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2007

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LOW TEMPERATURE NiTiFe SHAPE MEMORY ALLOYS: ACTUATOR ENGINEERING AND INVESTIGATION OF DEFORMATION MECHANISMS USING \textit{IN SITU} NEUTRON DIFFRACTION AT LOS ALAMOS NATIONAL LABORATORY

by

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2007

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Shape memory alloys are incorporated as actuator elements due to their inherent ability to sense a change in temperature and actuate against external loads by undergoing a shape change as a result of a temperature-induced phase transformation. The cubic so-called austenite to the trigonal so-called R-phase transformation in NiTiFe shape memory alloys offers a practical temperature range for actuator operation at low temperatures, as it exhibits a narrow temperature-hysteresis with a desirable fatigue response. Overall, this work is an investigation of selected science and engineering aspects of low temperature NiTiFe shape memory alloys.

The scientific study was performed using *in situ* neutron diffraction measurements at the newly developed low temperature loading capability on the Spectrometer for Materials Research at Temperature and Stress (SMARTS) at Los Alamos National Laboratory and encompasses three aspects of the behavior of Ni$_{46.8}$Ti$_{50}$Fe$_{3.2}$ at 92 K (the lowest steady state temperature attainable with the capability). First, in order to study deformation mechanisms in the R-phase in NiTiFe, measurements were performed at a constant temperature of 92 K under external loading. Second, with the objective of examining NiTiFe in one-time, high-stroke, actuator applications (such as in safety valves), a NiTiFe sample was strained to approximately 5% (the R-phase was transformed to B19' phase in the process) at 92 K and subsequently heated to full strain recovery under a load. Third, with the objective of examining NiTiFe in cyclic, low-stroke, actuator applications (such as in cryogenic thermal switches), a NiTiFe sample was strained to 1% at 92 K and subsequently heated to full strain recovery under load. Neutron diffraction spectra were recorded at selected time and stress intervals during these experiments. The spectra were
subsequently used to obtain quantitative information related to the phase-specific strain, texture and phase fraction evolution using the Rietveld technique.

The mechanical characterization of NiTiFe alloys using the cryogenic capability at SMARTS provided considerable insight into the mechanisms of phase transformation and twinning at cryogenic temperatures. Both mechanisms contribute to shape memory and pseudoelasticity phenomena. Three phases (R, B19' and B33 phases) were found to coexist at 92 K in the unloaded condition (nominal holding stress of 8 MPa). For the first time the elastic modulus of R-phase was reported from neutron diffraction experiments. Furthermore, for the first time a base-centered orthorhombic (B33) martensitic phase was identified experimentally in a NiTi-based shape memory alloy. The orthorhombic B33 phase has been theoretically predicted in NiTi from density function theory (DFT) calculations but hitherto has never been observed experimentally. The orthorhombic B33 phase was observed while observing shifting of a peak (identified to be \{021\}_{B33} between the \{111\}_R and \{100\}_{B19'} peaks in the diffraction spectra collected during loading. Given the existing ambiguity in the published literature as to whether the trigonal R-phase belongs to the \textit{P}3 or \textit{P}5\textit{3} space groups, Rietveld analyses were separately carried out incorporating the symmetries associated with both space groups and the impact of this choice evaluated. The constrained recovery of the B19' phase to the R-phase recorded approximately 4% strain recovery between 150 K and 170 K, with half of that recovery occurring between 160 K and 162 K. Additionally, the aforementioned research methodology developed for Ni_{46.8}Ti_{50}Fe_{3.2} shape memory alloys was applied to experiments performed on a new high temperature Ni_{29.5}Ti_{50.5}Pd_{20} shape memory alloys.
The engineering aspect focused on the development of (i) a NiTiFe based thermal conduction switch that minimized the heat gradient across the shape memory actuator element, (ii) a NiTiFe based thermal conduction switch that incorporated the actuator element in the form of helical springs, and (iii) a NiTi based release mechanism. Patents are being filed for all the three shape memory actuators developed as a part of this work.

This work was supported by grants from SRI, NASA (NAG3-2751) and NSF (CAREER DMR-0239512) to UCF. Additionally, this work benefited from the use of the Lujan Center at the Los Alamos Neutron Science Center, funded by the United States Department of Energy, Office of Basic Energy Sciences, under Contract No. W-7405-ENG-36.
Dedicated

to

My Parents and Late Uncle
ACKNOWLEDGMENTS

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TABLE OF CONTENTS

LIST OF TABLES ........................................................................................................................ xii
LIST OF FIGURES ...................................................................................................................... xiii
LIST OF ACRONYMS ............................................................................................................... xvii

CHAPTER ONE: INTRODUCTION ..............................................................................................1
  1.1 Motivation .................................................................................................................................1
  1.2 Organization .............................................................................................................................4

CHAPTER TWO: LITERATURE REVIEW ..................................................................................5
  2.1 Shape Memory Alloys ..................................................................................................................5
    2.1.1 Shape Memory Effect ..........................................................................................................6
    2.1.2 Superelasticity ......................................................................................................................8
  2.2 Shape Memory Alloy Actuators ..............................................................................................9
  2.3 NiTi Shape Memory Alloys .....................................................................................................11
    2.3.1 Hysteresis in NiTi Alloys ..................................................................................................12
    2.3.2 NiTiFe Alloys ....................................................................................................................12
    2.3.3 R-Phase in NiTi Alloys ......................................................................................................13
  2.4 Neutron Diffraction ................................................................................................................14
    2.4.1 Rietveld Refinement .........................................................................................................15
    2.4.2 Single Peak Fitting ............................................................................................................17

CHAPTER THREE: CRYOGENIC NEUTRON DIFFRACTION SETUP AND
MEASUREMENTS AT 92 K .............................................................................................................18
  3.1 Introduction ............................................................................................................................18
  3.2 Experimental Procedure ........................................................................................................19
    3.2.1 Neutron Diffraction Measurements on SMARTS ............................................................19
    3.2.2 Cryogenic Capability on SMARTS ..................................................................................20
    3.2.3 Sample Fabrication ...........................................................................................................22
    3.2.4 Experimental Temperature and Strain Parameters .........................................................23
5.5 Conclusions .................................................................................................................................68

CHAPTER SIX: CONSTRAINED RECOVERY EXPERIMENTS ..............................................................69
6.1 Introduction ....................................................................................................................................69
6.2 Experimental Procedure ..............................................................................................................70
  6.2.1 Sample Fabrication ..................................................................................................................70
  6.2.2 Experimental Setup and Method ............................................................................................70
  6.2.3 Neutron Data Analysis ............................................................................................................71
6.3 Results and Discussion ................................................................................................................72
  6.3.1 Constrained Recovery from B19’ Phase to R-Phase ............................................................72
  6.3.2 Constrained Recovery from R-Phase to B2 Phase ...............................................................76
6.4 Conclusions ...................................................................................................................................79

CHAPTER SEVEN: EXTENSION OF RESEARCH METHODOLOGY TO NiTiPd SHAPE MEMORY ALLOYS .................................................................................................................81
7.1 Introduction ....................................................................................................................................81
7.2 Experimental Procedures ..............................................................................................................83
  7.2.1 Sample Fabrication ..................................................................................................................83
  7.2.2 Experimental Setup ................................................................................................................83
7.3 Results and Discussion ................................................................................................................84
  7.3.1 Identification of NiTiPd Martensite Structure ......................................................................84
  7.3.2 Load-Bias Experiment ............................................................................................................86
  7.3.3 Stress-Induced Martensite Experiment .................................................................................92
7.4 Conclusions ...................................................................................................................................93

CHAPTER EIGHT: ACTUATOR DEVICE DEVELOPMENT ...................................................................96
8.1 Development of NiTiFe Thermal Conduction Switch - Prototypes ................................................96
  8.1.1 Introduction ............................................................................................................................96
  8.1.2 Shape Memory Alloy Actuators ..............................................................................................99
  8.1.3 Lunar Applications ..................................................................................................................99
  8.1.4 Shape Memory Alloy Element Fabrication and Testing .....................................................100
  8.1.5 Switch Testing .......................................................................................................................102
8.2 Shape Memory Alloy Based Release Mechanism .........................................................................104
Table 4.1: Experimental conditions and the corresponding phases present ..................................39
Table 4.2: R-phase atom positions for the three experimental conditions, refined with R-phase
belonging to the $P3$ space group ..................................................................................42
Table 4.3: R-phase atom positions for the three experimental conditions, refined with R-phase
belonging to the $P\bar{3}$ space group .............................................................................43
Table 4.4: Quality of fit parameters [9] for the two sets of Rietveld refinements ($P3$ and $P\bar{3}$ space
groups) ..........................................................................................................................43
Table 4.5: Strain evaluation using single peak fitting ..........................................................49
Table 4.6: Strain evaluation using Rietveld approach for the two sets of refinements at 216 K ($P3$
and $P\bar{3}$ space groups) ................................................................................................49
Table 7.1: Isotropic strains in the B2 phase with respect to cycle 1. The contributions of the
coefficient of thermal expansion (CTE) have been subtracted out ....................................90
Table 7.2: Lattice strains in the B2 phase for cycle 5 (300 MPa, 659 K) determined with respect
to cycle 1 (100 MPa, 464 K) ..........................................................................................92
LIST OF FIGURES

Figure 2.1: Transformation temperatures associated with the shape memory effect [17]...........7
Figure 2.2: Types of SMA actuators (a) one-way actuator, (b) biased two-way actuator, and (c) differential two-way actuator [17].................................................................................10
Figure 2.3: Isotropic scattering of neutron beam by a nucleus..............................................14
Figure 3.1: Schematic of the SMARTS diffractometer showing the incident and diffracted neutron beam during the application of compressive stress on the sample.........................20
Figure 3.2: Schematic of the SMARTS diffractometer with the cryogenic setup (top view) [8]..21
Figure 3.3: Comparison of the diffraction patterns obtained at room temperature and at 92 K, in the no-load condition (nominal holding stress of 8 MPa)..................................................24
Figure 3.4: Splitting of \{112\}_R and \{300\}_R peaks of diffraction patterns observed at 216 K and at 92 K.......................................................................................................................24
Figure 3.5: Macroscopic stress-strain curve obtained \textit{ex situ} at 92 K. ........................................25
Figure 3.6: Stress-induced transformation from R-phase to B19' phase above a stress of 68 MPa, during loading at 92 K.............................................................................................................26
Figure 3.7: Limited twinning in the R-phase and strain redistribution above 68 MPa due to the formation of stress-induced B19' phase during loading at 92 K.............................................26
Figure 3.8: Transformation hysteresis between B19' phase and R-phase, typical of shape memory alloys. The dotted lines qualitatively represent the region where the experiments were conducted...........................................................................................................27
Figure 3.9: Constrained recovery of the R-phase from the B19' phase during the heating of the 5% strained sample from 150 K to 170 K.........................................................................................28
Figure 3.10: Tilting of \{021\}_{B33} during loading at 92 K, observed as a peak movement between \{111\}_R and \{100\}_{B19'}. .....................................................................................................................30
Figure 3.11: Crystallographic correspondence between the cubic B2 and the orthorhombic B33 structures.................................................................................................................................30
Figure 3.12: Left – the monoclinic B19' unit cell with $\gamma = 97^\circ$. Right – the monoclinic B19' unit cell with $\gamma = 107^\circ$ and the orthorhombic B33 unit cell. The green rectangle shows the B33 {021} plane. (Figures modified from Huang \textit{et. al.}, Nature Materials, 2003 [57]). 30
Figure 4.1: Unit cell of R-phase using $P3$ space group (left) and $P\bar{3}$ space group (right). ....40
Figure 4.2: A typical GSAS Rietveld refinement output with the R-phase refined as belonging to the $P3$ space group (for spectrum obtained from the sample under a compressive stress of 44 MPa at 237 K) for diffracting lattice planes whose normals are parallel to the loading axis. The measured data are indicated by cross-marks and the calculated
profile is indicated by the solid-line curve. The line-marks below the profile pattern indicate the positions of all possible Bragg reflections. The lower graph shows the difference between the measured and calculated profile patterns. ........................................40

Figure 4.3: A typical GSAS Rietveld refinement output with the R-phase refined as belonging to the $P\bar{3}$ space group (for spectrum obtained from the sample under a compressive stress of 44 MPa at 237 K) for diffracting lattice planes whose normals are parallel to the loading axis. The measured data are indicated by cross-marks and the calculated profile is indicated by the solid-line curve. The line-marks below the profile pattern indicate the positions of all possible Bragg reflections. The lower graph shows the difference between the measured and calculated profile patterns. ........................................41

Figure 4.4: Section of normalized neutron diffraction spectra corresponding to R-phase {111} lattice plane reflections (most intense) for the various experimental conditions. The reflections shown here are from diffracting lattice planes whose normals are parallel to the loading axis. .......................................................................................................45

Figure 4.5: Section of normalized neutron diffraction spectra corresponding to R-phase {411} and {511} lattice plane reflections (second most intense) for the various experimental conditions. The reflections shown here are from diffracting lattice planes whose normals are parallel to the loading axis. ........................................................................................46

Figure 4.6: R-phase (111) axial distribution plots (refined as belonging to the $P3$ space group) for the various experimental conditions. $\phi$ is the angle between the (111) plane normal and the loading axis. .........................................................................................................47

Figure 4.7: R-phase (111) axial distribution plots (refined as belonging to the $P\bar{3}$ space group), for the various experimental conditions. $\phi$ is the angle between the (111) plane normal and the loading axis. .........................................................................................................48

Figure 5.1: Macroscopic stress-strain curve at 92 K. The symbols indicate the stresses at which neutron diffraction spectra were obtained and analyzed.................................................................54

Figure 5.2: Section of normalized neutron diffraction spectra observed in both banks during loading and unloading at 92 K. (a) The diffracting lattice planes are parallel to the loading axis (bank 1). (b) The diffracting lattice planes are perpendicular to the loading axis (bank 2). ........................................................................................................55

Figure 5.3: A typical GSAS Rietveld refinement output with the R, B19' and B33 phases refined for diffracting lattice planes whose normals are parallel to the loading axis. The measured data are indicated by cross-marks and the calculated profile is indicated by the solid-line curve. The line-marks below the profile pattern indicate the positions of all possible Bragg reflections. The lower graph shows the difference between the measured and calculated profile patterns. ........................................................................56

Figure 5.4: Volume fraction of various phases obtained by Rietveld refinement as a function of applied compressive load, (a) during loading and (b) during unloading. The typical error associated with the volume fraction determination is ±3%. ........................................57
Figure 5.5: Texture evolution in the R and B19' phases represented by the texture index during (a) loading and (b) unloading.................................................................57

Figure 5.6: R-phase (111) axial distribution plots during (a) loading and (b) unloading. φ is the angle between the (111) plane normal and the loading axis..............................58

Figure 5.7: B19' (100) axial distribution plots during (a) loading and (b) unloading. φ is the angle between the (100) plane normal and the loading axis...............................59

Figure 5.8: Lattice strains obtained from single peak fitting and Rietveld analysis for (a) R-phase {111} and (b) B19' {100} planes, during loading/unloading. The arrows indicate the loading and unloading direction. The typical errors associated with determination of d-spacing and lattice parameters (Rietveld) are ±0.0003Å and ±0.0002Å respectively.......................................................61

Figure 5.9: Anisotropic strains in B33 {021} planes with respect to {010} and {001} planes, during distortion of the B33 phase. The typical errors associated with determination of strains are ±0.0002Å...............................................................................................................62

Figure 6.1: Constrained recovery of the R-phase from B19' phase during the heating of the 5% strained NiTiFe sample from 150 K to 170 K.......................................................72

Figure 6.2: Displacement in the SMARTS load frame as a function of temperature during heating of the 5% strained NiTiFe sample from 150 K to 170 K........................................73

Figure 6.3: Phase fraction evolution of the B19' and R phases during constrained recovery of the 5% strained NiTiFe sample from 150 K to 170 K........................................73

Figure 6.4: Texture evolution in the B19' and R phases represented by texture index during constrained recovery of the 5% strained NiTiFe sample from 150 K to 170 K........74

Figure 6.5: (a) B19' (100) and (b) R-phase (111) axial distribution plots planes during constrained recovery of the 5% strained NiTiFe sample from 150 K to 170 K. φ is the angle between the corresponding plane normal and the loading axis..............75

Figure 6.6: Constrained recovery of the B2 phase from the R-phase during heating of the 1% strained NiTiFe sample from 231 K to 243 K, (a) showing R{411} and R{303} combining to form B2{210} and (b) showing R{300} and R{112} combining to form B2{110}........................................................................................................76

Figure 6.7: Phase fraction evolution of the R and B2 phases during constrained recovery of the 1% strained NiTiFe sample from 231 K to 243 K.................................................77

Figure 6.8: Texture evolution in the R and B2 phases represented by texture index during constrained recovery of the 1% strained NiTiFe sample from 231 K to 243 K.........78

Figure 6.9: (a) R-phase (111) planes and (b) B2 (100) axial distribution plots during constrained recovery of the 1% strained NiTiFe sample from 231 K to 243 K. φ is the angle between the corresponding plane normal and the loading axis.............................78

Figure 7.1: High temperature furnace on the SMARTS load frame [6].................................................................84
Figure 7.2: A typical GSAS Rietveld refinement output with B19' structure refined for
diffracting lattice planes whose normals are parallel to the loading axis. The measured
data are indicated by cross-marks and the calculated profile is indicated by the solid-
line curve. The line-marks below the profile pattern indicate the positions of all possible Bragg reflections. The lower graph shows the difference between the measured and calculated profile patterns.

Figure 7.3: A typical GSAS Rietveld refinement output with B19 phase refined for diffracting
lattice planes whose normals are parallel to the loading axis. The measured data are
indicated by cross-marks and the calculated profile is indicated by the solid-line curve. The line-marks below the profile pattern indicate the positions of all possible Bragg reflections. The lower graph shows the difference between the measured and calculated profile patterns.

Figure 7.4: Room temperature measurements at the applied load in each cycle, before heating. These spectra are from the bank 2 detector, where the diffracting lattice planes are perpendicular to the loading axis.

Figure 7.5: High temperature measurements for each cycle. These are from the bank 2 detector where the diffracting lattice planes are perpendicular to the loading axis.

Figure 7.6: (a) B19 (100) and (b) B19 (011) axial distribution plots at the maximum temperatures correspond to cycles 5, 6 and 7. \( \phi \) is the angle between the corresponding plane normal and the loading axis.

Figure 7.7: Section of normalized neutron diffraction spectra showing strains between the B2 \{100\} planes for cycles 1 and 7, at the maximum temperature. These spectra are from the bank 2 detector, where the diffracting lattice planes are perpendicular to the loading axis.

Figure 7.8: Macroscopic stress-displacement response corresponding to the stress-induced martensite experiment. The symbols represent the stresses at which neutron diffraction spectra were recorded.

Figure 7.9: Development of stress-induced martensite during cycling at 498 K. These spectra are from the bank 2 detector, where the diffracting lattice planes are perpendicular to the loading axis.

Figure 8.1: Differential scanning calorimeter (DSC) response of the NiTiFe wire used.

Figure 8.2: Switch performance between 200 K and room temperature.

Figure 8.3: The NiTiFe helical spring switch in, (a) the closed (extended) position at a room temperature of 298 K and (b) the open (contracted) position at 233 K.

Figure 8.4: The shape memory alloy release mechanism in, (a) before actuation and (b) after actuation, releasing a 100 lb load.

