_M$) provide the mechanisms for inducing the macroscopic strains, but exhibit limited microscopic strains.

Similar analysis to that described above for the martensite phase was carried out in the B2 phase. The austenite phase was also found to evolve with cycling, but not in the same way. The austenite phase primarily exhibited shifts in atomic spacing and peak broadening, but exhibited little change in peak intensities. Sections of normalized diffraction spectra corresponding to the B2 phase at 300 °C are shown in Figs. 9a-d for diffracting lattice planes perpendicular to the loading axis and in Figs. 9e-h for diffracting planes parallel to the loading axis. For reference, B19 spectra obtained at room temperature were included in the bottom of each plot. There were no significant changes in austenite peak intensities during cycling as shown summarized in Fig. 10a. With a cubic symmetry and an anticipated $\langle 001 \rangle$ burgers vector for the active slip system, no change in texture would be expected with deformation [80] consistent with the current analysis. Instead, most of the peaks evolved with cycling by changes in position and peak broadening, which is consistent with the unstable macroscopic strain-temperature behavior evident in Fig. 5.

The peak positions are affected not just by the introduction of applied strain into the system, but also by the generation of retained martensite. Retained martensite is evident by the appearance of new peaks at 300 °C in the B2 phase ($\{110\}_A$ peak splitting) as shown in Fig. 9f, and by asymmetric peak shapes indicative of peak overlaps as shown in Fig. 9b. The volume fraction of retained martensite was estimated to be 6% at the end of the 10th cycle. This mechanism is a contributing factor to the observed dimensional instabilities shown in Fig. 5. In addition to having to accommodate the phase change between two different lattice structures, which is a major source of defect generation [81], the presence of retained martensite creates additional incompatibilities between austenite grains, which have to be accommodated through irreversible mechanisms such as slip and or deformation twinning [82, 83].

Also of interest are the magnitude and anisotropy of the lattice strains developed in the austenite phase during thermomechanical cycling. Although the material is cubic at 300 °C, thermomechanical cycling appeared to introduce large lattice strains with a significant anisotropy (Fig. 11). This behavior would be consistent for a material with significant elastic anisotropy, which is the case for B2 NiTi [84] and is predicted for B2 NiTiPd alloys [85]. In fact, the strain development with cycling in Fig. 11 is qualitatively similar to what is observed during thermomechanical cycling of binary NiTi [86]. In both cases, for planes perpendicular to the loading direction, the largest strains develop on the {100} planes and continuously build with cycle count; {111} planes quickly develop a negative strain with cycling and other planes such as {110}, {210}, and {221} evolve very slowly or are almost constant in strain after a few cycles. The lattice strains parallel to the loading axis are also similar for the NiTiPd and NiTi [86] with strain being negative (Poisson's strains) and essentially constant with cycling except for {100}, which continues to increase in compression with cycling. This lattice strain evolution is the result of elastic anisotropy and resulting deformation mechanisms, which limit elastic strains on planes where deformation is occurring. Assuming $\langle 100 \rangle$ type slip is the primary slip in this $\text{Ni}_{24.3}\text{Ti}_{49.7}\text{Pd}_{26}$ B2 system, the buildup of strains on {100} planes can be explained by non-activation of this slip because of zero resolved shear stress on these planes. Since {100} is a hard orientation where there is no resolved shear stress for $\langle 100 \rangle$ type slip, (expected in these alloys), the strain is able to build to very high levels. The general qualitative similarity between this data (Fig. 11) and analogous results for binary NiTi, combined with the lack of texture development during cycling (Fig. 9), are also consistent with an expected $\langle 100 \rangle$ type slip system.

Finally, it is noted that most of the B2 phase peaks show peak broadening with cycling, which in this case is probably due to the significant buildup in lattice defects with cycling [87]. This broadening was quantified by measuring the full width at half maximum (FWHM) for various planes and plotted as a function of cycle number in Fig. 12. The peak width increased with thermomechanical cycling consistent with the accumulation of the macroscopic residual strain shown in Fig. 5.

