2005

Diffraction Studies Of Deformation In Shape Memory Alloys And Selected Engineering Components

Chandrasen Rathod

University of Central Florida

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DIFFRACTION STUDIES OF DEFORMATION IN SHAPE MEMORY ALLOYS AND SELECTED ENGINEERING COMPONENTS

by

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A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Mechanical Materials and Aerospace Engineering in the College of Engineering and Computer Science at the University of Central Florida Orlando, Florida

Fall Term
2005

Major Professor: Dr. Raj Vaidyanathan
ABSTRACT

Deformation phenomena in shape memory alloys involve stress-, temperature-induced phase transformations and crystallographic variant conversion or reorientation, equivalent to a twinning operation. In near equiatomic NiTi, Ti rich compositions can exist near room temperature as a monoclinic B19' martensitic phase, which when deformed undergoes twinning resulting in strains as large as 8%. Upon heating, the martensite transforms to a cubic B2 austenitic phase, thereby recovering the strain and exhibiting the shape memory effect. Ni rich compositions on the other hand can exist near room temperature in the austenitic phase and undergo a reversible martensitic transformation on application of stress. Associated with this reversible martensitic transformation are macroscopic strains, again as large as 8%, which are also recovered and resulting in superelasticity.

This work primarily focuses on neutron diffraction measurements during loading at the Los Alamos Neutron Science Center at Los Alamos National Laboratory. Three phenomena were investigated: First, the phenomena of hysteresis reduction and increase in linearity with increasing plastic deformation in superelastic NiTi. There is usually a hysteresis associated with the forward and reverse transformations in superelastic NiTi which translates to a hysteresis in the stress-strain curve during loading and unloading. This hysteresis is reduced in cold-worked NiTi and the macroscopic stress-strain response is more linear. This work reports on measurements during loading and unloading in plastically deformed (up to 11%) and cycled NiTi. Second, the tension-compression stress-strain asymmetry in martensitic NiTi. This work reports on measurements during tensile and compressive loading of polycrystalline shape-
memory martensitic NiTi with no starting texture. Third, a heterogeneous stress-induced phase transformation in superelastic NiTi. Measurements were performed on a NiTi disc specimen loaded laterally in compression and associated with a macroscopically heterogeneous stress state.

For the case of superelastic NiTi, the experiments related the macroscopic stress-strain behavior (from an extensometer or an analytical approach) with the texture, phase volume fraction and strain evolution (from neutron diffraction spectra). For the case of shape memory NiTi, the macroscopic connection was made with the texture and strain evolution due to twinning and elastic deformation in martensitic NiTi. In all cases, this work provided for the first time insight into atomic-scale phenomena such as mismatch accommodation and martensite variant selection.

The aforementioned technique of neutron diffraction for mechanical characterization was also extended to engineering components and focused mainly on the determination of residual strains. Two samples were investigated and presented in this work; first, a welded INCONEL 718 NASA space shuttle flow liner was studied at 135 K and second, Ti-6Al-4V turbine blade components were investigated for Siemens Westinghouse Power Corporation. Lastly, also reported in this dissertation is a refinement of the methodology established in the author’s masters thesis at UCF that used synchrotron x-ray diffraction during loading to study superelastic NiTi.

The Los Alamos Neutron Science Center is a national user facility funded by the United States Department of Energy, Office of Basic Energy Sciences, under Contract No. W-7405-ENG-36. The work reported here was made possible by grants to UCF from NASA (NAG3-2751), NSF
CAREER (DMR-0239512), Siemens Westinghouse Power Corporation and the Space Research Initiative.
ACKNOWLEDGMENTS

I would like to express my sincere gratitude to –

Prof. Raj Vaidyanathan, my advisor and mentor, for having confidence in my abilities and giving me an opportunity to study at UCF and work on interesting projects. Without his guidance, encouragement and help in many ways than I can imagine, this work would not have been possible.

Prof. Indranath Dutta, for having faith in my abilities and creating an invaluable opportunity to work at the Naval Postgraduate School.

Dr. Mark Bourke for his fruitful discussions and advice during my stay at Los Alamos Neutron Science Center. His willingness to help and act as a reference for my National Research Council (NRC) Proposal is very much appreciated. Prof. Desai for fruitful discussions, advice and interest in my professional welfare.

Profs. Suryanarayana and Kevin Coffey for their advice as thesis committee members, invaluable suggestions and interest in my welfare during stay at UCF. Their readiness to act as a reference to my NRC Proposal and for my professional growth is very much appreciated. Profs. Linan An, Helge Heinrich and Samar Kalita for serving on my final examination committee and for their readiness to help.