Figure 9.1: Behavior of Ni\textsubscript{46.8}Ti\textsubscript{50}Fe\textsubscript{3.2} shape memory alloy between room temperature and 92 K.
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
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<tbody>
<tr>
<td>ADF</td>
<td>Axial Distribution Function</td>
</tr>
<tr>
<td>$A_f$</td>
<td>Austenite finish</td>
</tr>
<tr>
<td>$A_p$</td>
<td>Austenite peak</td>
</tr>
<tr>
<td>$A_s$</td>
<td>Austenite start</td>
</tr>
<tr>
<td>CBED</td>
<td>Convergent Beam Electron Diffraction</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Function Theory</td>
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<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>EDM</td>
<td>Electrical Discharge Machining</td>
</tr>
<tr>
<td>GRC</td>
<td>Glenn Research Center</td>
</tr>
<tr>
<td>GSAS</td>
<td>General Structure Analysis System</td>
</tr>
<tr>
<td>HTSMA</td>
<td>High Temperature Shape Memory Alloy</td>
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<tr>
<td>KSC</td>
<td>Kennedy Space Center</td>
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<tr>
<td>$M_d$</td>
<td>Martensite desist</td>
</tr>
<tr>
<td>MEMS</td>
<td>Micro-Electro-Mechanical Systems</td>
</tr>
<tr>
<td>$M_f$</td>
<td>Martensite finish</td>
</tr>
<tr>
<td>$M_p$</td>
<td>Martensite peak</td>
</tr>
<tr>
<td>$M_s$</td>
<td>Martensite start</td>
</tr>
<tr>
<td>NASA</td>
<td>National Aeronautics and Space Administration</td>
</tr>
<tr>
<td>SMA</td>
<td>Shape Memory Alloy</td>
</tr>
<tr>
<td>SMARTS</td>
<td>Spectrometer for Materials Research at Temperature and Stress</td>
</tr>
<tr>
<td>SPF</td>
<td>Single Peak Fit</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>UCF</td>
<td>University of Central Florida</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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CHAPTER ONE: INTRODUCTION

1.1 Motivation

Shape memory alloys (SMAs) recover to a preset shape as a result of a temperature-induced phase transformation (shape memory effect) or a stress-induced phase transformation (pseudoelasticity) that is of the first order and thermoelastic. The strain recovery associated with the shape recovery is instantaneous (limited to the speed of sound in the material) besides generating large forces (as high as 500 MPa), resulting in their application as actuators. SMA actuators have remarkable potential for use in space applications due to the following advantages [1]: (i) high power to weight and stroke length to weight ratios; (ii) combination of sensor and actuator elements in a single component; (iii) clean, debris-less, spark-free, silent operation and (iv) capability of operating in zero gravity environments with small, controlled accelerations. In NiTi SMAs, the phase transformation usually takes place between a monoclinic, so-called martensite phase and a cubic, so-called austenite phase. The addition of Fe to the NiTi system shifts the martensitic transformation to lower temperatures while introducing an intermediate trigonal R-phase.

The prime motivation for this research comes from NASA’s requirement for a cryogenic thermal conduction switch for thermal management at cryogenic temperatures, and cryogenic safety mechanisms such as self-healing gaskets, valves and seals. NiTiFe SMA based actuators are ideal candidates for these mechanisms.
There is a need for better understanding the microscopic mechanisms concerning the trigonal R-phase transformation, B19' phase transformation and associated deformation phenomena for improving the design, the scope of application ranging from cryogenic actuators to micro-electromechanical systems (MEMS). This necessitates associated characterization techniques for the investigation of microscopic deformation mechanisms coupled with phase transformations and twinning, which occur in the actuator from temperature changes and application of forces, respectively. Among available advanced techniques, *in situ* neutron diffraction during loading at varying temperatures is uniquely suited for investigating the texture, strain and phase fraction evolution in bulk polycrystalline SMA samples [2-5]. Neutron diffraction measurements have been performed *in situ* during loading at ambient and high temperatures, but not at low temperatures. Again, the underlying deformation mechanisms using neutron diffraction have been studied for shape memory alloys at around room temperature. However, a clear understanding of deformation mechanisms at cryogenic temperatures is still lacking. Accordingly, a low temperature loading capability for *in situ* neutron diffraction measurements has been implemented on the Spectrometer for Materials Research at Temperature and Stress (SMARTS) [6] at Los Alamos National Laboratory, with capabilities as low as 90 K [7].

With the new cryogenic capability, *in situ* neutron diffraction measurements were performed on Ni\(_{46.8}\)Ti\(_{50}\)Fe\(_{3.2}\) at 92 K (the lowest attainable steady state temperature). The experiments focused on three aspects on the behavior of Ni\(_{46.8}\)Ti\(_{50}\)Fe\(_{3.2}\) in the context of real world engineering applications. First, in order to study deformation mechanisms and stress-induced transformations in the R-phase in Ni\(_{46.8}\)Ti\(_{50}\)Fe\(_{3.2}\), measurements were performed at a constant temperature of 92 K under external loading. Second, with the objective of examining
one-time, high-stroke, actuator applications (such as in safety valves), a Ni$_{46.8}$Ti$_{50}$Fe$_{3.2}$ sample was strained to approximately 5% at 92 K and subsequently heated to full strain recovery under a constant load. Third, with the objective of examining cyclic, low-stroke, actuator applications (such as in cryogenic thermal switches), a Ni$_{46.8}$Ti$_{50}$Fe$_{3.2}$ sample was strained to 1% at 92 K and subsequently heated to full strain recovery under a constant load. Neutron diffraction spectra were recorded at suitable stress or temperature intervals during these experiments that assisted in the monitoring of the phase-specific strain, texture and volume fraction evolutions.

In theory, the complete strain tensor can be determined by measuring strain in at least six orientations. Additionally, six banks of detectors would help in determining the preferred orientation in a textured sample satisfactorily. However, the unique combination of controlling temperature and external loads, limits the SMARTS diffractometer at Los Alamos National Laboratory where the present study was conducted, to only two banks of detectors [6]. There is a need to establish a methodology under these constraints, to quantitatively assess the data collected from NiTiFe systems based on time-of-flight neutron diffraction spectra acquired using SMARTS, under the influence of external loading and changes in temperature [8]. A variety of refinement techniques are available to analyze the diffraction data in general and the present study uses one such method, Rietveld analysis. Of the programs available for Rietveld analysis, GSAS (General Structure Analysis System) [9] is chosen for the present study in obtaining the texture, phase fraction, strain and crystal structure parameters. Additionally, the research methodology for Ni$_{46.8}$Ti$_{50}$Fe$_{3.2}$ shape memory alloys has been applied to experiments performed on new high temperature based Ni$_{29.5}$Ti$_{50.5}$Pd$_{20}$ shape memory alloys.
In addition to the scientific investigation using neutron diffraction measurements and subsequent analyses, efforts were focused on the engineering development of selected cryogenic NiTiFe based actuator devices. The engineering aspects were focused on the development of a (i) NiTiFe based thermal conduction switch that minimized the thermal gradient in the actuator element, (ii) NiTiFe based thermal conduction switch that incorporated the actuator element in the form of helical springs, and (iii) a NiTiFe based low-temperature release mechanism.

1.2 Organization

The work in this dissertation is organized as follows: Chapter 2 is a literature survey of shape memory alloys and briefly introduces the neutron diffraction technique and neutron spectra analysis. Chapter 3 discusses the cryogenic neutron diffraction setup on SMARTS, overview of experiments and the qualitative results. Chapter 4 addresses the ambiguity in the structure of the R-phase through diffraction spectra analyses [8]. Chapter 5 discusses the deformation behavior observed during uniaxial compressive loading of NiTiFe at 92 K based on Rietveld refinements. Chapter 6 provides a quantitative analysis of the two constrained recovery experiments performed on NiTiFe compression samples, i.e., from the B19' phase to the R-phase and the R-phase to the B2 phase. Chapter 7 is an extension of the research methodology presented in the previous chapters to the experiments performed on Ni\textsubscript{29.5}Ti\textsubscript{50.5}Pd\textsubscript{20} shape memory alloys using \textit{in situ} neutron diffraction. These include load-bias experiments and stress-induced martensite experiments. Chapter 8 presents engineering aspects and development of NiTi based actuators [10, 11]. Finally, Chapter 9 presents a summary and conclusions.
CHAPTER TWO: LITERATURE REVIEW

This chapter is a selected review of the literature on NiTi/NiTiFe shape memory alloys and briefly introduces neutron diffraction and neutron spectra analysis. Due to the stand-alone nature of each chapter in this dissertation, a more detailed review is available in the individual chapters as it relates to the observations.

2.1 Shape Memory Alloys

“Shape memory alloys” (SMAs) can recover from certain changes in shape or accumulated strain as a result of a temperature-induced phase transformation (shape memory effect) or a stress-induced phase transformation (pseudoelasticity). Typically, shape memory alloys accommodate extensive deformations (e.g., up to 8% strain) in their low-temperature, “weaker phase” by detwinning or by undergoing a stress-induced phase transformation to the “weaker phase” from their high temperature “stronger phase”. The strain recovery is instantaneous besides generating large forces (as high as 500 MPa), resulting in their application as actuators [12-15]. Even though a wide range of alloys are found to exhibit the shape memory effect or pseudoelasticity, NiTi alloys are of practical interest owing to a superior combination of material properties coupled with substantial strain recovery (up to 8%). The properties of SMAs are discussed below.
2.1.1 Shape Memory Effect

SMAs undergo a first-order (involving latent heat), thermoelastic martensitic transformation that is responsible for the shape memory effect. A martensitic transformation is defined as a lattice transformation where a shearing deformation is involved as a result of cooperative movement of atoms [12]. Although the transformation involves distortion of the parent unit cell, there is no diffusion of atoms associated with it. Due to this cooperative movement (displacive), there exists a one-to-one lattice correspondence between the parent austenite phase and the resulting martensite phase. In thermoelastic martensitic transformations, the martensite crystals, once nucleated, will grow or shrink corresponding to a decrease or increase in temperature. On the contrary, non-thermoelastic martensitic transformations proceed with the nucleation and growth of martensite within the parent phase as the temperature decreases, and an increase in the temperature results in the nucleation and growth of the parent phase within the martensitic phase (reverse transformation) [12].

When an SMA in its high-temperature, austenite phase is cooled (Figure 1.1), the martensitic transformation commences at $M_s$ (martensitic start temperature) and completes at $M_f$ (martensitic finish temperature). Upon heating (Figure 1.1), the reverse transformation from martensite to austenite begins at $A_s$ (austenitic start temperature). At $A_f$ (austenitic finish temperature), it completely transforms back to austenite [16]. Composition and thermo-mechanical treatments can significantly influence these transformation temperatures.
A certain number of symmetry-related variants are possible in the martensitic phase due to its low crystallographic symmetry. The microstructure of martensite shows different morphologies such as lath, plate, wedge or square shapes [18-20]. These morphologies have at least two variants (including habit plane variants) oriented in a certain fashion. The type of morphology depends on the crystal system as well as the stress state (both internal and external). For example, Bhattacharya [20] studied a wedge-like morphology and found that this microstructure is possible only as a coherent, energy minimizing microstructure when certain restrictive conditions on the lattice parameters are satisfied.

The self-accommodation (no net change in macroscopic shape) of martensite in SMAs helps produce zero macroscopic strain by orienting the variants of resultant martensite in various morphologies. When external stress is applied on SMAs in the martensitic state, an internal
rearrangement (consequence of energy minimization) takes place in such a way that the strain can be accommodated. This internal rearrangement take place in two ways: (i) the realignment of differently oriented morphologies in the favor of external stress (martensite reorientation in some cases [19]), and (ii) the realignment of different variants within a single morphology such that twinning or variant coalescence (detwinning in some cases [19]) takes place. Strictly speaking, the realignment of the morphology is not possible unless the crystal structure of the matrix surrounding the morphology, in addition to that inside the morphology, twins. In other words, realignment of individual morphologies, variant coalescence and/or twinning due to variant realignment takes care of the shape change without introducing dislocations (that result in permanent deformation). This strain-accommodation manifests as the “mushy” behavior of the martensitic phase. The amount of strain-accommodation depends on the number of variants a crystal system can form. For example, monoclinic martensite has 12 variants in contrast to 4 variants (excluding habit plane variants) in the trigonal R-phase, resulting in about 8% strain recovery for monoclinic martensite compared to about 1% in the R-phase in NiTi based alloys. During the reverse transformation, each variant of martensite transforms back to a single variant of austenite, resulting in the shape memory effect.

### 2.1.2 Superelasticity

Another unique property of certain shape memory alloys is superelasticity or pseudo-elasticity. In the presence of applied stress, the parent high symmetry structure undergoes a stress-induced transformation rather than slip. This happens at relatively lower temperatures (above the $M_s$ temperature) where the stress-induced transformation is favored rather than slip,
caused by the movement of dislocations. The transformed region when compared to the matrix (parent) has a different crystal structure that is of lower symmetry. Thus the presence of external stress promotes martensitic transformation. At temperatures above $M_d$ (martensite desist), the stress-induced martensite no longer forms (Figure 1.1). In the case of pseudoelasticity, the martensite formed from transformation of the parent structure is stable only in the presence of applied stress, in the absence of it, martensite reverts to the parent phase. However, at temperatures lower than $A_s$, the martensite formed can be stabilized.

2.2 **Shape Memory Alloy Actuators**

Shape memory alloys (SMAs) have potential for use in actuator elements due to the following advantages [1,17]: (i) They combine sensory and actuation functions. The SMA element inherently senses a change in temperature and actuates by undergoing a shape change as a result of a phase transformation. Consequently, the need for external electronic sensors and control is eliminated. (ii) They function in a clean, debris-less, spark-free manner. The shape change that is responsible for the actuator displacement is again an inherent material property. It is not associated with moving parts that require lubrication or electrical signals with a potential to spark. (iii) They have high power/weight and stroke length/weight ratios. The operating range includes strain and stress limits of 8% and 700 MPa, respectively, depending on the number of required cycles. (iv) They possess the ability to function in zero-gravity environments with small, controlled accelerations. The displacement strains are a result of a thermally induced phase transformation which can be controlled by the heat transfer rate. As a result, end-of-deployment shock loadings (associated with spring deployed structures) can be avoided in SMA-
based deployable structures, thus eliminating the overall complexity by avoiding the use of dampers. (v) They are reliable and offer design flexibility. SMA actuators can function in a linear or rotary manner (or a combination of the two). Typically, an SMA actuator utilizes the shape memory effect to generate force and motion. When compared to electronically controlled thermal actuators comprising a temperature sensing device (e.g., thermistor), an electronic processor (e.g., IC circuit) and electric actuator (e.g., motor), SMA actuators have fewer parts, higher reliability and lower fabrication costs. SMA actuators can be of one-way or two-way type (Figure 1.2).

![Diagram of SMA actuators](image)

Figure 2.2: Types of SMA actuators (a) one-way actuator, (b) biased two-way actuator, and (c) differential two-way actuator [17].

One-way SMA actuators (Figure 1.2a) are used where one-time actuation is necessary such as in safety devices, couplings, release mechanisms etc. In a one-way actuator, the SMA element acts against some force when the temperature reaches a pre-set temperature. Two-way
actuation can occur either in a biasing mode (Figure 1.2b) or a differential mode (Figure 1.2c). The biasing mode uses a bias spring opposing the SMA spring for actuation in either direction. When the temperature of the SMA element rises to a pre-set temperature, the SMA element being stronger as it undergoes a phase transformation, will act against the bias spring force actuating in one direction. As the temperature of the SMA element drops below a certain temperature, the bias spring force overcomes the SMA element force, thus acting in the opposite direction. Biasing mode operation is more commonly employed and offers enhanced flexibility in design. In the differential mode of operation, the bias spring is substituted by another SMA spring. Here actuation in either direction can be achieved by appropriately heating or cooling either of the two SMA elements. Applications requiring precise movement and high accuracy make use of the differential mode [21].

NiTi based SMAs are a preferred choice for designing actuators due to the following advantages: (i) able to accommodate large strains (up to 8%), (ii) high corrosion resistance [12, 16, 22], (iii) capable of operating in a relatively wide range of temperatures by slightly varying the composition or thermo-mechanical treatments [23-27], (iv) superior mechanical properties compared to other SMAs [28] and (v) high fatigue life of $\sim 10^6$ cycles when strains are restrained to $\sim 1\%$ [29].

### 2.3 NiTi Shape Memory Alloys

Near equiatomic NiTi undergoes a temperature-induced phase transformation close to room temperature, between a monoclinic martensite (B19' structure) and a cubic austenite (B2 structure). NiTi alloys exhibit behavior on the basis of composition (variation in Ni/Ti ratio or
addition of a third element replacing either Ni or Ti) and the history of thermo-mechanical treatments. The behavior can include one or more combinations of a shift in transformation temperatures, change in martensite structure, appearance of intermediate phases and changes in hysteresis. Accordingly, the shape memory effect and the superelastic response in NiTi alloys are subjected to compositional modifications and thermo-mechanical treatments.

2.3.1 Hysteresis in NiTi Alloys

Typically, there is hysteresis between the forward and reverse transformations in shape memory alloys. The transformation hysteresis is a result of elastic strain energy dissipation, the energy associated with frictional resistance to interface motion and similar dissipative processes [30-32]. Generally, thermal hysteresis ranges from 1.5-2 K for R-phase transformations, 10-15 K for certain NiTiCu alloys, 20-60 K for binary NiTi alloys and in excess of 100 K for NiTiNb alloys [22, 30]. Aspects such as alloy composition, thermal cycling, thermo-mechanical treatments, pre-deformation and external load influence the transformation hysteresis.

2.3.2 NiTiFe Alloys

The addition of Fe to the NiTi system decreases the martensitic transformation temperature and further introduces an intermediate trigonal R-phase. The cubic austenite to trigonal R-phase transformation in NiTiFe shape memory alloys offer a practical temperature range for actuator operation at low temperatures, as it exhibits a narrow temperature-hysteresis with a desirable fatigue response [33].
2.3.3 R-Phase in NiTi Alloys

The R-phase is considered to be derived from a rhombohedral distortion of the parent, cubic austenite phase [34-36]. The R-phase transformation exhibits a temperature hysteresis as low as 1.5 K, useful in designing certain types of actuators that operate in narrow temperature ranges. The maximum recoverable strain (approximately 1%) during the R-phase transformation is fairly low compared to the monoclinic B19' phase transformation [37]. However, the fatigue life of the R-phase is very good compared to the B19' phase [38].

The formation of the R-phase and the subsequent formation of the monoclinic B19' phase has been attributed to the presence of defects in the form of dislocations, precipitates, and/or impurity elements. The R-phase in NiTi based SMAs can be achieved by suppressing the martensitic transformation [23,39], i.e., by: (i) increasing the Ni content, (ii) ageing at lower temperatures (573-773 K) after solution treatment [40-42] to form Ni$_4$Ti$_3$ precipitates, (iii) annealing below the recrystallization temperature immediately after cold-working [40,41], (iv) adding a third element such as Fe, Co or Al [41,43] and (v) thermal cycling [44-46].
2.4 Neutron Diffraction

Figure 2.3: Isotropic scattering of neutron beam by a nucleus.

Whereas both neutrons and x-rays (laboratory sources) can be used for materials characterization, neutrons can provide information on the bulk behavior in materials. The most obvious difference between neutrons and x-rays is that neutrons interact with atoms via short-ranged nuclear interactions, as opposed to electron interactions in the case of x-rays. Since the nucleus is extremely small compared to the electron cloud in an atom, the neutrons can penetrate a material very deeply before being scattered (Figure 2.1). Crystal structure, residual stress, phase fraction in a multiphase system and texture are few examples of the information that can be obtained using this technique [47]. Furthermore, in situ neutron diffraction allows researchers to study in real time the mode of deformation mechanism in material systems, such as elastic deformation, twinning or stress-induced phase transformation. This is especially advantageous in the study of SMA alloys which twin at low-temperatures to accommodate strains and undergo multiple step phase transformations that are thermally or stress-induced.
2.4.1 Rietveld Refinement

The Rietveld refinement procedure was originally introduced for the analysis of constant wavelength neutron diffraction data [48, 49] and was subsequently used for the refinement of x-ray diffraction patterns in the late 1970s. In Rietveld analysis, the method of least squares is used to obtain the best possible fit between the entire observed pattern with the corresponding calculated pattern. This has many advantages; significant among them are the analysis of elastic strains owing to the change in lattice plane positions as a result of external loading, an account of the phase fraction evolution or twinning corresponding to changes in peak intensities and the analysis of preferential orientation (texture).