3.3 Post-isobaric thermomechanical cycling

The dimensional instability shown in Figs. 5b and 5d is undeniably an unfavorable factor for actuation purposes. Nonetheless, related behaviors associated with such instabilities may be of benefit to other applications, such as the ability to generate a strong two-way shape memory effect (TWSME). After thermomechanical cycling at 300 MPa, the sample was unloaded and cycled through the phase transformation under stress-free conditions. A TWSME strain of approximately 2% was obtained for the four stress-free thermal cycles (Fig. 5c), which is of significant value for applications requiring unbiased actuation at relatively high temperature. This TWSME can be developed several ways and can likely be stabilized by applying even simpler training routines [88]. This TWSME was attributed to a remnant microstructure that was developed during isobaric thermal cycling.

Upon unloading and thermal cycling under zero stress, *in situ* neutron diffraction results (Fig. 6, post-cycles 1 thru 4) show that the intensities of the examined B19 peaks did not revert back to the original nearly-texture free values, but varied only slightly compared to the isobarically cycled data. This is quantified by the IPFs of Fig. 7 showing the intensity at the (030)_M orientation in Fig. 7a decreasing slightly from a multiples of random distribution (MRD) of 12.5

after 10 isobaric thermal cycles to an MRD of approximately 9.1 after four stress-free thermal cycles. Likewise, that of the $(202)_M$ and $(102)_M$ orientations in Fig. 7b only decreased from an MRD of 3.5 to an MRD of approximately 2.7. Similar behaviors were observed for the B2 phase shown in Fig. 9 where the austenite peak positions did not revert back to the original state and the presence of retained martensite was still evident (Fig. 9f) after load removal and stress-free thermal cycling.

It is assumed that the retained texture in the $\text{Ni}_{24.3}\text{Ti}_{49.7}\text{Pd}_{26}$ alloy was “pinned” by the lattice defects that were generated during thermomechanical cycling. Thus, the microstructure of the post-cycled (steps $(i+ii+iii)$) material was examined in the TEM and general examples are shown in Figs. 13-14. After cycling, the majority of the martensite still consisted of elongated parallel plates, but the nature of the martensite had changed from “self-accommodated” in the aged condition (Fig. 1c) to predominantly “reoriented” with only one set of $\{111\}$ type I twins, as shown in Fig. 13a. The alternate plates labeled *A*, *B* and *C* in Fig. 13a show reoriented twin structure that is similar to that present in plates *D* and *E*, and also contain some detwinned areas with a complete loss of the originally present $\{111\}$ type I twins. This suggests that the preferred martensite twin variant that was aligned closest to the loading direction was favored after loading and cycling. In addition, a high density of dislocations (Fig. 13b, c) and some recovered regions bounded by subgrain boundaries (marked by arrows in Fig. 13b) were also observed in the microstructure. The interaction of dislocations with fine precipitates and anti-phase boundaries (arrows) is clearly seen in Figs. 13d and 14a. In addition, several new twinned structures were observed throughout the microstructure. These were more pronounced in the detwinned regions, as shown by arrows in Fig. 14c. Occasionally these were also observed in the plates containing an array of LIS $\{111\}$ type I twins; an example of one such intersecting inclined set is shown by

white arrows in Fig. 14b. Many of these twins appeared to originate from the martensite interplate boundaries where the dislocation density was somewhat higher. SADP of the circled area shown in Fig. 14c, suggested that these were $\{011\}$ compound twins, which are not the LIS but considered deformation twins for the B19 to B2 transformation [37, 64].

The “post-cycled” sample was heated *in situ* in the TEM to 300 °C to observe the microstructure of the austenite after thermomechanical cycling. The material had transformed to austenite but contained retained martensite plates and a high density of dislocations (Fig. 15a). Some dislocation loops and dislocation pinning at the precipitates were also observed (Fig. 15b). Thus, plastic deformation, deformation twins and retained martensite are all responsible for the irrecoverable strains generated in Fig. 5.

Further examination of the neutron spectra show that unloading followed by no-load thermal cycling did not relax all the accumulated lattice strains. This is true for both phases as shown in Fig. 8 for the B19 phase and in Fig. 11 for the B2 phase. In fact, some reflections revert to a compressive strain as evident by the $(020)_M$ lattice planes. These residual strains are a result of the buildup of lattice defects during thermomechanical cycling as shown in Figs. 13-15. Moreover, the peak breadths were also unrecovered after load removal. This suggests that the microstructural defects generated during cycling, while negatively impacting the dimensional stability of the alloy, do bias the martensitic transformation to yield the useful TWSME shown in Fig. 5.