Dr. Sven Vogel, Dr. Bjørn Clausen, Dr. Don Brown, Thomas Sisneros and Veronica Livescu at Los Alamos National Laboratory for discussions and helping me with neutron diffraction measurements. Karen Glidewell, Kari Stiles, Cynthia Harle and Angela Levitt for helping me with the paperwork.

Jen, Sudhir, Vinu, Sara and Tim, my colleagues in the work place, for their camaraderie and their endearing friendship. Jen and Sudhir in particular for the many wonderful discussions about books, philosophies and shape memory alloys. Sachin, Parag and Susheel for being good friends.

Rupali, my wife, for her immense love, support, encouragement and understanding and her efforts in weeding out the glaring typos in this thesis as well as in my NRC proposal.

Dr. Ritesh, for being such a loving brother; and

Most of all my Parents to whom I humbly dedicate my research work, for their continual love, inspiration and support and teaching me the values of honesty, sincerity, hard work and commitment. Above all I thank GOD for putting me in the midst of such wonderful people.
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<th>Description</th>
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<tbody>
<tr>
<td>SMA</td>
<td>Shape Memory Alloy</td>
</tr>
<tr>
<td>SME</td>
<td>Shape Memory Effect</td>
</tr>
<tr>
<td>SE</td>
<td>Superelasticity</td>
</tr>
<tr>
<td>LSE</td>
<td>Linear Superelasticity</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimeter</td>
</tr>
<tr>
<td>$A_f$</td>
<td>Austenite finish</td>
</tr>
<tr>
<td>$A_s$</td>
<td>Austenite start</td>
</tr>
<tr>
<td>EDM</td>
<td>Electrical Discharge Machining</td>
</tr>
<tr>
<td>$M_f$</td>
<td>Martensite finish</td>
</tr>
<tr>
<td>$M_s$</td>
<td>Martensite start</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>SMARTS</td>
<td>Spectrometer for MAterials Research at Temperature and Stress</td>
</tr>
<tr>
<td>DND-CAT</td>
<td>Dupont-Northwestern-Dow Collaborative Access Team</td>
</tr>
<tr>
<td>NPD</td>
<td>Neutron Powder Diffractometer</td>
</tr>
<tr>
<td>TIG</td>
<td>Tungsten Inert Gas</td>
</tr>
<tr>
<td>NASA</td>
<td>National Aeronautics and Space Administration</td>
</tr>
<tr>
<td>CTE</td>
<td>Coefficient of Thermal Expansion</td>
</tr>
</tbody>
</table>
CHAPTER 1:  INTRODUCTION

1.1 Motivation

The interest in NiTi shape memory alloys stems from the unique deformation phenomena they exhibit - twinning and stress/temperature-induced transformations. Recently, many articles have highlighted theoretical and commercial interests in thermoelastic martensitic transformations in shape memory alloys such as NiTi and its associated functionality\textsuperscript{1-3}. They classify martensitic transformations into two categories. In one case, the energy barrier to inelastic deformation (via lattice-invariant shear, as in twinning or slip) is no higher than the barrier to the phase change itself. These transformations are therefore irreversible, as observed in steels. In the other case, the energy barrier to lattice-invariant shear can be much higher than that pertaining to the phase change. Consequently, transformations of this type can occur with virtually no plasticity and can be reversible, as in the case of shape-memory alloys. The articles explain the unique property on the basis of a change in crystal symmetry during transformation. The need to understand the crystal symmetry change during a phase transformation in these alloys can be experimentally achieved by doing \textit{in situ} diffraction measurements under stress or temperature.

NiTi based alloys are functional materials for their excellent shape memory and mechanical properties. These alloys are characterized by their unique shape memory response which can be triggered by mechanical or thermal means. The thermal response typically involves twinning followed phase transformation, occurs in Ti rich alloys at room temperature, and is called the shape memory effect. On the other hand, the mechanical response involves phase transformation,
occurs in Ni rich alloys, and is called superelasticity. The superelasticity effect in NiTi is typically associated with a large stress-strain hysteresis. In cold-worked or cold-deformed NiTi, this stress-strain hysteresis is considerably reduced and the stress-strain behavior becomes almost linear with elastically recoverable strains as high as 4\% (i.e., the so called linear superelastic effect). This mechanical response has potential use in springs and is of great interest since the energy stored is almost four times than that of steel. The microstructural and micromechanical phenomena associated with this reduction in hysteresis are not well understood.