Based on the crystal structure of the material being refined, the intensity, $Y_{ei}$, can be calculated at every point in the spectrum and the position of the observed lattice reflections can be predicted. The calculated intensity depends on numerous factors and can be determined from the expression [50]:

$$Y_{ei} = s \sum_{K} L_K |F_K|^2 \phi (2\theta_i - 2\theta_K) P_K A + Y_{bi}$$  \hspace{1cm} (2.1)

where, $s$ is the scaling factor, $K$ is the $h$, $k$, and $l$ Miller indices for a Bragg reflection, $L_K$ includes the Lorentz, polarization and multiplicity factors, $F_K$ is the structure factor, $\phi$ is the reflection profile function, $2\theta_i$ is the observed position of the Bragg peak, $2\theta_K$ is the calculated position of the Bragg peak corrected for the zero-point error in the detector, $P_K$ is the preferred orientation function, $A$ is an absorption factor and $Y_{bi}$ is the background intensity at the $i^{th}$ step of the iteration process. Thus in order to obtain a good fit between the experimental and calculated patterns, a number of atom position, thermal, site occupancy, lattice, background, instrumental
and profile parameters are typically refined, among others. The profile function may include effects from microstrain and crystallite size related peak broadening, specimen and instrument source and geometry. The presence of preferred orientation necessitates the refinement for texture. For example in GSAS [9], two different models are used for the refinement of texture. The first, following the formulation of March and Dollase [51, 52], uses a cylindrical symmetrical version of an ellipsoidal model to describe texture. The second uses a generalized spherical-harmonic [53] description of the orientation distribution function. However, earlier studies have shown that the March-Dollase texture formulation is inadequate to account for evolving texture during martensitic transformations on SMARTS [3]. Accordingly, the generalized spherical-harmonic formulation is preferred over the March-Dollase formulation in this work. The sequence and/or number of parameters being simultaneously refined can influence whether the least square minimization algorithm settles in a local minimum as opposed to a global minimum. Thus in order to avoid arriving at such false minima [50], there is a need to both quantitatively and qualitatively evaluate the accuracy of the refinement. A qualitative check may include visual inspections as well as ensuring that the model considered has all the necessary parameters to describe both structural and diffraction effects. A quantitative check may utilize representative statistical parameters. Such statistical parameters include crystallographic residual factors ($R_{wp}$, $R_p$, etc.) and goodness of fit ($\chi^2$) that can help judge the quality of the fit [9].
2.4.2 Single Peak Fitting

The single peaks corresponding to specific $hkl$ reflections in the diffraction pattern can be fitted individually for lattice spacing $d_{hkl}^{\text{hkl}}$, to follow strains specific to different grain orientations with respect to the unloaded state. The strain for a specific $hkl$ plane is then given by:

$$
\varepsilon_{hkl} = \frac{d_{hkl}^{hkl} - d_{0}^{hkl}}{d_{0}^{hkl}} \tag{2.2}
$$

where $d_{0}^{hkl}$ is the corresponding “strain free” spacing. However, a small nominal compressive stress of 8 MPa (this was needed to keep the compression sample aligned at the SMARTS load frame) was used as the “strain free” unloaded state, ignoring the pre-existing intergranular stresses. The RAWPLOT program in GSAS [9] was used to fit the peaks individually.

Additionally, RAWPLOT allows quantification of intensity for a set of individual peak reflections. The ratio of intensities of peaks with respect to the unloaded state can follow the texture evolution. The ratio of peak intensity (normalized) for a specific $hkl$ plane is then given by:

$$
I_{hkl}^{\text{hkl}} = \frac{I_{hkl}^{\text{hkl}}}{I_{0}^{\text{hkl}}} \times \frac{I_{0}^{\text{Spectra}}}{I_{0}^{\text{Spectra}}} \tag{2.3}
$$

where $I_{hkl}^{\text{hkl}}$ is the intensity of a specific $hkl$ plane at a given stress state, $I_{0}^{\text{hkl}}$ is the corresponding unloaded state, $I_{0}^{\text{Spectra}}$ is the integrated peak intensity of the entire spectra at the corresponding stress state and $I_{0}^{\text{Spectra}}$ is the integrated peak intensity of the entire spectra corresponding to unloaded state. The normalization procedure accounts for the different count times while acquiring neutron diffraction spectra.
CHAPTER THREE: CRYOGENIC NEUTRON DIFFRACTION SETUP AND MEASUREMENTS AT 92 K

This chapter presents an overview of the cryogenic neutron diffraction setup [7] implemented on the Spectrometer for Materials Research at Temperature and Stress (SMARTS), and the experiments performed on Ni\textsubscript{46.8}Ti\textsubscript{50}Fe\textsubscript{3.2} at 92 K. The deformation behavior of a Ni\textsubscript{46.8}Ti\textsubscript{50}Fe\textsubscript{3.2} sample was studied under uniaxial compressive loading at 92 K. In addition, constrained recovery of the sample was studied that simulated the functioning of an SMA as an actuator under a bias force, by controlled heating of the sample at a constant load of 50 MPa from 92 K to room temperature. Neutron diffraction spectra were recorded at appropriate intervals during these experiments, facilitating the monitoring of the strain, texture and phase fraction evolution and thus the microscopic deformation mechanisms. The results presented here identify and outline the fundamental mechanisms and phenomenology, with details presented in subsequent chapters.

3.1 Introduction

Shape memory alloys undergo a first-order thermoelastic martensitic phase transformation as a consequence of an overall free-energy minimizing thermodynamic approach. In polycrystalline shape memory alloys, the phase transformation driven by chemical free-energy change competes with elastic strain energy, frictional resistance to interface motion and similar dissipative processes, which manifests as thermal hysteresis [31,32]. The unique lattice correspondence between austenite (parent) and martensite phases and strain-accommodation by
twinning or variant coalescence (detwinning) are responsible for the phenomena of shape memory and pseudoelasticity in shape memory alloys [12]. NiTiFe shape memory alloys are reported to undergo two-stage martensitic transformation, initially from a cubic austenite phase to a trigonal R-phase and subsequently to a monoclinic phase. By recourse to neutron diffraction technique at cryogenic temperatures under the application of stress in NiTiFe alloys, the phase transformations and deformation mechanisms were probed.

To investigate deformation mechanisms in Ni$_{46.8}$Ti$_{50}$Fe$_{3.2}$ at cryogenic temperatures using in situ neutron diffraction measurements, a novel 90 K loading capability [7] was implemented on the Spectrometer for Materials Research at Temperature and Stress (SMARTS) [6] at Los Alamos Neutron Science Center. Experiments were performed at 92 K (lowest possible steady state temperature attainable) that includes investigation of deformation mechanisms as well as constrained recovery experiments. This chapter is an overview of the qualitative observations made during these experiments. The quantitative analyses of the experiments are presented in Chapters 4 through 6.

### 3.2 Experimental Procedure

#### 3.2.1 Neutron Diffraction Measurements on SMARTS

The neutron diffraction measurements were conducted on SMARTS, a third generation neutron diffractometer at Los Alamos National Laboratory [6]. SMARTS (Figure 3.1) has two banks of detectors, bank 1 oriented for lattice planes whose normals are perpendicular to the axis of loading and bank 2 oriented for lattice planes whose normals are parallel to the axis of loading. The high temperature vacuum furnace and load frame facilitate research on materials
under high loads (250 kN) and high temperatures (1773 K). Recently, a cryogenic loading capability (Figure 3.2) was incorporated on the SMARTS diffractometer by the UCF research group [7], principally developed for the study of NiTiFe shape memory alloys. With the new cryogenic setup, samples can be cooled to temperatures as low as 90 K during loading and neutron spectra acquisition.

![Schematic of the SMARTS diffractometer](image)

Figure 3.1: Schematic of the SMARTS diffractometer showing the incident and diffracted neutron beam during the application of compressive stress on the sample.

### 3.2.2 Cryogenic Capability on SMARTS

The cryogenic capability on SMARTS (Figure 3.2) relies on conductively cooling the sample while in contact with the load-applying compression platens. The capability primarily consists of an aluminum vacuum chamber that minimizes convective heat losses, and prevents freezing of moisture and other gases in the atmosphere at low temperatures. It has two identical flanged cylindrical ports that were exactly opposite to each other that accommodated the insertion of two compression platens, connected to the push rods of the mechanical loading
system on SMARTS. The path for neutrons is provided via four rectangular windows at 90° to each other and positioned at 45° with respect to the flanged cylindrical ports.

![Diagram of SMARTS diffractometer with cryogenic setup](image)

Figure 3.2: Schematic of the SMARTS diffractometer with the cryogenic setup (top view) [8].

The cooling system consisted of conductively cooling the test sample via the load-applying platens that in turn were cooled by circulating liquid nitrogen through the internal cooling channels. A thermally insulating coupling system isolated the cold compression platens from the warm push rods (due to heat generated from the hydraulic actuators) of the SMARTS load frame. The cooling system consisted of a temperature control system that maintained a constant temperature under variable loading and also varied the temperature at constant loading. The temperature control system consisted of a custom program developed using LabVIEW software, a set of thin surface heaters mounted on the conical surface of each platen and thermocouples mounted at various locations on the test sample, platens, inlet and vent locations of the liquid nitrogen lines. The controller collected temperature data from the thermocouples.
and maintained the temperature through surface heaters. The temperature control system allowed the temperature of the test sample to be stabilized (± 1 K) at any temperature specified by the operator, at or above 92 K. This further required regulating the liquid nitrogen flow valves manually.

### 3.2.3 Sample Fabrication

A Ni$_{46.8}$Ti$_{50}$Fe$_{3.2}$ billet (nominal composition), fabricated by vacuum-induction-melting and vacuum-arc-remelting, was procured from Special Metals, NY. Cylindrical samples of 10 mm diameter by 24 mm length were cut from the billet by electrical discharge machining (EDM) for the neutron diffraction measurements. The samples were then solutionized at 1023 K for 1 hour in a vacuum furnace and immediately oil quenched to room temperature. Differential scanning calorimetry (DSC) at a rate of 0.33 Ks$^{-1}$, under nitrogen cover gas was used to determine the start and finish of the R-phase transformation from austenite and the corresponding reverse transformation to austenite from the R-phase. These temperatures were determined to be 236, 223, 227 and 239 ± 2 K, respectively. The transformation to monoclinic (B19') phase was below 120 K and was hence outside the operating range of the calorimeter used.
3.2.4 Experimental Temperature and Strain Parameters

The scientific study encompassed three aspects of the behavior of NiTiFe:

i. In order to study deformation mechanisms in the R-phase in NiTiFe, measurements were performed at a constant temperature of 92 K under external loading.

ii. With the objective of examining NiTiFe in cyclic, low-stroke, actuator applications (such as in cryogenic thermal switches), a NiTiFe sample was strained to 1% at 92 K and subsequently heated to full strain recovery under a constant external load.

iii. With the objective of examining NiTiFe in one-time, high-stroke, actuator applications (such as in safety valves), a NiTiFe sample was strained to approximately 5% at 92 K and subsequently heated to full strain recovery under a constant external load.

Neutron diffraction spectra were recorded at suitable stress and time intervals during these experiments, which assisted in the monitoring of the phase-specific strain, texture and phase fraction evolution using Rietveld refinements.

3.3 Results and Discussion

While cooling the sample to 92 K, the cubic B2 (austenite) transformed to the trigonal R-phase. Figure 3.3 shows the comparison of diffraction spectra for the B2 phase (cubic) at room temperature and the R-phase (trigonal) at 92 K, in the no-load condition (nominal holding stress of 8 MPa). The R-phase spectra are normalized with respect to the austenite spectra. Certain regions of the diffraction spectra are magnified for clarity. During the austenite to R-phase transformation, the \(\{110\}_{B2}\) peak splits to \(\{112\}_R\) and \(\{300\}_R\), respectively (Figure 3.3). This is
due to the unit cell elongation in the <111> crystallographic direction of the B2 phase and interpreted as the manifestation of the R-phase [54]. Similarly, the \{210\}_{B2} peak splits to \{303\}_R and \{411\}_R, respectively (Figure 3.3).

Figure 3.3: Comparison of the diffraction patterns obtained at room temperature and at 92 K, in the no-load condition (nominal holding stress of 8 MPa).

Figure 3.4: Splitting of \{112\}_R and \{300\}_R peaks of diffraction patterns observed at 216 K and at 92 K.
The splitting increases with cooling, due to a change in the angle ($\alpha$) of the trigonal unit cell. This is evident from comparing the diffraction patterns obtained at 92K with that at 216 K [55] (Figure 3.4). However, after a certain temperature, the angle ($\alpha$) becomes constant and so does the splitting.

Figure 3.5: Macroscopic stress-strain curve obtained ex situ at 92 K.

Once the sample was stabilized at 92 K, it was loaded to study the associated deformation mechanisms. An ex situ stress-strain curve (Figure 3.5) was generated at 92 K using a strain gauge, which was used to correlate the macroscopic behavior with the microscopic behavior obtained from neutron diffraction investigations.
When loaded at 92 K, the emergence of stress-induced B19' phase was noticed at a low stress of 68 MPa (Figure 3.6) with strain redistribution (not twinning) among lattice planes in the R-phase (Figure 3.7). This is because the propensity for R-phase to undergo a phase transformation (due to lower free-energy of monoclinic phase under stress at 92 K) is higher than
twinning. Furthermore, the bulk of the R-phase was transformed to B19' phase at approximately 5% strain and the transformed B19' phase was stabilized during unloading at a holding load of 8 MPa (Figure 3.6), unlike a near complete recovery to R-phase observed at 216 K [55]. This behavior can be attributed to the fact that the B19' phase was stabilized at a temperature lower than the reverse transformation temperature of B19' phase to R-phase, arising from the thermal hysteresis (Figure 3.8).

![Diagram](image)

Figure 3.8: Transformation hysteresis between B19' phase and R-phase, typical of shape memory alloys. The dotted lines qualitatively represent the region where the experiments were conducted.

### 3.3.1 Constrained Recovery Experiments

A NiTiFe compression sample was strained to 1% at 92 K and subsequently heated to full strain recovery under a constant load to simulate the working of cyclic, low-stroke actuators (such as in cryogenic thermal switches [29,33]). In another experiment, a NiTiFe compression sample was strained to approximately 5% (the R-phase transformed to B19' phase in the process) at 92 K and subsequently heated to full strain recovery under a constant load to simulate the working of one-time, high-stroke actuators (such as in a safety valves). The constrained recovery
experiments of 5% strained sample showed a significant recovery of 4% strain between 150 K and 170 K, even more significant was the bulk strain recovery of approximately 2% that took place between 160 K and 162 K (Figure 3.9). The Rietveld refinements using GSAS [9] suggested the phase fractions of B19' phase (space group P1121/m) and R-phase (space group P3) at 160 K to be 83.3 vol. % and 16.7 vol. % respectively, and at 162 K to be 46.3 vol. % and 53.7 vol. %, respectively.

Figure 3.9: Constrained recovery of the R-phase from the B19' phase during the heating of the 5% strained sample from 150 K to 170 K.

### 3.3.2 Elastic Modulus of the R-phase

The elastic moduli of various planes in the R-phase were calculated from the lattice strain observed (Figure 3.7), below 68 MPa, during loading at 92 K. The strain for a specific \( hkl \) plane was calculated using equation (2.2). The estimated elastic modulus at 92 K varied between 92.9 GPa for \{111\} planes to 113.8 GPa for \{322\} planes. A macroscopic stress-strain curve (Figure 3.4) was generated from the strain gauge readings and load frame data obtained at 92 K. The macroscopic elastic modulus (determined at stresses below 68 MPa) of the R-phase was found to be 90.9 GPa, in agreement with that obtained from the neutron measurements. The lack of
twinning at 92 K was consistent with the agreement between macroscopic and microscopic measurements [56].

### 3.3.3 Observation of Orthorhombic B33 Phase

One of the major contributions of the cryogenic neutron diffraction experiments was the experimental identification of the orthorhombic B33 phase at 92 K. The orthorhombic B33 phase has been theoretically predicted in NiTi from density function theory (DFT) calculations [57, 58], but has never been observed experimentally until now. The orthorhombic B33 phase was identified while observing a peak movement (Figure 3.10) between \{111\}_R and \{100\}_{B19'} peaks in the diffraction spectra collected during loading. Huang et al. [57] reported from DFT calculations that the stress-free martensite in NiTi has a base-centered orthorhombic symmetry (Cmcm) rather than the widely reported monoclinic symmetry (P2$_1$/m or P112$_1$/m). They found that the angle of the monoclinic structure associated with the minimum energy distortion is not the experimentally reported $\gamma \approx 98^\circ$, but rather having $\gamma = 107^\circ$. However, when $\gamma = 107^\circ$ it corresponds to base centered orthorhombic symmetry (B33) (Figures 3.11 and 3.12) rather than monoclinic symmetry. They proposed that the experimentally reported and observed monoclinic structure ($\gamma \approx 98^\circ$) of martensite is stabilized by internal residual stresses as well as external applied stresses.
Figure 3.10: Tilting of \{021\}_{B33} during loading at 92 K, observed as a peak movement between \{111\}_R and \{100\}_{B19'}.

Figure 3.11: Crystallographic correspondence between the cubic B2 and the orthorhombic B33 structures.

Figure 3.12: Left – the monoclinic B19' unit cell with $\gamma = 97^\circ$. Right – the monoclinic B19' unit cell with $\gamma = 107^\circ$ and the orthorhombic B33 unit cell. The green rectangle shows the B33 \{021\} plane. (Figures modified from Huang et. al., Nature Materials, 2003 [57]).
During cooling to 92 K in the no-load condition (nominal holding stress of 8 MPa), Ni$_{46.8}$Ti$_{50}$Fe$_{3.2}$ consisted primarily of the R-phase with approximately 17 vol. % monoclinic phase and approximately 12 vol. % orthorhombic phase. These values were estimated from Rietveld refinements using GSAS [9] of the acquired neutron diffraction pattern. We infer that the orthorhombic martensite was formed in stress-free areas, while monoclinic martensite in areas that experience internal stresses [57]. Upon loading, the R-phase undergoes a stress-induced transformation to monoclinic B19' phase. Furthermore, since the orthorhombic B33 is unstable under stress (shear or hydrostatic) [57] certain planes of B33 phase gradually distort at higher applied stresses. This distortion can be viewed as a change in monoclinic angle from $\gamma = 107^\circ$ to $\gamma = 97^\circ$ (Figure 3.12). Figure 3.10 shows the tilting of $\{021\}_{B33}$ planes associated with the distortion, in the diffraction spectra. Similar tilting was also observed in the $\{042\}_{B33}$ planes. The tilting of these planes starts at approximately 114 MPa and completes at approximately 210 MPa. Using Rietveld refinements, the lattice parameters for B33 at a holding stress of 8 MPa were determined to be $a = 2.911\text{Å}$, $b = 9.393\text{Å}$, $c = 3.806\text{Å}$, $\alpha = \beta = \gamma = 90^\circ$. These values are comparable to those predicted from theoretical DFT calculations.