4. Conclusions

Thermomechanical cycling of a Ni-rich $\text{Ni}_{24.3}\text{Ti}_{49.7}\text{Pd}_{26}$ high temperature shape memory alloy was investigated concurrent with microstructural examination using *in situ* neutron diffraction,

and augmented before and after thermomechanical cycling by transmission electron microscopy. The measured texture, lattice strains and microstructural observations were used to interpret the shape memory behavior including transformation strains, strain evolution, and residual deformation with and without load. From the presented data, the following conclusions were reached:

- The initial martensitic microstructure of the aged $\text{Ni}_{24.3}\text{Ti}_{49.7}\text{Pd}_{26}$ consisted primarily of $\{111\}$ type I twins, with presence of anti-phase boundary (APB) type structures, and a very fine precipitate phase of approximately $\leq 10\text{nm}$ in size.
- The material exhibited a biased transformation strain on the order of 3% under a 300 MPa stress, and two-way shape memory effect (TWSME) strain of 2% once the load was removed. In both cases, dimensional instabilities were present. The strain accumulation of about 1.5% ensued over ten load-biased thermomechanical cycles. This was attributed to the generation of lattice defects and the presence of retained martensite during cycling as revealed by TEM observations and peak broadening of the neutron spectra.
- Significant lattice strains developed with cycling in both the austenite and martensite phases, most of which were not recovered upon load removal. These residual strains biased the martensitic transformation during free thermal recovery, producing a significant TWSME. This was attributed to the martensite texture that was retained during post no-load thermal cycling as confirmed by the inverse pole figures obtained from neutron diffraction data.

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Tables:

Table 1. $\text{Ni}_{24.3}\text{Ti}_{49.7}\text{Pd}_{26}$ measured composition in atomic percent using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Figures:

Fig. 1. Microstructure of the aged $\text{Ni}_{24.3}\text{Ti}_{49.7}\text{Pd}_{26}$ alloy at room temperature. (a) SEM micrograph showing the martensite grains and micron size carbide particles, (b) energy-dispersive x-ray spectroscopy (EDS) spectrum of the particles in 1a, (c) bright field TEM image showing the general microstructure of the alloy, (d) selected area diffraction patterns (SADP) of the circled area in 1c, (e,f) anti-phase boundaries (red arrows) within the twin plates and a nm size fine precipitate phase circled in (f).

Fig. 2. Microstructure of the aged $\text{Ni}_{24.3}\text{Ti}_{49.7}\text{Pd}_{26}$ alloy at RT and 300 °C. TEM bright field images showing (a,c) martensite microstructure and its selected area diffraction patterns (SADP) at room temperature, (b,d) same region (as in (a)) transformed to austenite and its SADP at 300° C; (e) bright field and (f) dark field images showing a region of higher density of fine precipitate phase in the B2 matrix. Extra spots in 2d (marked P) correspond to the precipitate phase [69, 70].

Fig. 3. Neutron diffraction patterns for $\text{Ni}_{24.3}\text{Ti}_{49.7}\text{Pd}_{26}$ with diffracting lattice planes parallel to the loading axis with no externally applied load. (a) Orthorhombic martensite at room temperature and (b) cubic austenite at 300 °C. The measured data are indicated by cross marks in red and the calculated profile (Rietveld refinement) is indicated by the solid green line. The tick-marks below the profile pattern indicate the reflections used in the refinement. The lower magenta curve is the difference between the measurement and refinement.

Fig. 4. Initial martensitic texture measured at room temperature prior to cycling (the loading axis is at the center of the pole figures).

Fig. 5. Macroscopic strain-temperature response of $\text{Ni}_{24.3}\text{Ti}_{49.7}\text{Pd}_{26}$ during (a) the initial two no-load thermal cycles, (b) the ten load-biased thermal cycles at 300 MPa, and (c) the four post thermal cycles at 0 MPa showing development of a two-way shape memory effect (TWSME). The strain data is also plotted against the cycle number for (d) showing the strain accumulation in both phases at the end of each thermal cycle, (e) the transformation strains versus cycle number, and (f) the residual or unrecovered strains for each cycle.