Neutron diffraction studies can be used to study micromechanical phenomena \textit{in situ} during phase transformations in these alloys. Thus, the objective of this work was to study the linear superelastic behavior in NiTi. \textit{In situ} neutron diffraction during loading at Los Alamos National Laboratory was used to investigate the effects of plastic deformation on the stress induced transformation in superelastic NiTi. These experiments gathered neutron diffraction spectra \textit{in situ} during loading and attempted to characterize the stress-strain curve of NiTi with different amounts of plastic deformation and subsequent mechanical cycling. In addition, this study was also focused on extending this characterization technique or methodology to study the differences in deformation phenomena in shape memory NiTi under tension and compression. Furthermore, this work also focuses on a spatially heterogeneous stress-induced transformation in superelastic NiTi under a biaxial stress state. This study made use of a novel sample geometry, that of a thin US quarter sized NiTi disc loaded in compression, to produce a heterogeneous stress state in the sample. Finally, this work extends the neutron diffraction mechanical characterization methodology to engineering components – Inconel 718 coupons and Ti-6Al-4V turbine blade components.
1.2 Organization

The work in this dissertation extends the author’s masters thesis work at UCF\textsuperscript{4,5}. The primary focus of the masters thesis work was to establish a methodology to quantify texture, phase fraction and strain evolution during loading and unloading in superelastic NiTi wire using synchrotron X-rays\textsuperscript{3}. The current work started with using \textit{in situ} neutron diffraction during loading as a complimentary technique to analyze bulk samples in contrast to thin geometries which are more suitable for synchrotron X-ray studies. The work in this dissertation is organized as follows:

Chapter 2 provides a brief introduction to shape memory alloys and an overview of recent advances in understanding these materials, their unique properties and applications. Chapter 3 discusses briefly neutron radiation, its properties and application followed by introducing the neutron diffraction methodology and neutron spectra analysis by single peak and Rietveld refinement.

Chapters 4 through 6 of this dissertation outline the work that was carried out at the University of Central Florida, Orlando, FL and Los Alamos National Laboratory, Los Alamos, NM from October 2002 to July 2005. Chapters 4, 5 and 6, outlines the \textit{in situ} neutron diffraction methodology applied to (a) plastically deformed superelastic NiTi, in order to investigate hysteresis reduction and increased linearity in stress strain response (b) diffraction measurements during tensile and compressive loading of shape memory NiTi, in order to link the macromechanical and micromechanical behaviors in tension and compression and examine the reasons for the differences; and (c) measurements from a superelastic NiTi disk specimen loaded laterally in compression and associated with a macroscopically heterogeneous stress state,
respectively. The work described in these chapters is in the process of being submitted to three journals\textsuperscript{6-8}.

Chapter 7 documents a refinement of the author’s masters thesis work at UCF also in the process of being submitted for a journal publication\textsuperscript{9}. Chapter 8 constitutes the work which was undertaken separately for National Aeronautics and Space Administration (NASA) and Siemens Westinghouse Power Corporation in collaboration with Los Alamos National Laboratory. The section of this work is published in Ref. [10,11]. Finally, Chapter 9 lists conclusions.
CHAPTER 2: SHAPE MEMORY ALLOYS

Shape memory alloys are of considerable scientific and commercial interest because of its unique deformation behavior and its ability to memorize shapes. This chapter discusses briefly the history of shape memory alloys, recent advances in understanding these materials, their unique properties and its various applications.

2.1 Shape Memory Alloys

Shape Memory Alloys (SMAs) refer to a unique class of alloys that remember their original shape (or pre-deformation shape) when heated from a relatively lower temperature. Heating results in a reversible phase transformation from a low symmetry phase to a high symmetry phase, followed by associated recovery of all the accumulated strain. Generally, shape memory alloys can accommodate large deformation (e.g., up to 8%) in their low-temperature, low symmetry martensite phase. The strain recovery can take place against large forces (up to 500 MPa), resulting in their application as actuators. Even though many alloys are found to exhibit the shape memory effect, only those alloys that recover considerable amounts of strain (or exert significant force) are of prime importance. These include NiTi alloys and copper based alloys such as Cu-Al-Ni and Cu-Zn-Al.

In 1932 Arne Ölander, a Swedish physicist, was the first to report the thermoelastic transformation of martensite when working with an alloy of Au and Cd. Following his discovery, the shape memory phenomenon as a result of the thermoelastic behavior of the martensite phase was widely reported by Kurdjumov and Chang and Read. In 1962, Buehler...
and Wang at the U.S. Naval Ordinance Laboratory discovered the shape memory effect in an equiatomic alloy of Ni and Ti, which is considered a breakthrough in the field of SMAs\textsuperscript{18}. This alloy was named Nitinol, acronym for Nickel-Titanium Naval Ordinance Laboratory. Since then, interest in the field of SMAs has increased immensely with significant advances in the understanding of SMA phenomena.