### 3.4 Conclusions

A novel cryogenic capability was implemented on the Spectrometer for Materials Research at Temperature and Stress (SMARTS) at Los Alamos National Laboratory. The deformation behavior of Ni$_{46.8}$Ti$_{50}$Fe$_{3.2}$ was studied at 92 K using this capability.

i. The cubic B2 phase transformed to trigonal R-phase during cooling. During the transformation, the $\{110\}_{B2}$ peak split into $\{112\}_{R}$ and $\{300\}_{R}$, respectively. This was
due to the unit cell elongation in the <111> crystallographic direction of the B2 phase associated with the formation of R-phase. A very similar splitting was observed for the \{210\}_{B2} peak to \{303\}_R and \{411\}_R, respectively. The splitting increased with cooling and was evident from comparing the diffraction patterns obtained at 92K with that at 216 K.

ii. When loaded at 92 K, the emergence of a stress-induced B19' phase was noticed at a low stress of 68 MPa, with strain redistribution among lattice planes in the R-phase. Bulk of the R-phase was transformed to the B19' phase at approximately 5% strain and the transformed B19' phase was stabilized during unloading to a holding load of 8 MPa. This behavior was attributed to the fact that the B19' phase was be stabilized at a temperature lower than the reverse transformation temperature of the B19' phase to the R-phase, arising from the thermal hysteresis.

iii. The constrained recovery experiments of the 5% strained sample showed a significant recovery of 4 % strain between 150 K and 170 K, and with approximately half of that occurring between 160 K and 162 K.

iv. The estimated elastic modulus of lattice planes varied between 92.9 GPa for \{111\} planes to 113.8 GPa for \{322\} planes. This was in excellent agreement with the macroscopic elastic modulus of 90.9 GPa. The lack of twinning in the R-phase below 68 MPa was consistent with this agreement between macroscopic and microscopic measurements.

v. A base-centered orthorhombic B33 phase was experimentally identified for the first time in NiTi based alloys. The orthorhombic B33 phase was observed while identifying a peak movement between \{111\}_R and \{100\}_{B19} peaks in the diffraction spectra collected during
loading. During cooling to 92 K in the no-load condition (nominal holding stress of 8 MPa), Ni$_{46.8}$Ti$_{50}$Fe$_{3.2}$ consisted primarily of the R-phase with approximately 17 vol. % monoclinic phase and approximately 12 vol. % orthorhombic phase. It was inferred that orthorhombic martensite was formed in stress-free areas, while monoclinic martensite in areas that experienced internal stresses. Upon loading, the R-phase underwent a stress-induced transformation to monoclinic B19' phase. Since the orthorhombic B33 was unstable under stress, certain planes of the B33 phase gradually distorted at higher applied stresses. This distortion was viewed as a change in the monoclinic angle from $\gamma = 107^\circ$ to $\gamma = 97^\circ$. The tilting of $\{021\}_{B33}$ planes was observed in the diffraction spectra, which started at approximately 114 MPa and completed at approximately 210 MPa.
CHAPTER FOUR: CHOICE OF R-PHASE SPACE GROUP

This chapter describes a methodology to quantify the textures, strains and phase fractions using the General Structure Analysis System (GSAS) [9] for Rietveld refinement of neutron diffraction spectra [8]. Emphasis is placed on evaluating the choice of P3 and P\textsuperscript{3} space groups for the R-phase in the refinements and the impact of this choice on the quantitative analyses of spectra. Furthermore, this chapter sets the stage for using Rietveld refinement of R-phase in NiTiFe during mechanical loading at low temperatures and the same methodology has been followed for Rietveld refinement of the R-phase in subsequent chapters.

4.1 Introduction

Shape memory alloys are incorporated as actuator elements due to their inherent ability to sense a change in temperature and actuate against external loads by undergoing a shape change, as a result of a temperature-induced phase transformation [12-15]. Among various alloy classes, NiTi-based shape memory alloys are more often used due to an advantageous combination of material properties and shape memory behavior [12,22]. However, the B19' monoclinic (martensite) to B2 cubic (austenite) phase transformation associated with shape memory phenomenology in binary NiTi alloys exhibits hysteresis (usually between 1.5-145 K) and typically occurs around 50-70 K above or below ambient temperature. The addition of Fe to the NiTi system suppresses the martensitic transformation temperature and stabilizes an intermediate trigonal R-phase. The R-phase transformation in NiTiFe alloys offers a useful window for low
temperature actuator operation while exhibiting reduced transformation hysteresis and a favorable fatigue response [33]. In order to better utilize the R-phase transformation in actuator design there is a need to understand fundamental deformation mechanisms associated with it. Such an understanding can be aided tremendously by the use of advanced mechanical characterization techniques.

Among available diffraction techniques, \textit{in situ} neutron diffraction at stress and temperature is uniquely suited to following the texture, strain and phase fraction evolution in a bulk polycrystalline shape memory alloy sample [2-5]. Whereas both neutrons and X-rays (from conventional laboratory sources) can be used for materials characterization, neutrons can penetrate further (several mm) into the sample and can thus provide insights that are representative of bulk behavior. Crystal structures, residual strains, phase fractions (in multiphase systems) and textures are among the breadth of information that can be obtained using this technique.

Neutron diffraction measurements have routinely been performed during \textit{in situ} loading at ambient and high temperatures. However, there have previously been no measurements performed during loading at cryogenic temperatures. With the objective of investigating deformation in the R-phase, a capability for \textit{in situ} neutron diffraction during loading at cryogenic temperatures was implemented at Los Alamos National Laboratory for the first time and is outlined in chapter 3. In theory, the accuracy and completeness of texture, strain and phase fraction measurements increase with the number of measurement orientations and/or detector area coverage. However, in practice, difficulties arise in accurately orienting large samples with auxiliary equipment (e.g., load frame and vacuum chamber), from “shadows” cast from such
equipment and from errors associated with sample shifts and changes in the diffraction sampling volume. As a result of the aforementioned considerations, the present study was conducted on the SMARTS diffractometer at Los Alamos National Laboratory utilizing a polychromatic beam from a spallation neutron source with detectors in two fixed orientations. There is then a need to establish a methodology to quantitatively follow the strain, texture and phase fraction evolution with this limited detector area coverage. The objective of this chapter is to establish such a methodology using Rietveld refinement of neutron spectra (in the General Structure Analysis System (GSAS) [9]) that is not merely focused on structure identification (like, e.g., a transmission electron microscopy investigation would) but uniquely includes the combined analyses of strain, texture and phase fraction information representative of the bulk in the sample. Here we note that such a methodology has previously been established for the cubic phase in NiTi [3] but is now done here for the trigonal phase.

4.2 Experimental Procedure

4.2.1 Sample Fabrication

Cylindrical compression samples of 10 mm diameter by 24 mm length were used for this experiment. The sample fabrication was similar to that discussed in section 3.2.3.

4.2.2 Neutron Diffraction and Low Temperature Loading

The neutron diffraction measurements were conducted on the SMARTS [6], using the newly developed cryogenic loading capability [7], principally developed for the study of NiTiFe
shape memory alloys. Neutron diffraction spectra were collected under three experimental conditions in this study:

i. At 216 K, under a compressive stress of 30 MPa

ii. At 216 K, under a compressive stress of 313 MPa

iii. At 237 K, under a compressive stress of 44 MPa.

The accumulated count time in each of the above experiments was 19 minutes or more (23, 19 and 27 minutes, respectively) at a nominal beam current of 100 $\mu A$ in order to obtain adequate intensity from a diffraction volume of about 1 cm$^3$.

4.3 Results and Discussion

4.3.1 Rietveld Refinement

As justified in a subsequent section, the initial structural parameters for the refinement were taken from Ref. [60, 63] and the following general methodology implemented in GSAS in the order indicated:

i. Lattice parameters were refined following the introduction of space groups, histograms and atom parameters (initial atom positions, fractional occupancies and thermal factors). This was followed by a refinement of absorption coefficients. For the two-phase specimen, a constraint (sum adding to unity) was imposed for the refinement of phase fractions.

ii. The profile coefficients, including the Gaussian variance, isotropic strain and anisotropic strain fitting parameters were then refined. The profile function that fitted the data best
was a convolution of two back-to-back exponentials with a Gaussian. The profile coefficients were initially refined independently and subsequently refined simultaneously with the lattice parameter. In the presence of strain (i.e., the externally loaded condition), the strain fitting parameters were refined first and then the variance. For cases where the quantitative determination of strain was the objective, the isotropic and anisotropic strain fitting parameters were not refined, but instead only the lattice parameter and the variance were refined.

iii. In the next step, the presence of texture was accounted for by the use of a generalized spherical harmonic description of the orientation distribution function [53]. To begin with, the sample orientation relative to the incident neutron and detector banks was appropriately considered. Additionally, the order of the harmonic was considered in an incremental manner such that the order used did not statistically improve the refinement with the next higher order.

iv. Following the introduction of texture, the profile parameters were refined again, which were followed by refinements of the thermal parameters and atom positions.

v. Finally, zero point error/sample height problems were corrected if necessary.

### 4.3.2 Phase Identification

Based on the DSC results, as expected, the phase transformation to the R-phase was complete under the first two experimental conditions at 216 K. The stresses of 30 and 313 MPa resulted in elastic deformation of the R-phase and not a stress-induced transformation of the R-phase to B19' martensite. From the DSC measurements, the reverse transformation from the R-
phase to austenite was expected to start at 227 K and finish at 239 K. However, under a compressive stress of 44 MPa at 237 K (the third experimental condition), the transformation is expected to finish at a temperature higher than 239 K, which results in a substantial amount of the R-phase remaining at 237 K as it transforms to the B2 austenite. A summary of the phases present under the three experimental conditions is shown in Table 4.1.

Table 4.1: Experimental conditions and the corresponding phases present

<table>
<thead>
<tr>
<th>Experimental Condition</th>
<th>Temperature (K)</th>
<th>Stress (MPa)</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>216</td>
<td>30</td>
<td>R-phase</td>
</tr>
<tr>
<td>2</td>
<td>216</td>
<td>313</td>
<td>R-phase</td>
</tr>
<tr>
<td>3</td>
<td>237</td>
<td>44</td>
<td>R-phase + Austenite</td>
</tr>
</tbody>
</table>

4.3.3 Structure Identification

The R-phase is considered to be derived from a rhombohedral distortion of the parent, cubic austenite phase [34-36]. However, the structure of the R-phase has been under debate for some time. A considerable amount of research has been done in understanding the crystal structure of R-phase using a variety of characterization techniques such as X-ray diffraction (XRD), transmission electron microscopy (TEM), synchrotron diffraction and neutron diffraction [54, 59-65]. Hara et. al. [61] suggested the space group to be \( P3 \), employing various techniques such as convergent beam electron diffraction (CBED), electron diffraction considering dynamic scattering, and x-ray diffraction using Rietveld method. Schryvers and Potapov [62] utilizing nanoprobe electron diffraction patterns recommended the structure \( P3 \overline{3} \) rather than \( P3 \) (Figure 4.1), even though they obtained a better refinement with \( P3 \), considering the interatomic distances of constituent atoms. They claim that the variation in the interatomic distances is smaller by choosing \( P3 \overline{3} \) than \( P3 \). More recently, Sitepu [64] and Khalil-Allafi [65] obtained
better results with $P\bar{3}$, by using synchrotron and neutron diffraction data that were refined by the Rietveld method.

![Image of unit cell of R-phase using $P3$ space group (left) and $P\bar{3}$ space group (right).]

**Figure 4.1:** Unit cell of R-phase using $P3$ space group (left) and $P\bar{3}$ space group (right).

![Graph showing a typical GSAS Rietveld refinement output with the R-phase refined as belonging to the $P3$ space group (for spectrum obtained from the sample under a compressive stress of 44 MPa at 237 K) for diffracting lattice planes whose normals are parallel to the loading axis. The measured data are indicated by cross-marks and the calculated profile is indicated by the solid-line curve. The line-marks below the profile pattern indicate the positions of all possible Bragg reflections. The lower graph shows the difference between the measured and calculated profile patterns.]

**Figure 4.2:** A typical GSAS Rietveld refinement output with the R-phase refined as belonging to the $P3$ space group (for spectrum obtained from the sample under a compressive stress of 44 MPa at 237 K) for diffracting lattice planes whose normals are parallel to the loading axis. The measured data are indicated by cross-marks and the calculated profile is indicated by the solid-line curve. The line-marks below the profile pattern indicate the positions of all possible Bragg reflections. The lower graph shows the difference between the measured and calculated profile patterns.
Figure 4.3: A typical GSAS Rietveld refinement output with the R-phase refined as belonging to the $P\overline{3}$ space group (for spectrum obtained from the sample under a compressive stress of 44 MPa at 237 K) for diffracting lattice planes whose normals are parallel to the loading axis. The measured data are indicated by cross-marks and the calculated profile is indicated by the solid-line curve. The line-marks below the profile pattern indicate the positions of all possible Bragg reflections. The lower graph shows the difference between the measured and calculated profile patterns.

Given the ambiguity, both space groups $P\overline{3}$ and $P3$ were considered in Rietveld refinement of spectra obtained in this study under the various experimental conditions. Figure 4.2 shows a representative GSAS Rietveld refinement output (for spectrum obtained from the sample under a compressive stress of 44 MPa at 237 K) using the space group $P3$ for the R-phase in the presence of austenite. Figure 4.3 is the corresponding output for the R-phase with the space group $P\overline{3}$. The atom positions were also refined for each of the three experimental conditions. Tables 4.2 and 4.3 show results from refining atom positions using space groups $P3$ and $P\overline{3}$, respectively. The comparative results of evaluating the refinement for space groups $P3$ and $P\overline{3}$ are discussed in the subsequent sections.
and $P\overline{3}$ in terms of refinement quality of fit parameters ($\chi^2$, $R_{wp}$ and $R_p$) are given in Table 4.4.

The refinement quality of fit parameters for all three experimental conditions do not show notable differences between space groups $P3$ and $P\overline{3}$.

Table 4.2: R-phase atom positions for the three experimental conditions, refined with R-phase belonging to the $P3$ space group

<table>
<thead>
<tr>
<th>Atom positions</th>
<th>Parameters Refined</th>
<th>216 K, 30 MPa</th>
<th>216 K, 313 MPa</th>
<th>237 K, 44 MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti 1(0, 0, 0)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ti 2(1/3, 2/3, z)</td>
<td>z</td>
<td>0.0792</td>
<td>0.0817</td>
<td>0.0740</td>
</tr>
<tr>
<td>Ti 3(2/3, 1/3, z)</td>
<td>z</td>
<td>0.121</td>
<td>0.0227</td>
<td>0.0065</td>
</tr>
<tr>
<td>Ti 4(x, y, z)</td>
<td>x, y, z</td>
<td>0.3328, -0.0056, 0.3618</td>
<td>0.3345, -0.0046, 0.3611</td>
<td>0.3375, -0.0020, 0.3545</td>
</tr>
<tr>
<td>Ti 5(x, y, z)</td>
<td>x, y, z</td>
<td>0.6753, 0.0094, 0.6838</td>
<td>0.6784, 0.0094, 0.6868</td>
<td>0.6748, 0.0128, 0.6825</td>
</tr>
<tr>
<td>Ni 1(0, 0, z)</td>
<td>z</td>
<td>0.4710</td>
<td>0.4685</td>
<td>0.4690</td>
</tr>
<tr>
<td>Ni 2(1/3, 2/3, z)</td>
<td>z</td>
<td>0.5510</td>
<td>0.5483</td>
<td>0.5421</td>
</tr>
<tr>
<td>Ni 3(2/3, 1/3, z)</td>
<td>z</td>
<td>0.4204</td>
<td>0.4183</td>
<td>0.4274</td>
</tr>
<tr>
<td>Ni 4(x, y, z)</td>
<td>x, y, z</td>
<td>0.3186, -0.0211, 0.8580</td>
<td>0.3191, -0.0207, 0.8582</td>
<td>0.3199, -0.0227, 0.8572</td>
</tr>
<tr>
<td>Ni 5(x, y, z)</td>
<td>x, y, z</td>
<td>0.6858, 0.0194, 0.1593</td>
<td>0.6861, 0.0200, 0.1605</td>
<td>0.6850, 0.0189, 0.1582</td>
</tr>
</tbody>
</table>
Table 4.3: R-phase atom positions for the three experimental conditions, refined with R-phase belonging to the $P\bar{3}$ space group

<table>
<thead>
<tr>
<th>Atom positions</th>
<th>Refined parameters</th>
<th>216 K, 30 MPa</th>
<th>216 K, 313 MPa</th>
<th>237 K, 44 MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti 1(0, 0, 0)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ti 2(1/3, 2/3, z)</td>
<td>z</td>
<td>0.0280</td>
<td>0.0290</td>
<td>0.0236</td>
</tr>
<tr>
<td>Ti 3(x, y, z)</td>
<td>x</td>
<td>0.3321</td>
<td>0.3313</td>
<td>0.3312</td>
</tr>
<tr>
<td></td>
<td>y</td>
<td>-0.0070</td>
<td>-0.0083</td>
<td>-0.0069</td>
</tr>
<tr>
<td></td>
<td>z</td>
<td>0.3417</td>
<td>0.3416</td>
<td>0.3441</td>
</tr>
<tr>
<td>Ni 1(0, 0, 1/2)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ni 2(1/3, 2/3, z)</td>
<td>z</td>
<td>0.5643</td>
<td>0.5622</td>
<td>0.5589</td>
</tr>
<tr>
<td>Ni 3(x, y, z)</td>
<td>x</td>
<td>0.3225</td>
<td>0.3228</td>
<td>0.3219</td>
</tr>
<tr>
<td></td>
<td>y</td>
<td>-0.0194</td>
<td>-0.0188</td>
<td>-0.0199</td>
</tr>
<tr>
<td></td>
<td>z</td>
<td>0.8527</td>
<td>0.8539</td>
<td>0.8556</td>
</tr>
</tbody>
</table>

Table 4.4: Quality of fit parameters [9] for the two sets of Rietveld refinements ($P3$ and $P\bar{3}$ space groups)

<table>
<thead>
<tr>
<th>Experimental Condition</th>
<th>$P3$</th>
<th>$P\bar{3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\chi^2$</td>
<td>$R_{wp}$</td>
</tr>
<tr>
<td>216 K, 30 MPa</td>
<td>4.495</td>
<td>4.88</td>
</tr>
<tr>
<td>216 K, 313 MPa</td>
<td>4.566</td>
<td>5.48</td>
</tr>
<tr>
<td>237 K, 44 MPa</td>
<td>5.318</td>
<td>5.36</td>
</tr>
</tbody>
</table>

4.3.4 Texture Determination

A generalized spherical harmonic description of the orientation distribution function was used to account for the evolving texture in the R-phase and the processing induced texture in the parent B2 austenite phase. It should be noted that refining for texture despite limited detector area coverage may in some cases merely serve to improve the quality of the refinement rather than represent crystallographic phenomena. Incorporating data from both detectors and accounting for cylindrical symmetry in the sample, a 24th order spherical-harmonic description was used. This order was arrived at by iterating from lower orders and
qualitatively/quantitatively examining the refinement, until increasing the order of the harmonic did not improve the refinement.

The quantification of texture can be defined by a single parameter, the texture index $J$ [66]:

$$J = \frac{1}{2} \left[ f(g) \right]^2 \text{d}g \quad (4.1)$$

where $f(g)$ is the orientation distribution function that maps the probability of each of the possible grain orientations with respect to the external sample dimensions and the integration is over all orientation space. $J$ lies between unity and infinity, corresponding to random orientations and to a single crystal, respectively. The texture index of the R-phase was 19.4 using the space group $P3$ and 25.2 with the space group $P\overline{3}$ for the measurements at 216 K, under a compressive stress of 30 MPa. Correspondingly, the texture index was 35.7 using the space group $P3$ and 42.1 with the space group $P\overline{3}$ for the measurements at 216 K, under a compressive stress of 313 MPa. However, for the measurement at 237 K (where both R-phase and austenite co-exist), the space group $P\overline{3}$ resulted in an unrealistic texture index when compared to normalized spectra as discussed in a later section.

The space group $P3$ has the lowest possible symmetry in the trigonal system, while space group $P\overline{3}$ has a center of symmetry. By using electron diffraction data from small single crystalline R-phase regions, Schryvers and Potapov [62] demonstrated that atoms in the R-phase are located in centrosymmetric positions thus belonging to the space group $P\overline{3}$ rather than the space group $P3$. This may be true considering that the diffraction measurements represented single crystalline regions. However, for the case of neutron diffraction, the measurements are
representative of much larger polycrystalline areas. Following preferential phase transformation (i.e., some variants of R-phase transforming earlier to austenite when compared to others) in the bulk, a heterogeneous strain distribution may result that causes a loss of the center of symmetry. This has previously been reported for ferroelectric metals [67, 68]. The space group $P3$ rather than the space group $P\overline{3}$ better captures this loss of center of symmetry. This may explain the unrealistically high texture index for a fit with the space group $P\overline{3}$.