Fig. 6. Normalized B19 neutron diffraction spectra acquired at room temperature during thermal cycling. Reflections are from (a-d) lattice planes perpendicular and (e-h) lattice planes parallel to the loading direction. The conditions are: (i) initial two no-load cycles (pre-cycles 0-2), (ii) ten load-biased thermomechanical cycles at 300 MPa (cycles 1-10), and (iii) post thermal cycling at 0 MPa (post-cycle 1-4).

Fig. 7. Inverse pole figures (IPFs) for martensitic $\text{Ni}_{24.3}\text{Ti}_{49.7}\text{Pd}_{26}$ from (a) diffracting planes perpendicular to the loading direction and (b) diffracting planes parallel to the loading direction.

Cycle numbers correspond to the conditions shown in Fig. 6. A unique multiples of random distribution (MRD) scale was adopted for each data set (a and b), and the maximum and minimum MRD values are recorded within each IPF.

Fig. 8. Lattice strains associated with several B19 reflections (a) perpendicular and (b) parallel to the loading direction. Cycle numbers correspond to the same sample conditions as shown in Figs. 6 and 7.

Fig. 9. Normalized B2 neutron diffraction spectra acquired at 300 °C during thermal cycling. Reflections are from (a-d) lattice planes perpendicular and (e-h) lattice planes parallel to the loading direction. The conditions are: *i*) B19 spectrum taken at room temperature for reference *(ii)* initial two no-load cycles (pre-cycles 1-2), *(iii)* ten load-biased thermomechanical cycles at 300 MPa (cycles 1-10), and *(iv)* post thermal cycling at 0 MPa (post-cycle 1-3). The missing load-biased cycles 6 and 8 are due to loss of neutron beam during cycling.

Fig. 10. Normalized integrated peak intensities for reflections perpendicular to the loading direction measured in (a) the austenite phase at 300 °C, and (b) the martensite phase at room temperature. Note the change in vertical scale in (a) and (b).

Fig. 11. Lattice strains associated with several B2 reflections (a) perpendicular and (b) parallel to the loading direction. Cycle numbers correspond to the same sample conditions as shown in Fig. 9.

Fig. 12. Full-width of half-maximum (peak broadening) of the B2 austenite $\text{Ni}_{24.3}\text{Ti}_{49.7}\text{Pd}_{26}$ measured at 300 °C (a) perpendicular and (b) parallel to the loading direction. Cycle numbers correspond to the same sample conditions as shown in Fig. 9.

Fig. 13. Room temperature TEM images of “Post-cycled” $\text{Ni}_{24.3}\text{Ti}_{49.7}\text{Pd}_{26}$ alloy (a) showing detwinning (regions marked X) and preferentially oriented twins in plates (A-E), (b,c) a high density of dislocations, (d) dislocation pinning and looping around precipitates.

Fig. 14. Room temperature TEM images of “Post-cycled” $\text{Ni}_{24.3}\text{Ti}_{49.7}\text{Pd}_{26}$ alloy (a) showing (a) dislocation interaction with anti-phase boundaries, (b,c) appearance of new twins (white lines and red arrows), (d) selected area diffraction patterns (SADP) from the circled area in (c).

Fig. 15. Microstructure of the “post-cycled” alloy at 300 °C. TEM bright field images showing (a) a high density of dislocations and retained martensite plates in the B2 austenite; the inset shows the selected area diffraction patterns (SADP) from the circled area confirming the presence of martensite. (b) Dislocation interaction with precipitates.

Table 1

ICP Run	Sample ID	Sample weight	Measured composition (at.%)					
		mg	Ni	Ti	Pd	C	N	O
Run1-A	Ni-49.7Ti-26Pd (A)	171.5	23.99	48.87	27.13	0.401	0.044	0.1030
Run1-B	Ni-49.7Ti-26Pd (B)	174.8	24.06	48.70	27.24			
ICP Run 2			Ni	Ti	Pd	C	N	O
Run2-A	Ni-49.7Ti-26Pd (A)	171.5	23.87	49.37	26.76	0.389	0.043	0.1020
Run2-A	Ni-49.7Ti-26Pd (B)	174.8	23.88	49.35	26.78			

Figure1

Figure2

Figure3

Figure4

Figure5

Figure6

B19 lattice planes $\perp$ to loading direction

B19 lattice planes $\parallel$ to loading direction

Figure7

(a)

(b)

Figure8

Figure9

Figure10

Figure11

Figure12

Figure13

Figure14

Figure15