Previous studies on NiTi\textsuperscript{1,19-24} have shown improvement in understanding the fundamentals of mechanical properties in NiTi shape memory and superelastic behavior. Many topics dealt with aspects like crystallography, texture, hysteresis and order disorder transformation. Recently, due to advances in technical facilities, data acquisition and data analysis at National Laboratories with advanced instruments have increased the opportunities to take science to a higher level. For example, Vaidyanathan and co-workers have carried out a series of experiments on superelastic NiTi and NiTi-TiC and systematically characterized their mechanical behavior through the determination of texture, phase fraction and strain evolution with applied stress\textsuperscript{20,21}. In Ref. [23] they investigated the effects of cycling on superelastic NiTi. Parallelly, Chang and Wu\textsuperscript{25} studied the textures in cold worked and annealed NiTi, while Zheng and co-workers\textsuperscript{26} studied the linear superelasticity effect in cold drawn NiTi with transmission electron microscopy. Hysteresis aspect in shape memory alloys was the focus of research for Delaey and co-workers\textsuperscript{27}. More recently, progress has been continued in magnetic SMAs. For example, recent research efforts to reduce hysteresis in Ni-Mn-Ga are underway by James et. al.,\textsuperscript{28}. The major properties of SMAs are discussed below.
2.2 Shape Memory Effect

The shape memory effect is the ability of SMAs to remember its pre-deformation shape when it is heated from a relatively lower temperature ($T < M_f$ or martensitic finish temperature). During this heating process, a reversible phase transformation takes place from the low-temperature, martensitic phase to the high-temperature ($T > A_f$ or austenite finish temperature) austenitic phase. The shape memory effect can be of two types, namely, the one-way shape memory effect and the two-way shape memory effect (see Figure 2-1). If the alloy remembers only its high-temperature shape, it is called the one-way shape memory effect. If in addition to the high-temperature shape the alloy remembers its low-temperature shape (deformed shape), it is called the two-way shape memory effect. This two-way shape memory effect is achieved by “biasing” or “training” the SMA specimen, where it is cycled several times between its low-temperature shape and high-temperature shape.

2.3 Superelasticity

Another unique property of certain shape memory alloys is superelasticity or pseudo-elasticity. Unlike the shape memory effect, superelastic behavior takes place without any temperature change, and this phenomenon is observed within a narrow range of temperatures just above the $A_f$ (austenitic finish temperature). Here large strains are possible during mechanical loading, due to the formation of stress-induced martensite (Figure 2-2). Unloading results in the conversion of unstable martensite back to austenite with concomitant recovery of all the accumulated macroscopic strain. The advantage of superelastic alloys is large strains, however disadvantage of these alloys are large stress-strain hysteresis and nonlinear nature of the stress-strain curve.
2.4 Linear Superelasticity

Linear superelasticity is superelasticity in cold worked NiTi where hysteresis and nonlinear behavior is reduced as a function of cold work. Thus plastic deformation in NiTi reduces hysteresis and stress-strain response is more linear and has potential application in springs. The linear stress-strain curve of these alloys is of great interest as elastic energy in these alloys is four times compared to stainless steel (Figure 2-3).

2.5 Applications of Shape Memory Alloys

The unique properties of SMAs have generated impressive commercial and theoretical interest and have consequently led to their application for varied uses in several fields. Each year more and more products are coming into market. Some of the earliest applications included connectors, control valves, temperature switches, coffee maker, sterilizer etc. From application perspective, SMAs evolved with mere collection of ideas in early sixties, and followed by mass scale fabrication of devices in the late seventies and eighties.

SMAs applications can be broadly classified as

- Industrial applications - e.g., aeronautics, electronics, agriculture
- Medical applications - e.g., medicine, dentistry
- Consumer applications - e.g., domestic appliances and clothing

Examples of the above mentioned application are numerous and their in-depth discussion is beyond the scope of this dissertation. Only few applications are presented in Figure 2-4 to
highlight the various ways in which the properties of SMAs can be used. More details can be found elsewhere²⁴,²⁹,³⁰.

2.6 Figures

Figure 2-1: Schematic of one way and two way shape memory effects
Figure 2-2: Schematic of superelastic effect

Figure 2-3: Phenomena of superelasticity and linear superelasticity. For comparison, the elastic response of stainless steel is also shown.
Figure 2-4: Applications based on shape memory and superelastic properties. The alloys associated with the application are also indicated.30

Shape memory applications

- actuator (NiTi, NiTiFe)
- SMA coupling (NiTiFe, NiTiNb)
- coffee maker (NiTiCu)
- air conditioner flaps (NiTiFe)
- rice cooker (NiTiCu)
- control valves (NiTi, NiTiCu)
- water mixing (NiTi)
- bathtub adapter (NiTi)
- assembly rings (CuZnAl) etc.