Figure 4.4: Section of normalized neutron diffraction spectra corresponding to R-phase $\{111\}$ lattice plane reflections (most intense) for the various experimental conditions. The reflections shown here are from diffracting lattice planes whose normals are parallel to the loading axis.
Figures 4.4 and 4.5 represent the normalized intensities of the two most intense peak reflections for the three experimental conditions. The most intense peak corresponds to the \{111\} planes, while the less intense peak corresponds to the \{411\} and \{5\bar{1}1\} planes. It can be seen that the intensity of the first peak decreases while that of the second peak increases with external loading, representative of texture evolution. Furthermore, during the phase transformation at 237 K, the changes in intensities are relatively higher showing substantial texture evolution. The texture evolution in the sample can be represented by the texture index as well as axial distribution plots. While the texture index is merely a number that represents trends in the texture evolution, a more detailed representation is given by axial distribution plots. In an axial distribution plot, the y-axis is a measure of the number of grains that are at an angle $\phi$ between the normal to the chosen plane and the loading axis (in this case), compared to a
randomly oriented polycrystal. Thus a random polycrystalline sample would be represented by a horizontal line at unity. There is no physical significance associated with values less than zero, which in these plots is an outcome of the global normalization procedure. Figures 4.6 and 4.7 show the axial distribution plots of the (111) plane for all the three experimental conditions, using both space groups $P3$ and $P\overline{3}$, respectively. Again here, the choice of the space group $P\overline{3}$ unrealistically overestimates the strength of the texture when correlated with individual peak reflections in Figure 4.4.

Figure 4.6: R-phase (111) axial distribution plots (refined as belonging to the $P3$ space group) for the various experimental conditions. $\phi$ is the angle between the (111) plane normal and the loading axis.
Figure 4.7: R-phase (111) axial distribution plots (refined as belonging to the $P\bar{3}$ space group), for the various experimental conditions. $\phi$ is the angle between the (111) plane normal and the loading axis.

### 4.3.5 Strain Determination

The shift in peak positions represents (elastic) lattice strains and can be measured from either single peak fitting or lattice parameter refinement from the Rietveld method. As mentioned previously in chapter 2, the single peak method relies on fitting each $hkl$ plane individually for the lattice spacing, $d^{hkl}$ and the strain for a specific $hkl$ plane is given by equation (2.2). The three most intense peaks were used for single peak fitting, corresponding to the {111}; {411} and {511}; and {222} planes, respectively. As previously described, the Rietveld method refines lattice parameters ($a$ and $c$ in this case) that inherently average all the lattice planes that diffract in a particular bank of detectors. For strain determination, the histogram from the Bank 2 detector (representing measurements from lattice planes whose normals are parallel to the axis of loading) was considered and only the variance (among profile coefficients) was refined with the
lattice parameter. The lattice parameter obtained from Rietveld refinement was used to obtain the lattice spacings, \( d^{hk l} \) of the aforementioned planes from:

\[
\frac{1}{(d^{hk l})^2} = \frac{4}{3} \left[ \frac{h^2 + hk + k^2}{a^2} \right] + \frac{l^2}{c^2}
\]  

(4.2)

The strain for a specific \( hkl \) plane was then obtained using equation (2.2). This strain, together with the increase in the applied stress, \( \sigma_{\text{applied}} \), was used to determine a plane-specific elastic modulus, \( E_{hkl} \), from:

\[
E_{hkl} = \frac{\sigma_{\text{applied}}}{\varepsilon_{hkl}}
\]  

(4.3)

Table 4.5: Strain evaluation using single peak fitting

<table>
<thead>
<tr>
<th>lattice planes</th>
<th>( d^{111} ) at 30 MPa (Å)</th>
<th>( d^{111} ) at 313 MPa (Å)</th>
<th>( E ) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>{111}</td>
<td>3.0092</td>
<td>2.9969</td>
<td>68</td>
</tr>
<tr>
<td>{411} and {511}</td>
<td>1.3409</td>
<td>1.3366</td>
<td>87</td>
</tr>
<tr>
<td>{222}</td>
<td>1.5043</td>
<td>1.4981</td>
<td>70</td>
</tr>
</tbody>
</table>

The typical error associated with d-spacing determination is ±0.0003.

Table 4.6: Strain evaluation using Rietveld approach for the two sets of refinements at 216 K (\( P3 \) and \( P\bar{3} \) space groups)

<table>
<thead>
<tr>
<th>lattice planes</th>
<th>( d^{111} ) at 30 MPa (Å)</th>
<th>( d^{111} ) at 313 MPa (Å)</th>
<th>( E ) (GPa)</th>
<th>( d^{111} ) at 30 MPa (Å)</th>
<th>( d^{111} ) at 313 MPa (Å)</th>
<th>( E ) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>{111}</td>
<td>7.3370 Å</td>
<td>7.3134 Å</td>
<td>68</td>
<td>7.3371 Å</td>
<td>7.3140 Å</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>5.2616 Å</td>
<td>5.2302 Å</td>
<td></td>
<td>5.2611 Å</td>
<td>5.2291 Å</td>
<td></td>
</tr>
<tr>
<td>{411} and {511}</td>
<td>1.3407</td>
<td>1.3362</td>
<td>83</td>
<td>1.3408</td>
<td>1.3363</td>
<td>85</td>
</tr>
<tr>
<td>{222}</td>
<td>1.5046</td>
<td>1.4984</td>
<td>69</td>
<td>1.5046</td>
<td>1.4984</td>
<td>69</td>
</tr>
</tbody>
</table>

The typical error associated with lattice parameter determination is ±0.0002.
Tables 4.5 and 4.6 show the elastic moduli determined in the aforementioned manner for
the measurements at 216 K using both single peak and Rietveld analyses, with space groups \( P3 \)
and \( P\bar{3} \), respectively. The results are the same for the lattice reflections considered. Here we
note that we have reported moduli from two strain measurements in order to highlight the
agreement between single peak and Rietveld approaches for strain determination. These values
were checked with additional measurements (not reported here) and remained within error.

### 4.3.6 Phase Fraction Determination

In the presence of additional phases, the refinement for phase fraction involved setting of
phase and histogram constraints. During the phase transformation at 237 K, the refinements with
\( P3 \) showed a weight fraction of 44 vol. % for austenite (remaining R-phase), while that with \( P\bar{3} \)
was 38.50 vol. %. These values are within the estimated errors of \( \pm 3 \) vol. %. A qualitative
inspection of the diffraction spectra along with the thermal history suggested that the presence of
austenite was in the range of 30 to 50 vol. % at 237 K. Again, the Rietveld analyses for phase
fractions at 237 K using space groups \( P3 \) and \( P\bar{3} \) produced comparable results.

### 4.4 Conclusions

Given an existing ambiguity in the published literature as to whether the trigonal R-phase
belongs to the \( P3 \) or \( P\bar{3} \) space groups, Rietveld analyses were separately carried out
incorporating the symmetries associated with both space groups and the impact of this choice
evaluated. No statistical differences in the refinement quality were noted for structure, strain and

50
phase fraction analyses between the choice of $P3$ or $P\overline{3}$ space groups. The accuracy of the refinement for strain determination was confirmed by comparing single peak fitting and Rietveld approaches which resulted in comparable results for the three sets of reflections considered. The accuracy of the texture and phase fraction determination was confirmed from visual inspection of raw spectra. For texture analyses, the choice of the $P\overline{3}$ space group resulted in unrealistically high texture indices (when compared to qualitative analyses). This was attributed to the heterogeneous strain in the diffracting volume resulting in a loss of the center of symmetry. In summary, this work has thus set the stage for using Rietveld refinement to quantitatively follow the strain, texture and phase fraction evolution in the R-phase of NiTiFe during mechanical loading at low temperatures on the SMARTS neutron diffractometer at Los Alamos National Laboratory.
CHAPTER FIVE: DEFORMATION BEHAVIOR OF SHAPE MEMORY NiTiFe DURING MECHANICAL LOADING AT 92 K

This chapter discusses the deformation behavior observed during uniaxial compressive loading of Ni$_{46.8}$Ti$_{50}$Fe$_{3.2}$ at 92 K. Neutron diffraction spectra were recorded at appropriate intervals during this experiment, facilitating the quantitative monitoring of the strain, texture and phase fraction evolution and thus the microscopic deformation mechanisms.

5.1 Introduction

NiTiFe based shape memory alloys are promising candidates for certain actuator applications due to introduction of a trigonal R-phase between the characteristic phase transformation from the cubic (B2) and the monoclinic (B19') phases typically observed in equiatomic NiTi. In doing so, the monoclinic (B19') phase transformation temperatures are lowered to the low temperature/cryogenic regime. However, little is known about the microscopic deformation behavior and mechanisms exhibited by these alloys at cryogenic temperatures. In order to study the deformation behavior of the R-phase, experiments were performed at 92 K in Ni$_{46.8}$Ti$_{50}$Fe$_{3.2}$ under external loading with the objective of following the texture, strain and phase fraction evolution. A qualitative overview of the deformation behavior observed during loading of Ni$_{46.8}$Ti$_{50}$Fe$_{3.2}$ at 92 K was discussed in chapter 3. This chapter provides a quantitative analysis of the strain, texture and phase fraction evolution based on Rietveld refinements.
5.2 **Experimental Procedure**

5.2.1 Sample Fabrication

A cylindrical compression sample of 10 mm diameter by 24 mm length was used for this experiment. The sample fabrication was similar to that discussed in section 3.2.3.

5.2.2 Experimental Setup and Method

The experimental setup is explained in section 3.2.2. A compression test (rather than a tension test, limited by the cryogenic capability) was performed at 92 K, while collecting neutron diffraction spectra at selected stress intervals. An effective compressive holding load of 8 MPa was applied to sample after sustaining vacuum inside the chamber. The general experimental procedure consists of cooling the sample to 92 K and the sample was loaded as the temperature stabilized. The sample was loaded at a rate of 0.167 MPa/s in load control mode during elastic deformation and was switched to position control at the onset of twinning (plateau in the stress-strain curve). The accumulated count time during each stress interval was 27 minutes at a nominal beam current of 100 μA in order to obtain adequate intensity from a diffraction volume of about 1 cm$^3$. Figure 5.1 shows the stress-strain response of the NiTiFe sample, generated *ex situ* under identical conditions at 92 K. The symbols on the stress-strain curve indicate the stresses at which the *in situ* neutron diffraction spectra were obtained and analyzed.
Figure 5.1: Macroscopic stress-strain curve at 92 K. The symbols indicate the stresses at which neutron diffraction spectra were obtained and analyzed.

5.2.3 Neutron Spectra Analysis

Neutron diffraction spectra collected at 92 K in the no-load condition (nominal holding stress of 8 MPa) revealed that the alloy was mainly R-phase, with approximately 17 vol. % monoclinic B19' phase and approximately 12 vol. % orthorhombic B33 phase [Chapter 3]. Orthorhombic (B33) martensite was predicted as the structure possessing the lowest energy in NiTi alloys from first-principle density function theory (DFT) calculations [57,58]. We reported direct observation of the orthorhombic (B33) martensite, identified experimentally for the first time [Chapter 3]. The orthorhombic (B33) martensite that distorts at higher loads can be viewed as resulting from a change in the angle of the monoclinic unit cell from $\gamma = 107^\circ$ to $97^\circ$.

The structural parameters for the R-phase ($P3$ space group) were taken from Ref. [8, 60], for the B19' phase ($P112_1/m$ space group) were obtained from Ref. [69, 70] and for the B33 phase (Cmcm space group) were obtained from Ref. [57]. The space group of the R-phase was considered to be $P3$ for the reasons already explained in Chapter 4.
5.3 Results

Figure 5.2 shows the normalized neutron diffraction spectra collected during loading and unloading, from both banks of detectors on SMARTS. The spectra are normalized with respect to the area under the curve. It contrasts the preference of certain planes in the B19' phase in bank 1 and bank 2 during loading. By using neutron diffraction data from the two banks of detectors and with a generalized spherical harmonic texture formulation in the Rietveld refinement procedure, the volume fraction of various phases were quantified at various stress levels as indicated in Figure 5.2. The orthorhombic (B33) martensite was taken into consideration for Rietveld refinements until a load of 210 MPa, where the distortion was expected to be completed [Chapter 3]. Figure 5.3 shows a typical Rietveld refinement output using GSAS. The volume fraction of the three phases (R-phase, B19' phase and B33 phase) are presented as a function of

Figure 5.2: Section of normalized neutron diffraction spectra observed in both banks during loading and unloading at 92 K. (a) The diffracting lattice planes are parallel to the loading axis (bank 1). (b) The diffracting lattice planes are perpendicular to the loading axis (bank 2).
applied load in Figure 5.4. The results obtained from Rietveld refinement during the loading part are distinguished from the unloading part.

Figure 5.3: A typical GSAS Rietveld refinement output with the R, B19' and B33 phases refined for diffracting lattice planes whose normals are parallel to the loading axis. The measured data are indicated by cross-marks and the calculated profile is indicated by the solid-line curve. The line-marks below the profile pattern indicate the positions of all possible Bragg reflections. The lower graph shows the difference between the measured and calculated profile patterns.
Figure 5.4: Volume fraction of various phases obtained by Rietveld refinement as a function of applied compressive load, (a) during loading and (b) during unloading. The typical error associated with the volume fraction determination is ±3%.

Figure 5.5: Texture evolution in the R and B19' phases represented by the texture index during (a) loading and (b) unloading.
As mentioned previously in chapter 4, the quantification of texture can be defined by a single parameter, the texture index $J$ [equation (4.1)]. Figure 5.5 shows the texture evolution in the R and B19' phases quantified in terms of texture index during loading and unloading. While the texture index is merely a number that represents trends in the texture evolution, a more detailed representation is seen in axial distribution plots as described previously in Chapter 4.

Figure 5.6: R-phase \((1\bar{1}1)\) axial distribution plots during (a) loading and (b) unloading. $\phi$ is the angle between the \((1\bar{1}1)\) plane normal and the loading axis.
Figure 5.7: B19' (100) axial distribution plots during (a) loading and (b) unloading. \( \phi \) is the angle between the (100) plane normal and the loading axis.

Figure 5.6 shows axial distribution plots for the R-phase (1\overline{1}1) plane in NiTiFe during loading and unloading. Similarly, Figure 5.7 shows axial distribution plots for B19' phase (100) plane in NiTiFe during loading and unloading. These two planes were prominent and present during the entire load-unload sequence in the bank 2 detector, where the diffracting lattice planes are perpendicular to the loading axis. Measurements at intermediate stresses were left out in Figures 5.6 and 5.7, for clarity. Texture evolution in the B33 phase is not reported due to the presence of a shearing type mechanism associated with distortion in the \( \gamma \) angle (linked to a change in symmetry from orthorhombic to monoclinic), rather than twinning [chapter 3].

The shift in peak positions represents lattice strains and can be measured from either single peak fitting or lattice parameter refinement from the Rietveld method. As previously mentioned in chapter 2, the single peak method relies on fitting each \( hkl \) plane individually for the lattice spacing, \( d^{hkl} \). The strain for a specific \( hkl \) plane is then given by equation (2.2). Strains from individual lattice plane reflections using single peak fitting are reported only for
separated peaks (i.e., non-overlapping) in the R and B19' phases. These correspond to \{111\} planes in the R-phase and \{100\} planes in the B19' phase, from the bank 2 detector (representing measurements from the diffracting lattice planes that are perpendicular to the loading axis). The Rietveld method refines lattice parameters that inherently average all the lattice planes that diffract in a particular bank of detectors. For strain determination, only the histogram from the bank 2 detector was considered. The lattice parameters obtained from Rietveld refinement were used to obtain the lattice spacing, $d^{hkl}$ of the aforementioned planes using [71, 72] equation (4.2) for the R-phase and

$$\frac{1}{(d^{hkl})^2} = \frac{1}{\sin^2 \gamma} \left[ \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2 \sin^2 \gamma}{c^2} - \frac{2hk \cos \gamma}{ab} \right]$$

for the B19' phase  \hspace{1cm} (5.1)

It should be noted that $\gamma$ (instead of $\beta$) is the monoclinic angle, since the space group is $P1121/m$.

Figure 5.8 (a) shows the lattice strains obtained from single peak fitting and Rietveld analysis of R-phase \{111\} planes during loading and unloading. Similarly, Figure 5.8 (b) shows the lattice strains obtained from single peak fitting (SPF) and Rietveld analysis of B19' \{100\} planes during loading and unloading.
Figure 5.8: Lattice strains obtained from single peak fitting and Rietveld analysis for (a) R-phase \{111\} and (b) B19' \{100\} planes, during loading/unloading. The arrows indicate the loading and unloading direction. The typical errors associated with determination of d-spacing and lattice parameters (Rietveld) are ±0.0003Å and ±0.0002Å respectively.

GSAS [9] allows the lattice strains be evaluated in two ways, (1) by refining the lattice parameter and (2) by refining three fitting parameters, $\alpha$, $\beta$, and $\gamma$ (after fixing the lattice parameters). Since the diffraction peaks of orthorhombic B33 phase were very small compared to the R-phase and the B19' phase, the lattice strains in the B33 phase were evaluated using the second method. The strain for a specific $hkl$ plane is then given by:

$$\varepsilon_{hkl} = \frac{\alpha}{C} + \frac{\beta \cos \phi}{C} + \frac{\gamma}{C}$$

(5.2)

where, $C$ denotes the diffractometer constant that converts time-of-flight data to d-spacing [9]. The first term in equation (5.2) represents the isotropic contribution of strain, while the second and third terms represent the anisotropic contribution of strain for non-cubic and cubic
symmetries, respectively. The third term is irrelevant for orthorhombic symmetry and the interplanar angle ($\cos \phi$) in the second term is given by [71]:

$$\cos \phi = \frac{h_1 h_2}{a^2} + \frac{k_1 k_2}{b^2} + \frac{l_1 l_2}{c^2}$$

$$\left( \frac{h_1^2}{a^2} + \frac{k_1^2}{b^2} + \frac{l_1^2}{c^2} \right) \left( \frac{h_2^2}{a^2} + \frac{k_2^2}{b^2} + \frac{l_2^2}{c^2} \right)$$

Figure 5.9: Anisotropic strains in B33 \{021\} planes with respect to \{010\} and \{001\} planes, during distortion of the B33 phase. The typical errors associated with determination of strains are ±0.0002Å.

Figure 5.9 shows the anisotropic strains in B33 \{021\} planes during the distortion of the B33 phase, calculated with respect to the \{010\} and \{001\} planes. The isotropic strains remained relatively constant at approximately 0.6% in compression, during distortion.
5.4 Discussion

5.4.1 Macroscopic Behavior of NiTiFe at 92K

The macroscopic stress-strain curve generated *ex situ* (Figure 5.1) shows a plateau at stresses lower than 100 MPa. Typically, a plateau in the stress-strain response of shape memory alloys signifies the presence of twinning and/or stress-induced phase transformation. A qualitative examination of neutron diffraction spectra collected at different stress levels (Figure 5.2) confirms a stress induced transformation of the trigonal R-phase to the monoclinic B19' phase. Furthermore, the appearance of different peaks of B19' phase at each bank of detectors indicates the preference of variants of B19' phase for compression and tension. The diffraction spectra of lattice planes perpendicular to the loading axis that experience compression are acquired in bank 2, while those of lattice planes parallel to the loading axis that experience tension are acquired in bank 1. Figure 5.2 shows that the B19' variants with \{100\} planes perpendicular to the loading axis are preferred in bank 2 and B19' variants with \{011\} planes parallel to the loading axis are preferred in bank 1. This is in accordance with the published literature [73, 74] that suggests a preference for B19' \{100\} planes in compression and B19' \{011\} planes in tension.

The bulk of the R-phase was transformed to the B19' phase at the maximum load of 425 MPa and the transformed B19' phase was stabilized during unloading at a holding load of 8 MPa. This stabilization can be attributed to the fact that the B19' phase was retained at a temperature lower than the reverse transformation temperature (above 140 K) of B19' phase to R-phase, arising from the thermal hysteresis.
5.4.2 Phase Fraction Evolution

Figure 5.4 shows the volume fraction of the trigonal R-phase, the monoclinic B19' phase and the orthorhombic B33 phase obtained by Rietveld refinement, plotted at various stresses during loading and unloading. As mentioned previously, the base centered orthorhombic B33 cell can be viewed as a monoclinic cell with an angle \( \gamma = 107^\circ \) [57,58]. The orthorhombic B33 phase that is inherently unstable at higher loads will distort its monoclinic angle from \( \gamma = 107^\circ \) to \( \gamma = 97^\circ \) [Chapter 3]. This distortion can be regarded as a shearing type of mechanism (observed in martensitic transformations) and starts at a load of approximately 114 MPa and completes at a load of approximately 210 MPa. Consequently, the orthorhombic B33 phase was accounted for in Rietveld refinements until 210 MPa. The Rietveld refinements predict the volume fraction of B33 to be fairly constant at approximately 12 vol. %.

During the initial part of the loading, until 68 MPa, the volume fraction of the three phases remain constant. Subsequently, the trigonal R-phase undergoes a stress-induced transformation to monoclinic B19' phase. The maximum volume fraction of monoclinic B19' phase observed at the peak load of 425 MPa was 84%.

5.4.3 Texture Evolution

The texture evolution in the trigonal R-phase and the monoclinic B19' phase is illustrated by the texture index in Figure 5.5. Additionally, axial distribution plots of the \((1\bar{1}1)\) plane and the \((100)\) plane show a detailed evolution of texture respectively in Figures 5.6 and 5.7. \( \phi \) is the angle between the respective plane normal and the loading axis. Hence the distributions at \( \phi = 0^\circ \) and \( \phi = 90^\circ \) represents banks 2 and 1 respectively. In Figure 5.5, the R-phase is textured at a
holding load of 8 MPa. This is believed to be due to the starting texture of parent B2 austenite phase, arising from the alloy processing. During loading, the texture of the R-phase increases while that of the B19' decreases. Two factors can contribute to this variation. First, due to the preferential transformation (i.e., some variants of R-phase transforming earlier when compared to others) of R-phase to B19' phase in certain areas. If there is no preferential disappearance but random transformation to B19' phase, the axial distribution of each stress level would overlap one another. Second, due to the stress assisted twinning (or detwinning). This is addressed in the next section. The decrease in the texture of the B19' phase could be the need for the variants of B19' to satisfy strain compatibility (previously also seen in superelastic NiTi [73]).

5.4.4 Strain Evolution

The lattice strains obtained from single peak fitting and Rietveld refinement (Figure 5.8) agree with each other, taking into account the errors associated with the strain determination. As previously described, the Rietveld method refines lattice parameters that inherently average all the lattice planes that diffract in a particular bank of detectors. Thus the strains obtained through lattice parameter refinement using the Rietveld method will have the contribution from all the diffraction peaks associated with a specific phase. At low stress, below 68 MPa, the R-phase bears most of the strain (represented by ‘oa’) as illustrated in Figures 5.8 (a) and (b). In this regime, the R-phase is elastic in nature and we reported an elastic modulus that varies between 92 GPa to 114 GPa from individual lattice planes in Chapter 3. These values are in good agreement with the elastic modulus of 91 GPa obtained from the linear portion of the macroscopic stress-strain curve (Figure 5.1). Upon further loading, the stress-induced
transformation starts and the R-phase sheds a portion of the load to the B19' phase (represented by ‘ab’). The rest of the loading curve is comparatively linear for B19' \{100\} planes and bears most of the load subsequently. Although the intensity of R-phase \{111\} planes is diminishing with load, it bears certain amount of strain as seen in Figure 5.8 (a). The change in sign of the slope is puzzling and more work has to be done to understand this behavior.

The maximum microscopic strain obtained in B19' \{100\} plane using single peak fitting and the Rietveld method is approximately 0.5% at the maximum load of 425 MPa. However, the macroscopic strain (Figure 5.1) is 10 times larger than the microscopic strain. Considering load partitioning between the B19' phase (84% volume fraction) and the R-phase (16% volume fraction), this disparity would be even larger. This is because the microscopic strain is elastic where as the macroscopic strain is a mixture of elastic and inelastic strains. The inelasticity of the macroscopic strain can be explained by means of the internal rearrangement (consequence of energy minimization) of martensite in shape memory alloys. This internal rearrangement can take place in two ways: (i) the realignment of differently oriented morphologies of martensite (B19' phase and R-phase) in the favor of external stress (martensite reorientation in some cases [19]), and (ii) the realignment of different variants within a single morphology such that twinning or variant coalescence (detwinning in some cases [19]) takes place. Strictly speaking, the realignment of the morphology is not possible unless the crystal structure of the matrix surrounding the morphology, in addition to that inside the morphology, twins. In other terms, realignment of individual morphologies, variant coalescence and/or twinning due to variant realignment takes care of the difference (between macroscopic and microscopic strains) without introducing dislocations (that result in permanent deformation). This correlates with the twinning (or detwining) observed through texture index and axial distribution plots. It has been recently
known that twinning decreases the macroscopic elastic modulus of the shape memory material in the martensitic state [56]. This further suggests the disparity between macroscopic and microscopic strains. It should be noted that twinning in B19' phase is more pronounced than that of R-phase, due to significantly larger number of variants possible in the B19' phase [20]. Furthermore, the propensity for twinning increases with decrease in temperature (at 92 K). During unloading there was a large strain relaxation observed in R-phase between 425 MPa and 350 MPa. Concomitantly, a surge in texture (Figure 5.5b) was observed suggesting detwinning in the R-phase.

The inelastic part of the macroscopic strain (Figure 5.1) was not recovered during unloading. In shape memory alloys, the residual macroscopic strain imposed on the martensite phase can be recovered by heating. Justifying that, the macroscopic strains recovered during heating. Bulk of that recovery took place during the B19' to R-phase transformation and the remainder during the R-phase to B2 austenite phase transformation.

Figure 5.9 shows the anisotropic strains associated with \{021\} planes in the B33 orthorhombic phase, during its distortion (between 114 MPa and 210 MPa). Tilting of \{021\} and \{042\} planes was observed in the diffraction spectra collected at bank 2, between \{111\} R-phase and \{100\} B19' phase planes, while loading [Chapter 3]. The intense anisotropic strains (with isotropic strains remaining constant) suggest the shearing type mechanism associated with cooperative movement of atoms.
5.5 Conclusions

The SMARTS spectrometer was used to acquire neutron diffraction spectra in situ during uniaxial compression loading of a Ni$_{46.8}$Ti$_{50}$Fe$_{3.2}$ shape memory alloy sample at 92 K. The neutron diffraction spectra, representative of bulk measurements, were subjected to the Rietveld method using GSAS for quantitative determination of phase fractions, textures, and strains of the respective phases. The neutron diffraction spectra collected under a holding load of 8 MPa revealed that the trigonal R-phase was the dominant phase, with approximately 17 vol. % monoclinic B19' phase and approximately 12 vol. % orthorhombic B33 phase. Upon loading, at a stress lower than 100 MPa, the trigonal R-phase underwent a stress-induced transformation to the monoclinic B19' phase. The volume fraction of the orthorhombic B33 phase remained constant. However, the orthorhombic B33 phase that is unstable at higher loads distorted to the monoclinic B19' phase. This distortion was viewed as a change in the monoclinic angle from $\gamma = 107^\circ$ to $\gamma = 97^\circ$. The bulk of the R-phase transformed to the B19' phase at the maximum load of 425 MPa and the transformed B19' phase was stabilized during unloading to a holding load of 8 MPa. During loading, the texture of the R-phase increased while that of the B19' decreased. This was attributed to the preferential transformation and stress assisted twinning (or detwinning). The lattice strains obtained through single peak fitting and the Rietveld method suggested that the R-phase carried the load until 68 MPa. Upon further loading the bulk of the load was transferred to the evolving B19' phase. The discrepancy between macroscopic and microscopic strains was attributed to detwinning. Additionally, the intense anisotropic strains (with isotropic strains remaining constant) in B33 orthorhombic phase suggested a shearing type mechanism associated with cooperative movement of atoms.
CHAPTER SIX: CONSTRAINED RECOVERY EXPERIMENTS

This chapter presents a quantitative analysis of the two constrained recovery experiments performed on Ni$_{46.8}$Ti$_{50}$Fe$_{3.2}$ shape memory alloy samples, i.e., from the B19' phase to the R-phase and the R-phase to the B2 phase.

6.1 Introduction

Shape memory alloys combine the functions of a sensor and an actuator in a single element, by sensing a change in temperature and actuating against external loads as a result of a temperature-induced phase transformation [1]. In situ neutron diffraction is uniquely suited for investigating microscopic mechanisms on a bulk shape memory polycrystalline sample subjected to phase transformations (from temperature changes) and external stresses (from bias forces). Accordingly, bulk NiTiFe shape memory alloy samples were subjected to two constrained recovery (recovery of macroscopic strain under a constant stress) experiments in the context of real world engineering actuator applications. First, with the objective of examining NiTiFe in one-time, high-stroke, actuator applications, a Ni$_{46.8}$Ti$_{50}$Fe$_{3.2}$ compression sample was strained to approximately 5% (the R-phase was transformed to B19' phase in the process) at 92 K and subsequently heated to full strain recovery under a load. Second, with the objective of examining NiTiFe in cyclic, low-stroke, actuator applications, a Ni$_{46.8}$Ti$_{50}$Fe$_{3.2}$ compression sample was strained to 1% at 92 K and subsequently heated to full strain recovery under a load. Neutron diffraction spectra were recorded at suitable temperature intervals during these
experiments that assisted in the monitoring of the phase-specific texture and volume fraction
evolutions. A qualitative overview of the constrained recovery experiments was presented in
chapter 3. This chapter provides a quantitative analysis of the phase fraction and texture
evolution based on Rietveld refinements.

6.2 Experimental Procedure

6.2.1 Sample Fabrication

Cylindrical compression samples of 10 mm diameter by 24 mm length were used for the
constrained recovery experiments. The sample fabrication was similar to that discussed in
section 3.2.3.

6.2.2 Experimental Setup and Method

The experimental setup is outlined in section 3.2.2. In the first experiment, a
\( \text{Ni}_{46.8}\text{Ti}_{50}\text{Fe}_{3.2} \) shape memory alloy compression sample was strained to approximately 5% at 92
K. The neutron diffraction spectra collected under no-load condition (nominal holding stress of 8
MPa), \( \text{Ni}_{46.8}\text{Ti}_{50}\text{Fe}_{3.2} \) consisted primarily of trigonal R-phase with approximately 17 vol. %
monoclinic B19' phase and approximately 12 vol. % orthorhombic B33 phase [Chapter 3].
During the application of stress (up to a macroscopic strain of 5%), the trigonal R-phase
experienced a stress-induced transformation to monoclinic B19' phase. Subsequently, the sample
was unloaded and held at a constant stress of 50 MPa. The stress-induced monoclinic B19' phase
along with macroscopic strain (deformation) was retained during unloading. Thereafter the
sample was heated (at a constant stress of 50 MPa) through the B19' phase to R-phase transformation range (150–170 K) in a controlled manner, with neutron diffraction spectra collected at selected temperature intervals. The accumulated count time during each temperature interval was 27 minutes at a nominal beam current of 100 μA in order to obtain adequate intensity from a diffraction volume of about 1 cm$^3$.

In the second experiment, a Ni$_{46.8}$Ti$_{50}$Fe$_{3.2}$ shape memory alloy compression sample was strained to approximately 1% at 92 K. Subsequently, the sample was unloaded and held at a constant load of 50 MPa. Thereafter the sample was heated (at a constant load of 50 MPa) through the R-phase to B2 phase transformation range (231–243 K) in a controlled manner, with neutron diffraction spectra collected at selected temperature intervals. As with the previous experiment, the accumulated count time during each temperature interval was 27 minutes at a nominal beam current of 100 μA in order to obtain adequate intensity from a diffraction volume of about 1 cm$^3$.

### 6.2.3 Neutron Data Analysis

The structural parameters for the R-phase ($P3$ space group) were taken from Ref. [8, 60] and the B19' phase ($P112_1/m$ space group) were taken from Ref. [69, 70]. The space group of the R-phase was considered to be $P3$ for the reasons already explained in Chapter 4.
6.3 Results and Discussion

6.3.1 Constrained Recovery from B19' Phase to R-Phase

Figure 6.1 shows the recovery of the R-phase from the B19' phase under a constant load of 50 MPa. Here a section of the neutron diffraction spectra (normalized with respect to area) are offset with respect to increasing temperature. The intensities of {011} B19' phase planes diminish while that of {111} R-phase planes intensify, during heating. The displacement from the SMARTS load frame (Figure 6.2) displayed a 1 mm deflection (for 24 mm sample length) during heating from 150 K to 170 K. This corresponds to approximately 4% bulk recovery in strain (the machine compliance need not be taken into account, since the load remains the same and CTE is negligible). Even more significant was the bulk strain recovery of approximately 2% that took place between 160 K and 162 K.

Figure 6.1: Constrained recovery of the R-phase from B19' phase during the heating of the 5% strained NiTiFe sample from 150 K to 170 K.
Figure 6.2: Displacement in the SMARTS load frame as a function of temperature during heating of the 5% strained NiTiFe sample from 150 K to 170 K.

Figure 6.3: Phase fraction evolution of the B19' and R phases during constrained recovery of the 5% strained NiTiFe sample from 150 K to 170 K.

Figure 6.3 shows the phase fraction evolution of the B19' phase and the R-phase during the constrained recovery from 150 K to 170 K obtained through Rietveld refinements using GSAS [9]. The phase fraction is quantified in terms of volume fraction of the phases. The
Rietveld refinements suggest that the volume fractions of the B19' phase and the R-phase at 160 K to be 83.3 vol. % and 16.7 vol. %, respectively and at 162 K to be 46.3 vol. % and 53.7 vol. %, respectively [chapter 3].

The texture evolution in the B19' and R phases, represented by texture index is shown in Figure 6.4. It shows that the nascent texture of the R-phase is high and decreases with increasing phase fraction. This is due to the preferential transformation (i.e., some variants of the B19' phase transforming earlier when compared to others) of the B19' phase to the R-phase in certain areas within the sample. At the same time, the texture of the B19' phase is lower initially and increases with decreasing phase fraction. Again, as the transformation is preferential certain variants of the B19' phase get transformed to the R-phase when compared to others. A more detailed evolution in texture is portrayed by axial distribution plots, in terms of sample space. Figure 6.5 show the axial distribution plots of (a) B19' (100) plane and (b) R-phase (111) plane, during constrained recovery of the sample from 150 K to 170 K.

![Graph showing texture evolution](image)

Figure 6.4: Texture evolution in the B19' and R phases represented by texture index during constrained recovery of the 5% strained NiTiFe sample from 150 K to 170 K.
Figure 6.5: (a) B19' (100) and (b) R-phase (111) axial distribution plots planes during constrained recovery of the 5% strained NiTiFe sample from 150 K to 170 K. $\phi$ is the angle between the corresponding plane normal and the loading axis.

This constrained recovery of the R-phase from the B19' phase (especially between 160 K and 162 K) validates the use of NiTiFe in high-stroke, actuator applications such as in safety valves. In such devices, the actuation required is one-time (for most cases) with sufficient stroke as the temperature approaches a pre-determined value. This value depends on the composition of the shape memory material, along with the history of thermo-mechanical treatments.
6.3.2 Constrained Recovery from R-Phase to B2 Phase

Figure 6.6: Constrained recovery of the B2 phase from the R-phase during heating of the 1% strained NiTiFe sample from 231 K to 243 K, (a) showing R\{411\} and R\{303\} combining to form B2\{210\} and (b) showing R\{300\} and R\{112\} combining to form B2\{110\}.

Figure 6.6 shows the recovery of the B2 phase from the R-phase under a constant load of 50 MPa. Here two sections of the neutron diffraction spectra (normalized with respect to area) are offset with respect to increase in temperature. In Figure 6.6(a), the R-phase \{303\} planes and the R-phase \{411\} planes combine to form the B2 \{210\} planes. Similarly in Figure 6.6(b), the R-phase \{112\} planes and the R-phase \{300\} planes combine to form the B2 \{110\} planes. Figure 6.7 shows the phase fraction evolution of the R-phase and the B2 phase during constrained recovery from 231 K to 243 K obtained through Rietveld refinements using GSAS [9].
The texture evolution in the R and B2 phases, represented by the texture index is shown in Figure 6.8. The texture of the R-phase is lower initially and increases with decreasing phase fraction. This is due to the preferential transformation (i.e., some variants of the R-phase transforming earlier when compared to others) of the R-phase to the B2 phase in certain areas within the sample. Given that the B2 phase has only one variant when compared to the R-phase, the texture in the B2 phase is fairly constant during the recovery. A more detailed evolution in texture is portrayed by the axial distribution plots, in terms of sample space. Figure 6.9 show the texture evolution represented by axial distribution plots of (a) R-phase (111) plane and (b) B2 (100) plane, during constrained recovery of the sample from 231 K to 243 K.
Figure 6.8: Texture evolution in the R and B2 phases represented by texture index during constrained recovery of the 1% strained NiTiFe sample from 231 K to 243 K.

Figure 6.9: (a) R-phase \((1\bar{1}1)\) planes and (b) B2 (100) axial distribution plots during constrained recovery of the 1% strained NiTiFe sample from 231 K to 243 K. \(\phi\) is the angle between the corresponding plane normal and the loading axis.
This constrained recovery of the B2 phase from the R-phase simulates the functioning of the SMA in an actuator against a bias force. Further it validates the use of NiTiFe in cyclic, low-stroke, actuator application such as a thermal conduction switch. In such devices, the make or break actuation action has to be cyclic with a favorable fatigue behavior.

6.4 Conclusions

The SMARTS spectrometer was used to acquire neutron diffraction spectra in situ during two constrained recovery experiments performed on Ni\textsubscript{46.8}Ti\textsubscript{50}Fe\textsubscript{3.2} shape memory alloy samples, i.e., from the B19’ phase to the R-phase and the R-phase to the B2 phase. First, with the objective of examining NiTiFe in one-time, high-stroke, actuator applications, a Ni\textsubscript{46.8}Ti\textsubscript{50}Fe\textsubscript{3.2} compression sample was strained to approximately 5% at 92 K and subsequently heated to full strain recovery under a load. Second, with the objective of examining NiTiFe in cyclic, low-stroke, actuator applications, a Ni\textsubscript{46.8}Ti\textsubscript{50}Fe\textsubscript{3.2} compression sample was strained to 1% at 92 K and subsequently heated to full strain recovery under a load. The neutron diffraction spectra, representative of bulk measurements, were subjected to Rietveld method using GSAS for quantitative determination of phase fractions and textures of the respective phases. The bulk recovery in strain for the first experiment recorded approximately 4% strain recovery between 150 K and 170 K, with a significant strain recovery of approximately 2% that took place between 160 K and 162 K. The Rietveld refinements suggested the volume fractions of the B19’ phase and the R-phase at 160 K to be 83.3 vol. % and 16.7 vol. %, respectively and at 162 K to be 46.3 vol. % and 53.7 vol. %, respectively. The texture evolution exhibit a preferential transformation of the B19’ to the R-phase. The bulk recovery in strain for the second experiment recorded
approximately 1% between 231 K and 243 K, with a preferential transformation from the R to the B2 phase.
CHAPTER SEVEN: EXTENSION OF RESEARCH METHODOLOGY TO NiTiPd SHAPE MEMORY ALLOYS

This chapter presents an extension of the research methodology established in previous chapters to experiments performed on Ni$_{29.5}$Ti$_{50.5}$Pd$_{20}$ shape memory alloys using in situ neutron diffraction. These include load-bias experiments and stress-induced martensite experiments. Neutron diffraction spectra were recorded at appropriate intervals during these experiments, facilitating the monitoring of the strain, texture and phase fraction evolution and thus the microscopic deformation mechanisms in Ni$_{29.5}$Ti$_{50.5}$Pd$_{20}$ shape memory alloys.

7.1 Introduction

Although shape memory alloys (SMAs) have potential in room temperature and low temperature applications, the potential for high temperature applications is enormous when appropriate alloys are engineered. This is especially true for the automobile, aerospace and turbo-machinery (power generation) related applications. Recently there have been substantial efforts for the development of high temperature shape memory alloys (HTSMAs) by ternary and quaternary additions of elements such as Au, Pt, Pd, Hf, or Zr to the binary NiTi alloy system. The integration of HTSMAs into the devices operating at high temperatures can improve the performance and efficacy of such devices. For example, with the help of HTSMAs, aerospace engines can be designed to operate at improved efficiencies under a variety of flight conditions.

While most HTSMAs exhibit shape memory behavior under stress-free conditions, relatively fewer have the capability to produce work output (for functioning as actuators) under
the influence of external load. These include bulk NiTiPt [75] and NiTiPd [76] alloys, and NiTiHf thin films [77,78]. Furthermore, the useful work output in these alloys decreases with an increase in transformation temperatures above 573 K. This reduction in work output has been attributed to the deterioration of mechanical properties in the austenite phase [79]. The austenitic yield strength becomes lower than the martensitic yield strength with higher transformation temperatures, resulting in “shape setting” the material at the new stress level. It should be noted that “shape setting” in shape memory alloys is performed by heating the confined shape memory element (under stress) to a temperature where the applied stress is greater than the yield strength of the material at that temperature.

Under these circumstances, there is a need to understand the microscopic mechanisms that cause deterioration in mechanical behavior. Such an understanding can help in fabricating HTSMAs that can function satisfactorily at temperatures above 573 K. Amidst various in situ characterization techniques available, in situ neutron diffraction at temperature and stress is uniquely suited to following the texture, strain and phase fraction evolution in a bulk polycrystalline shape memory alloy sample [2-5]. The high temperature loading capability at SMARTS is ideally suited for such neutron diffraction studies.

For the first time Ni$_{29.5}$Ti$_{50.5}$Pd$_{20$ high temperature shape memory alloys were subjected to in situ neutron diffraction measurements at elevated temperatures during loading on SMARTS at Los Alamos National Laboratory. Two sets of experiments were preformed on these alloys. In the first set, the experiments consisted of applying a constant stress while thermally cycling between room and elevated temperatures. Two cycles each were performed at stresses of 100, 200 and 300 MPa, respectively. In the second set, the stress induced martensitic transformation
was investigated from the austenite phase by mechanically cycling at elevated temperatures. Neutron diffraction spectra were recorded at appropriate intervals during these experiments, facilitating the monitoring of the strain, texture and phase fraction evolution and thus the microscopic deformation mechanisms.

7.2 **Experimental Procedures**

7.2.1 Sample Fabrication

The Ni$_{29.5}$Ti$_{50.5}$Pd$_{20}$ compression samples (identified as extrusion # 59) of 9.5 mm diameter by 23.9 mm length were supplied by NASA-GRC for the neutron diffraction experiments. The alloy was made from high purity elemental constituents by vacuum induction melting in a graphite crucible. The melt was cast in a cylindrical copper mold of 25.4 mm diameter by 102 mm length. The ingot was then homogenized in a vacuum furnace at 1323 K for 72 hrs. The ingot was subsequently hot extruded at 1173 K into the required diameter and sliced into the required length by EDM [80, 81].

7.2.2 Experimental Setup

The elevated temperature loading capability (Figure 7.1) at SMARTS [6] was used for the neutron diffraction studies on Ni$_{29.5}$Ti$_{50.5}$Pd$_{20}$. Two thermocouples were mounted on the samples for temperature measurement. The output from the thermocouples was used to control the temperature of the sample using LabVIEW software. The accumulated count time during
each neutron window was 24 minutes at a nominal beam current of 100 $\mu$A in order to obtain adequate intensity from a diffraction volume of about 1 cm$^3$.

Figure 7.1: High temperature furnace on the SMARTS load frame [6].

7.3 Results and Discussion

7.3.1 Identification of NiTiPd Martensite Structure

Given the lack of prior literature on NiTiPd martensite structure, a decision was made to separately refine (using the Rietveld method) diffraction spectra from martensite using the monoclinic B19' structure as well as the orthorhombic B19 structure. The structural parameters for the B19' ($P112_1/m$ space group) were taken from Ref. [66,67] and that of the B19 phase (Pmcm space group) were taken from Ref. [82]. Figures 7.2 and 7.3 show the Rietveld refinement outputs using GSAS with the monoclinic B19' structure and the orthorhombic B19
structure, respectively. Using the Rietveld refinement procedure, the monoclinic B19’ structure lattice parameters were determined to be a=2.798Å, b=4.687Å, c=4.415Å, α=β=90° and γ=90.42°, against typical values of a=2.89Å, b=4.64Å, c=4.12Å, α=β=90° and γ=97° for a binary NiTi alloy. The refinement quality of fit parameters were χ²=3.504, Rwp=6.94 and Rp=5.06. The orthorhombic B19 lattice parameters were determined to be a=2.797Å, b=4.687Å, c=4.426Å and α=β=γ=90°. The refinement quality of fit parameters were χ²=3.571, Rwp=6.19 and Rp=4.50. It should be noted that the monoclinic angle (γ) of the B19’ unit cell approached 90°, validating that the structure is indeed orthorhombic. Furthermore, the crystallographic residual factors (Rwp and Rp) were better for the orthorhombic B19 structure.

Figure 7.2: A typical GSAS Rietveld refinement output with B19' structure refined for diffracting lattice planes whose normals are parallel to the loading axis. The measured data are indicated by cross-marks and the calculated profile is indicated by the solid-line curve. The line-marks below the profile pattern indicate the positions of all possible Bragg reflections. The lower graph shows the difference between the measured and calculated profile patterns.
Figure 7.3: A typical GSAS Rietveld refinement output with B19 phase refined for diffracting lattice planes whose normals are parallel to the loading axis. The measured data are indicated by cross-marks and the calculated profile is indicated by the solid-line curve. The line-marks below the profile pattern indicate the positions of all possible Bragg reflections. The lower graph shows the difference between the measured and calculated profile patterns.

7.3.2 Load-Bias Experiment

The load-bias experiment was performed on the NiTiPd sample by applying selected loads and then thermally cycling between room temperature and a temperature of \((A_f + 25)\) K. The austenite finish \((A_f)\) temperature was qualitatively recognized by identifying the disappearance of martensite peaks during heating (diffraction spectra were collected at 5 minute intervals). Two thermal cycles each were performed at compressive stresses of 100, 200 and 300 MPa, respectively in sequence and a last cycle was performed at 100 MPa. Before the start of each cycle, the sample was unloaded to a holding load (7 MPa) and reloaded again. Neutron
diffraction spectra were collected at the holding load and applied load at room temperature, at the
applied load at \((A_f + 25)\) K, and at the applied load back to room temperature, in each cycle.

Figure 7.4: Room temperature measurements at the applied load in each cycle, before heating.
These spectra are from the bank 2 detector, where the diffracting lattice planes are
perpendicular to the loading axis.

Figure 7.4 shows the qualitative texture evolution from selected normalized diffraction
spectra as a function of each cycle in the martensitic phase (room temperature), before heating.
The sample has a starting texture where majority of the B19 \{011\} planes are orientated
perpendicular to the loading axis. This is due to the processing induced texture from hot
extrusion. With cycling as observed in the bank 2 detectors, where the diffracting planes are
perpendicular to the loading axis, the intensity of B19 \{100\} planes increase at the expense of
B19 \{011\} planes. This behavior is typical of monoclinic B19' martensite in NiTi based alloys,
where the \{100\} planes are oriented perpendicular to compression and \{011\} planes are oriented
perpendicular to tension [73,74]. Furthermore, monoclinic B19' and orthorhombic B19 are crystallographically related in NiTi based alloys by comparable planes [83].

Figure 7.5 shows a section of the normalized diffraction spectra obtained at high temperature for each cycle. The load and the corresponding temperature at which the measurements were made are indicated along with the cycle number. A limit of 673 K (400° C) was put on the maximum temperature to avoid macroscopic strains being permanently set (or shape-setting at that temperature). Cycles 5 to 7 show residual martensite indicated by less intense peaks corresponding to the B19 {100} planes. With each cycle there is a peak shift as well as peak broadening. At the same stress there seems to be considerable amount of strain developing with cycling. Additionally, the temperature for ($A_f + 25$) K is increasing with the same load cycles.
As previously mentioned, the texture evolution in a cylindrical sample can be represented by axial distribution plots. Figure 7.6 shows the axial distribution plots of (a) B19 (100) planes and (b) B19 (011) planes, corresponding to residual B19 martensite at high temperature for cycles 5 to 7. The axial distribution plots show that there is slight change in texture in the residual martensite from cycles 5 through 7.

Figure 7.6: (a) B19 (100) and (b) B19 (011) axial distribution plots at the maximum temperatures correspond to cycles 5, 6 and 7. $\phi$ is the angle between the corresponding plane normal and the loading axis.

As previously mentioned in chapter 2, the shift in peak positions represents lattice strains and can be measured from either single peak fitting or lattice parameter refinement from the Rietveld method. The single peak method relies on fitting each $hkl$ plane individually for the lattice spacing, $d^{hkl}$ and the strain for a specific $hkl$ plane is given by equation (2.2).

The Rietveld method refines lattice parameters that inherently average all the lattice planes that diffract in a particular bank of detectors. For strain determination, only the histogram
from the bank 2 detector was considered. As previously discussed in chapter 5, GSAS [9] allows the lattice strains be evaluated in two ways, (1) by refining the lattice parameter and (2) by refining three fitting parameters, $\alpha$, $\beta$, and $\gamma$ (after fixing the lattice parameters). The strain for a specific $hkl$ plane is then given by equation (5.2).

The first term in equation (5.2) represents the isotropic contribution of strain, while the second and third terms represent the anisotropic contribution of strain for non-cubic and cubic symmetries, respectively. The second term is irrelevant for cubic symmetry and $A_{hkl}$ in the third term is given by:

$$A_{hkl} = \frac{h^2k^2 + h^2l^2 + k^2l^2}{(h^2 + k^2 + l^2)^2}$$  \hspace{1cm} (7.1)

Table 7.1 shows the isotropic strains calculated using the Rietveld method corresponding to various cycles with respect to cycle 1 for the B2 phase. The contributions from the coefficient of thermal expansion (CTE) were subtracted out in evaluating the strains.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Applied Load (MPa)</th>
<th>Temperature (K)</th>
<th>$\varepsilon$ (100)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-100</td>
<td>464</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>-100</td>
<td>490</td>
<td>-0.00016</td>
</tr>
<tr>
<td>3</td>
<td>-200</td>
<td>502</td>
<td>-0.0039</td>
</tr>
<tr>
<td>4</td>
<td>-200</td>
<td>604</td>
<td>-0.0054</td>
</tr>
<tr>
<td>5</td>
<td>-300</td>
<td>659</td>
<td>-0.01032</td>
</tr>
<tr>
<td>6</td>
<td>-300</td>
<td>672</td>
<td>-0.01357</td>
</tr>
<tr>
<td>7</td>
<td>-100</td>
<td>603</td>
<td>-0.01078</td>
</tr>
</tbody>
</table>
Figure 7.7: Section of normalized neutron diffraction spectra showing strains between the B2 \{100\} planes for cycles 1 and 7, at the maximum temperature. These spectra are from the bank 2 detector, where the diffracting lattice planes are perpendicular to the loading axis.

Table 7.1 shows high strains developed during the load-bias cycling. A qualitative representation of the strain can be obtained from Figure 7.7 that shows a peak shift in the B2 \{100\} planes between cycle 1 and 7. These strains may develop due to the mismatch between the lattices, under applied load and the corresponding high stresses may explain the deterioration in mechanical properties such as yield strength in the austenite phase at high temperatures. Further analysis of strain within various lattice planes that accounts for the anisotropy is shown in Table 7.2. Here the lattice strains corresponding to cycle 5 are determined on the basis of cycle 1.
Table 7.2: Lattice strains in the B2 phase for cycle 5 (300 MPa, 659 K) determined with respect to cycle 1 (100 MPa, 464 K).

<table>
<thead>
<tr>
<th>Lattice planes</th>
<th>Strain (considering CTE)</th>
<th>Rietveld</th>
<th>Single Peak Fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>{100}</td>
<td>-0.01049</td>
<td>-0.01044</td>
<td></td>
</tr>
<tr>
<td>{110}</td>
<td>-0.00160</td>
<td>-0.00067</td>
<td></td>
</tr>
<tr>
<td>{111}</td>
<td>-0.00130</td>
<td>-0.00396</td>
<td></td>
</tr>
</tbody>
</table>

7.3.3 Stress-Induced Martensite Experiment

In the second set of experiments, the stress-induced martensitic transformation was investigated from the austenite phase by mechanically cycling Ni_{29.5}Ti_{50.5}Pd_{20} compression samples at 498 K. Figure 7.7 shows the macroscopic response curve for two cycles in the stress-induced martensite experiment. It shows the first cycle with a plateau and residual macroscopic strain, and the second cycle as a mostly linear curve.

Figure 7.8: Macroscopic stress-displacement response corresponding to the stress-induced martensite experiment. The symbols represent the stresses at which neutron diffraction spectra were recorded.
Figure 7.9: Development of stress-induced martensite during cycling at 498 K. These spectra are from the bank 2 detector, where the diffracting lattice planes are perpendicular to the loading axis.

Figure 7.8 shows selected normalized diffraction spectra as a function of cyclic loading. The first cycle shows stress-induced martensite at higher loads and residual martensite upon unloading. Furthermore, there is a considerable shift in the B2 \{100\} planes before and after loading that signifies residual strain. This residual strain can be expected to stabilize the stress-induced martensite upon unloading. In the second cycle, the residual martensite is consistent with the linear response corresponding to the macroscopic behavior [32].

7.4 Conclusions

The SMARTS spectrometer was used to acquire neutron diffraction spectra in situ during load-bias and stress-induced martensite experiments performed on Ni$_{29.5}$Ti$_{50.5}$Pd$_{20}$ shape memory
alloys. The neutron diffraction spectra, representative of bulk measurements, were subjected to the Rietveld method using GSAS for quantitative determination of phase fractions, textures, and strains of the respective phases. Using the initial spectra collected from the room temperature martensite, Rietveld refinements were performed separately considering the monoclinic B19' structure and the orthorhombic B19 structure. The monoclinic angle ($\gamma$) with B19' approached 90°, validating that the structure is indeed orthorhombic. Furthermore, the crystallographic residual factors ($R_{wp}$ and $R_p$) were better for the orthorhombic B19 structure. During load-bias experiments, the intensity of the B19 {100} planes increased at the expense of the B19 {011} planes for room temperature measurements on bank 2 (the diffracting planes are perpendicular to the loading axis). Cycles 5 through 7 showed residual martensite at elevated temperatures indicated by less intense peaks representing B19 {100} planes. Peak shifts as well as peak broadening were reported with cycling at elevated temperature. The axial distribution plots show that there is a slight change in texture at various orientations (along $\phi$) in the residual martensite from cycles 5 through 7. The strain measurements using Rietveld and single peak fits indicate development of high strains during the load-bias cycling. These strains may develop due to the mismatch between the lattices under applied load. The high stresses associated with these strains may explain the deterioration in mechanical properties such as yield strength in the austenite phase at high temperatures. The stress-induced martensitic experiments, by mechanically cycling Ni$_{29.5}$Ti$_{50.5}$Pd$_{20}$ compression samples at 498 K, showed the first cycle with a plateau and residual macroscopic strain, and the second cycle with a more linear response. The first cycle showed stress-induced martensite at higher loads and residual martensite upon unloading. There was a considerable shift in the B2 {100} planes before and after loading, signifying residual strain. Residual stress was expected to stabilize the stress-induced martensite upon unloading. The
residual martensite from the first cycle was consistent with the macroscopic linear response in the second cycle.
CHAPTER EIGHT: ACTUATOR DEVICE DEVELOPMENT

This chapter focuses on the development of NiTi based shape memory alloy actuators. The NiTi helical springs in the thermal conduction switch described in the author’s master’s thesis [17] was replaced with NiTiFe springs and tested. Following that work and Lemanski [84], a design recommendation (patent pending) was made to minimize the heat gradient in the SMA actuator element in a cryogenic thermal conduction switch. This recommendation was implemented as a part of this work. Additionally, development of a NiTi based release mechanism was pursued. Such a mechanism can be potentially considered for use in debris-less separation mechanisms at room temperature to replace current pyrotechnic based release mechanisms, including booster separation chemical motors.

8.1 Development of NiTiFe Thermal Conduction Switch - Prototypes

8.1.1 Introduction

Shape memory alloys (SMAs) are used as actuator elements due to their intrinsic ability to sense a change in temperature and actuate against external loads (e.g., a bias spring) by undergoing a shape change. This ability, called the shape memory effect (SME), is attributed to a first-order, thermoelastic, martensitic phase transformation that takes place during the temperature change [12,15,83]. The temperature-induced phase transformation in SMAs results in an associated strain recovery against large stresses (e.g., as high as 500 MPa), making them superior actuator materials. In NiTi SMAs, this phase transformation usually takes place between
a monoclinic, so-called martensite phase and a cubic, so-called austenite phase. The temperature at which the phase transformation takes place is sensitive to composition and thermomechanical processing [83]. Furthermore, the addition of a third element in small quantities promotes a significant shift in the transformation temperatures and the possible introduction of an additional intermediate phase. The addition of Fe to the NiTi system shifts the martensitic transformation to lower temperatures while introducing an intermediate trigonal R-phase.

Typically, there is hysteresis between the forward and reverse transformations. The transformation hysteresis is a result of elastic strain energy dissipation, the energy associated with frictional resistance to interface motion and similar dissipative processes [31,32]. The cubic to R-phase transformation exhibits a temperature hysteresis as low as 1.5 K, compared to hystereses typically in excess of 10 K for a cubic to monoclinic martensitic transformation. Due to the very low transformation hysteresis, they are useful in designing actuators that operates between narrow temperature ranges. However, the maximum recoverable strain (1% approximately) is lower when compared to the monoclinic to cubic martensitic transformation (8% approximately) [37]. Furthermore, the fatigue life of the R-phase is superior when compared to the monoclinic martensite phase [85].

The motivation for this work arises from the National Aeronautics and Space Administration (NASA) Kennedy Space Center’s (KSC) requirement for thermal management at cryogenic temperatures. The initial objective was focused on NASA’s efforts to support methane liquefaction for future Mars missions [1,17,33]. However, recently the scope was extended to address the requirements of future lunar missions. The original objective was to design, construct and test an SMA thermal conduction switch to facilitate thermal conduction of
approximately 8 watts between two liquid reservoirs held at 118 K and 92 K (boiling points of liquid methane and liquid oxygen, respectively). This switch is expected to control the liquid methane temperature and pressure in a zero boil-off system by allowing on-demand heat transfer between two reservoirs kept at separate temperatures, in an efficient and autonomous manner. The first prototype switch to demonstrate proof-of-concept was developed by Droney et al. in 2003 that used a commercially available NiTi alloy, and operated between an ice-water mixture and hot water [86]. Subsequently, a low temperature version of the conduction switch that used NiTi helical springs was developed by Krishnan et al. in 2003 [1,17]. A third version of the switch using NiTiFe alloy strips for the actuator element was developed and tested by Lemanski et al. in 2005. That switch operated in the low temperature range and used the R-phase but exhibited limited stroke [33].

The cryogenic range thermal switches currently employed range from gas gap and liquid gap thermal switches that rely on convective heat transfer between two surfaces to externally actuated thermal switches. The sensors and active controls in such systems make them more complicated and expensive, yet less efficient than the proposed switch. Furthermore, gas gap switches are restricted to long cycle times, tend to exhibit poor thermal isolation in their open state and have low heat transfer ratios between open and closed states. Other systems using conduction bands make use of mechanical means to generate sufficient thermal contact and may not be reliable. SMA thermal switches have the potential to limit these problems.

This work, while addressing the extension to possible use on lunar missions, reports on modifying the previously reported helical spring switch [1,17] by using NiTiFe as the SMA element in order that significant stroke coupled with low thermal hysteresis can be achieved.
8.1.2 Shape Memory Alloy Actuators

SMAs exhibit significantly lower apparent modulus in their martensite phase compared to the austenite phase. This apparent lowering of modulus in the martensite phase is not solely representative of elastic deformation, but in addition is attributed to deformation twinning [56]. The lower symmetry of martensite, compared to the parent austenite, generates multiple variants that undergo deformation twinning. The design of SMA elements for actuators makes use of this macroscopic difference in modulus between the austenite and martensite states [21,87].

Among martensitic phase transformations in NiTi-based SMAs, the trigonal R-phase holds promise as it possesses reduced transformation hysteresis. However, the shape recovery associated with the R-phase transformation (approximately 1% strain) is significantly lower than that of the monoclinic phase transformation (approximately up to 8% strain). The use of helical SMA springs can compensate for this design limitation as springs produce greater stroke when compared to straight elements such as thin strips and wires [33]. Another advantage of helical springs is that the stress distribution in the helical spring is more uniform when compared to strips used in a bending mode (e.g., Ref. [33]) where there is a higher stress concentration in the middle of the element. A non-uniform stress distribution in the element can reduce the fatigue life and additionally increase the hysteresis associated with the phase transformation.

8.1.3 Lunar Applications

Current NASA plans for a crewed lunar outpost are expected to be targeted around the lunar south pole where direct exposure to the sun occurs about 70% of the time and temperature extremes are moderate. The temperature varies from approximately 120 K to 160 K during a
period of 28 earth days [88]. This region has elevated quantities of hydrogen and possibly water ice at the bottoms of deep craters. The lunar outpost is expected to incorporate in situ resource utilization approaches and the switch developed in this work has the potential to be used for liquefaction of oxygen and zero boil-off control during day/night cycles. Other potential uses include operations where variable heat transfer is required, including residual propellant scavenging, chill down of equipment, and long term storage of ascent module propellants.

Compared to Mars, wherein the switch needs to be enclosed in vacuum to prevent convective heat transfer, heat leakage on the Moon will be through radiation. Designs for the switch need to account for this radiative heat exchange to ensure the switch accurately senses the system temperature. Also, there is a potential issue regarding lunar dust that could increase friction in mechanisms, degrade seals and add significant thermal resistance between contact surfaces.

8.1.4 Shape Memory Alloy Element Fabrication and Testing

Ni$_{47.07}$Ti$_{49.66}$Fe$_{3.27}$ wire of 0.216 cm diameter was selected for the SMA springs. Following SMA spring theory [21,87], the NiTiFe wire was set into 3 helical springs of mean diameter 2.6 cm and 4 turns in order to obtain a maximum recovery force of 16 N per spring and a stroke of 0.5 cm, limiting the strain to within 1%. The shape setting was carried out at 773 K for 20 minutes followed by an ice-water quench.
Figure 8.1: Differential scanning calorimeter (DSC) response of the NiTiFe wire used.

Differential scanning calorimeter (DSC) measurements of transformation temperatures were performed on the NiTiFe wire before and after the shape-setting procedure (Figure 7.1). The samples were tested from 300 K to 230 K using a Perkin-Elmer Diamond DSC at a rate of 0.33 Ks\(^{-1}\) under nitrogen cover gas. The results show the austenite to R-phase transformation during cooling and the reverse transformation during heating. The first sample, represented by the solid black line, is the NiTiFe wire (as received) before any heat treatment. The second sample, represented by the dashed line, received a heat treatment of 773 K for 20 minutes during the shape-setting procedure and was subsequently ice-water quenched. The start and finish of the austenite to R-phase transformation and the corresponding reverse transformation from the R-phase to austenite were determined to be 268, 244, 254 and 277 ± 2 K, respectively, for NiTiFe wire before heat treatment. The corresponding temperatures for the NiTiFe wire after shape-setting were 265, 247,
262 and 272 ± 2 K. The transformation to martensite was below 120 K and was hence outside the operating range of the calorimeter used. The temperature hysteresis did not change appreciably during the shape-setting procedure. However, a slightly sharper peak was observed after the heat treatment for both the austenite to R-phase transformation and the reverse transformation. Even though the transformation temperatures of the composition currently selected are different from the exact temperatures required in final application, the goal here is the validation and demonstration of the use of the R-phase in actuating helical spring based switches. Furthermore, ongoing work at the University of Central Florida that focuses on tailoring the composition of NiTiFe for specific cryogenic applications shows that R-phase transformations can be lowered to the cryogenic regime by modifying the Ni/Ti ratio and Fe content with suitable thermomechanical treatments [89].

8.1.5 Switch Testing

In order to evaluate the performance of the switch, testing was conducted using liquid nitrogen to actuate the NiTiFe SMA springs. The purpose of the experiment was to verify the switch performance in terms of the temperature hysteresis and to obtain an initial estimate of the magnitude of the displacement of the switch. In order to determine the hysteresis, data for both the heating and cooling portions of the thermal cycle were recorded. Temperature vs. displacement data were obtained and are shown in Figure 7.2. Figure 7.3 shows the switch in the closed (extended) position at room temperature and in the open (contracted) position at a temperature of 233 K. A contraction of 4.11 mm was measured.
Figure 8.2: Switch performance between 200 K and room temperature.

Figure 8.3: The NiTiFe helical spring switch in, (a) the closed (extended) position at a room temperature of 298 K and (b) the open (contracted) position at 233 K.

A displacement of the order of 4 mm was measured in repeated experiments, whereas the displacement reported in Ref. [33] (with NiTiFe strips in a bending mode) was approximately 1 mm [33]. This enhanced displacement will help in achieving superior thermal isolation in the open state of the switch. Additionally, the contact force can also be better tailored over the
displacement range. Furthermore, this substantiates the earlier claim of superior stroke with a helical element instead of a bending element. The temperature vs. displacement graph also confirms a small temperature hysteresis despite thermal gradients that develop across the SMA elements during thermal cycling of the switch that result in a non-uniform phase transformation across the length of the spring.

8.2 Shape Memory Alloy Based Release Mechanism

The author and Dr. Raj Vaidyanathan supervised a senior design team (2006-7) at UCF, in developing a NiTi shape memory based release mechanism [11]. This mechanism was intended as a replacement to existing technologies used by NASA in launch vehicles. Existing methodologies rely on pyrotechnic charges that break hold-down bolts, and chemical motors that separate the solid rocket boosters during shuttle launches. In direct comparison to existing methodologies, this mechanism provides for:

i. Debris-less and spark-free release

ii. Controlled release – by controlling the heat input to the actuator

iii. Release of heavy loads by employing mechanical advantage – in the prototype a shape memory alloy actuator that is in the form of a spring (0.085 inch diameter wire, 5 turns, mean internal diameter and length of about 0.6”) removes a holding pin that in turn causes a spring-loaded bearing to rotate and release a hitch that holds as large as 1000 lbs

iv. Release in zero-gravity environments
v. Modular and fail-safe design that separates the actuator module from the load-bearing module, facilitating protection of the actuator module from extreme environments.

Figure 8.4: The shape memory alloy release mechanism in, (a) before actuation and (b) after actuation, releasing a 100 lb load.

Figure 8.4 shows the shape memory alloy based release mechanism releasing a 100 lb load. The details of the mechanism can be found in Ref. [11] and a patent has been filed.

8.3 Conclusions

The fabrication and testing of an SMA switch using Ni$_{47.07}$ Ti$_{49.66}$ Fe$_{3.27}$ helical springs has been presented as part of ongoing efforts to develop and improve upon the design of SMA thermal conduction switches for thermal management at cryogenic temperatures. Such a switch can provide on-demand heat transfer between two reservoirs at different temperatures, to meet NASA’s requirements for advanced spaceport applications. The utilization of a cubic to trigonal (R-phase) phase transformation in NiTiFe SMAs reduces the transformation hysteresis.
Additionally, the utilization of helical NiTiFe SMA springs produces superior stroke (order of 4 mm) compared to straight elements (order of 1 mm) such as thin strips and wires, and provides improved thermal isolation in the open state. The contact force can also be better tailored over the displacement range. Furthermore, a more uniform stress distribution in the helical springs when compared to strips (used in a bending mode) increases the fatigue life and decreases the hysteresis. As with previous versions of the switch, the thermal gradients that develop across the SMA elements during thermal cycling of the switch have proven to be problematic. The testing of another prototype of the switch that minimizes the thermal gradient within the SMA element incorporating a key configuration change is currently underway. The details of the switch are not disclosed due to proprietary reasons.

The development of a NiTi based release mechanism was pursued. Such a mechanism can be potentially considered for use in debris-less separation mechanisms at room temperature to replace current pyrotechnic based release mechanisms, including booster separation chemical motors. A prototype was implemented using NiTi, as the author and Dr. Raj Vaidyanathan supervised a senior design team project at UCF. Patents are being filed for all the three actuator mechanisms developed as a part of this dissertation work.
CHAPTER NINE: CONCLUSION

Due to the stand-alone nature of each chapter in this dissertation, an appropriate conclusion was included at the end of each chapter. This chapter summarizes all of them together for convenience.

9.1 Conclusion

A novel cryogenic capability was implemented by the UCF research group on the Spectrometer for Materials Research at Temperature and Stress (SMARTS) at Los Alamos National Laboratory that can vary temperatures between 300 K and 90 K, while collecting neutron diffraction spectra in situ during loading. The deformation behaviors of Ni$_{46.8}$Ti$_{50}$Fe$_{3.2}$ shape memory alloys were studied for the first time at 92 K using this capability.

i. The room temperature cubic B2 phase transformed to the trigonal R-phase during cooling. During the transformation, the \{110\}_B phase split into \{112\}_R and \{300\}_R, respectively. This was due to the unit cell elongation in the \langle111\rangle crystallographic direction of the B2 phase associated with the formation of the R-phase. A very similar splitting was observed for the \{210\}_B peak to \{303\}_R and \{411\}_R, respectively. The splitting increased with cooling and was evident while comparing the diffraction patterns obtained at 92K with that at 216 K.

ii. When loaded at 92 K, the emergence of a stress-induced B19' phase was noticed at a low stress of 68 MPa, with strain redistribution among lattice planes in the R-phase. Bulk of the R-phase transformed to the B19' phase at approximately 5% strain and the
transformed B19' phase was stabilized during unloading to a holding load of 8 MPa. This behavior was attributed to the fact that the B19' phase is stabilized at a temperature lower than the reverse transformation temperature of the B19' phase to the R-phase, arising from the thermal hysteresis.

iii. The estimated elastic modulus of lattice planes varied between 92.9 GPa for \{111\} planes to 113.8 GPa for \{322\} planes. This was in excellent agreement with the measured macroscopic elastic modulus of 90.9 GPa. The lack of twinning in the R-phase below 68 MPa was consistent with this agreement between macroscopic and microscopic measurements.

iv. The base-centered orthorhombic B33 phase was experimentally identified for the first time in NiTi based alloys. The orthorhombic B33 phase was observed while identifying a diffraction peak shifting between the \{111\}_R and \{100\}_{B19'} peaks in the diffraction spectra collected during loading. During cooling to 92 K in the no-load condition (nominal holding stress of 8 MPa), Ni\textsubscript{46.8}Ti\textsubscript{50}Fe\textsubscript{3.2} consisted primarily of the R-phase with approximately 17 vol. % monoclinic phase and approximately 12 vol. % orthorhombic phase. It was inferred that orthorhombic martensite was formed in stress-free areas, while monoclinic martensite formed in areas that experienced internal stresses. Upon loading, the R-phase underwent a stress-induced transformation to monoclinic B19' phase. Since the orthorhombic B33 was unstable under stress, certain planes of B33 phase gradually distorted at higher applied stresses. This distortion was viewed as a change in the monoclinic angle from \(\gamma = 107^\circ\) to \(\gamma = 97^\circ\). The tilting of the \{021\}_{B33} planes was
observed in the diffraction spectra, which started at approximately 114 MPa and finished at approximately 210 MPa.

v. Given an existing ambiguity in the published literature as to whether the trigonal R-phase belongs to the $P3$ or $P\bar{3}$ space groups, Rietveld analyses were separately carried out incorporating the symmetries associated with both space groups and the impact of this choice evaluated. No statistical differences in the refinement quality were noted for structure, strain and phase fraction analyses between the choice of $P3$ or $P\bar{3}$ space groups. The accuracy of the refinement for strain determination was confirmed by comparing single peak fitting and Rietveld approaches which resulted in comparable results for the three sets of diffraction patterns considered. The accuracy of the texture and phase fraction determination was confirmed from visual inspection of raw spectra. For texture analyses, the choice of the $P\bar{3}$ space group resulted in unrealistically high texture indices (when compared to qualitative analyses). This was attributed to the heterogeneous strain in the diffracting volume resulting in a loss of the center of symmetry.

vi. The neutron diffraction spectra acquired \textit{in situ} during uniaxial compression loading of Ni$_{46.8}$Ti$_{50}$Fe$_{3.2}$ shape memory alloy at 92 K, were subjected to the Rietveld method using GSAS for quantitative determination of phase fractions, textures, and strains of the respective phases. The neutron diffraction spectra collected under the no-load condition (nominal holding stress of 8 MPa), Ni$_{46.8}$Ti$_{50}$Fe$_{3.2}$ consisted primarily of the trigonal R-phase with approximately 17 vol. % monoclinic B19' phase and approximately 12 vol. % orthorhombic B33 phase. Upon loading, at a stress lower than 100 MPa, the trigonal R-
phase underwent a stress-induced transformation to the monoclinic B19' phase. The volume fraction of the orthorhombic B33 phase remained constant, until distortion to monoclinic B19' phase. The bulk of the R-phase was transformed to the B19' phase at the maximum load of 425 MPa and the transformed B19' phase was stabilized during unloading to a holding load of 8 MPa. During loading the texture of the R-phase increased while that of the B19' decreased. This was attributed to the preferential transformation and stress assisted detwinning. The lattice strains obtained through single peak fitting and the Rietveld method suggested that the R-phase carried the load until 68 MPa. Upon further loading, the bulk of the load was transferred to the evolving B19' phase. The discrepancy between the macroscopic and microscopic strains was attributed to detwinning. Additionally, the magnitude of the anisotropic strains (with isotropic strains remaining constant) in the B33 orthorhombic phase suggested a shearing type mechanism associated with a cooperative movement of atoms. Based on this work, a complete schematic of the behavior of Ni$_{46.8}$Ti$_{50}$Fe$_{3.2}$ shape memory alloy is represented in Figure 9.1.

vii. Neutron diffraction spectra was acquired *in situ* during two constrained recovery experiments performed on Ni$_{46.8}$Ti$_{50}$Fe$_{3.2}$ shape memory alloy samples, i.e., from B19' phase to R-phase and R-phase to B2 phase. First, with the objective of examining NiTiFe in one-time, high-stroke, actuator applications, a Ni$_{46.8}$Ti$_{50}$Fe$_{3.2}$ compression sample was strained to approximately 5% at 92 K and subsequently heated to full strain recovery under a load. Second, with the objective of examining NiTiFe in cyclic, low-stroke, actuator applications, a Ni$_{46.8}$Ti$_{50}$Fe$_{3.2}$ compression sample was strained to 1% at 92 K and subsequently heated to full strain recovery under a load. The neutron diffraction
spectra, representative of bulk measurements, were subjected to the Rietveld method using GSAS for quantitative determination of phase fractions and textures of the respective phases. The bulk recovery in strain for the first experiment recorded approximately 4% strain recovery between 150 K and 170 K, with a strain recovery of approximately 2% that took place between 160 K and 162 K. The Rietveld refinements suggested the volume fractions of the B19' phase and the R-phase at 160 K to be 83.3 vol. % and 16.7 vol. %, respectively and at 162 K to be 46.3 vol. % and 53.7 vol. %, respectively. The texture evolution exhibit a preferential transformation of the B19' phase to the R-phase. The bulk recovery in strain for the second experiment recorded approximately 1% strain recovery between 231 K and 243 K, with a preferential transformation from the R to the B2 phase.
The research methodology for Ni$_{46.8}$Ti$_{50}$Fe$_{3.2}$ shape memory alloys was applied to experiments performed on Ni$_{29.5}$Ti$_{50.5}$Pd$_{20}$ shape memory alloys. Neutron diffraction spectra were acquired in situ during load-bias and stress-induced martensite experiments performed on Ni$_{29.5}$Ti$_{50.5}$Pd$_{20}$ shape memory alloys. The neutron diffraction spectra, representative of bulk measurements, were subjected to the Rietveld method using GSAS for quantitative determination of phase fractions, textures, and strains of the respective phases. Using the initial spectra collected from the room temperature martensite, Rietveld refinement was separately performed considering the monoclinic B19' structure and the orthorhombic B19 structure. The monoclinic
angle ($\gamma$) with B19' approached 90°, validating that the structure is indeed orthorhombic. Furthermore, the crystallographic residual factors ($R_{wp}$ and $R_p$) were better for the orthorhombic B19 structure. During load-bias experiments, the intensity of the B19 {100} planes increased at the expense of the B19 {011} planes for room temperature measurements in bank 2 (the diffracting planes are perpendicular to the loading axis). Cycles 5 through 7 showed residual martensite at elevated temperature indicated by small peaks representing B19 {100} planes. Peak shifts as well as peak broadening was reported with cycling at elevated temperature. The axial distribution plots show that there is slight change in the texture in the residual martensite from cycles 5 through 7. The strain measurements using Rietveld and single peak fits indicate development of high strains during the load-bias cycling. These strains may develop due to the mismatch between the lattices under applied load. The high stresses associated with these strains may explain the deterioration in the mechanical properties such as yield strength in the austenite phase at high temperatures. The stress-induced martensitic experiments, by mechanically cycling Ni$_{29.5}$Ti$_{50.5}$Pd$_{20$ compression samples at 498 K, showed the first cycle to have a plateau in the stress-strain curve and residual macroscopic strain, and the second cycle with a more linear response. The first cycle showed stress-induced martensite at higher loads and residual martensite upon unloading. There was a considerable shift in the B2 {100} planes before and after loading, signifying residual strain. The resulting residual stress was expected to stabilize the stress-induced martensite upon unloading. The residual martensite from the first cycle was consistent with the macroscopic linear response in the second cycle.

The fabrication and testing of an SMA switch using Ni$_{47.07}$ Ti$_{49.66}$ Fe$_{3.27$ helical springs has been presented as part of ongoing efforts to develop and improve upon the design of SMA thermal conduction switches for thermal management at cryogenic temperatures. Such a switch
can provide on-demand heat transfer between two reservoirs at different temperatures, to meet NASA’s requirements for advanced spaceport applications. The utilization of a cubic to trigonal (R-phase) phase transformation in NiTiFe SMAs reduces the transformation hysteresis. Additionally, the utilization of helical NiTiFe SMA springs produces superior stroke (order of 4 mm) compared to straight elements (order of 1 mm) such as thin strips and wires, and provides improved thermal isolation in the open state. The contact force can also be better tailored over the displacement range. Furthermore, a more uniform stress distribution in the helical springs when compared to strips (used in a bending mode) increases the fatigue life and decreases the hysteresis. As with previous versions of the switch, the thermal gradients that develop across the SMA elements during thermal cycling of the switch have proven to be problematic. The testing of another prototype of the switch that minimizes the thermal gradient within the SMA element incorporating a key configuration change is currently underway. The details of the switch are not disclosed due to proprietary reasons.

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