Superelastic applications

- self-expanding stent in external carotid artery (NiTi)
- eyeglass frame (NiTi)
- orthodontic wire (NiTiCu, NiTi)
- paint gun (NiTi)
- cellular antenna (NiTiCu)
- guide wire (NiTi)
- clothes - leisure (NiTi)
- fishing line (NiTi) etc.
CHAPTER 3: NEUTRON RADIATION AND SCATTERING

Neutrons are a very unique and valuable tool for the probing structure of matter. They behave as particles which scatter off various objects and also like quantum-mechanical waves which diffract to form interference patterns. This chapter briefly discusses neutron radiation, its properties and applications. In this chapter, neutron diffraction technique for mechanical characterization is also described followed by neutron spectra analysis with single peak and Rietveld analysis.

3.1 Neutron Radiation and its Sources

Neutrons are a valuable tool when the need arises to characterize the structure of matter. They are especially useful in characterizing living matter and synthetics which are composed of light elements such as carbon, oxygen, hydrogen etc. Neutrons also reveal details about magnetic properties of certain materials that cannot be obtained by any other way. Such investigations can help in deciding the material that can be used for magnetic storage or superconductivity. Due to these advantages, in relatively short time, neutron scattering techniques became an essential tool for materials scientists, physicists, chemists and so on. They all used neutrons to study the ways of improving materials properties, making it stronger, lighter, more wear resistant and more flexible to meet specific needs. It was quickly realized that the need of growing number of people who used neutron radiation sources for their research required dedicated sources of radiation. In United States, currently four neutron sources are operated by the Office of Basic Energy Sciences – two reactor sources (at Brookhaven National Laboratory in New York and at Oak Ridge National Laboratory in Tennessee), and two spallation neutron source (at Argonne
National Laboratory in Illinois and at Los Alamos National Laboratory in New Mexico). There is one more spallation source currently under construction (at Oak Ridge National Laboratory in Tennessee) and will provide the most intense pulsed beam in the world for scientific research and industrial development. The operation of this spallation source will start from 2006. Details of spallation and reactor sources and their in-depth discussions are beyond the scope of this dissertation and can be found elsewhere.\(^\text{31}\)

### 3.2 Properties of Neutrons and their Applications

Neutrons are neutral particles which provide them a capability to penetrate deeply into materials. This characteristic is very useful in non-destructive probing of bulk materials. Second characteristic feature of neutrons is its magnetic moment that enables the study of magnetic structure and magnetic fluctuations in materials. Furthermore, they possess wavelengths (0.01 to 3 nm) similar to atomic d-spacing and can be used to probe crystal structures and atomic spacings in the materials. Neutrons also possess spins and thus can be formed into polarized neutron beams to study nuclear (atomic) orientations and used in coherent (elastic scattering, e.g., diffraction technique) as well as incoherent (inelastic scattering, e.g., measurement of phonon frequencies) scattering experiments. In addition, the energies of thermal neutrons are similar to the energies of elementary excitation in solids and can be used to study molecular vibrations and lattice modes in materials. Another unique property of neutrons is their ability to interact with nuclei of atoms in contrast to other conventional scattering sources such as X-ray and electrons.\(^\text{32}\) (which interact with clouds of electrons thereby making them sensitive to light atoms).
Thus, the idea of using neutron scattering originates due to its characteristic features and advantages over other types of radiation - high penetration depth, sensitive to magnetic fluctuations and ability to probe light elements. Applications of neutron scattering are numerous and their detailed discussion is beyond the scope of this dissertation and can be found elsewhere\textsuperscript{31,32}. Only neutron scattering for mechanical characterization is discussed below. In principle, X-rays, neutrons and electrons can be used in analogous ways. Nevertheless, there are several distinguishing features, which make neutron radiation a superior tool that can be used to probe structure in materials research. Neutron scattering is powerful tool in determining how atoms are arranged in individual crystals and how crystals are oriented in polycrystalline materials. In addition, neutron scattering can reveal changes that occur in crystal structures as the material is exposed to changing pressures, temperatures, or other environmental variables. Understanding how processing alters materials structure provides important clues on how to improve material properties (e.g., to produce a new material for cryogenic actuators) or to determine how material will behave in extreme conditions.

3.3 Neutron Diffraction

Neutron diffraction is a phenomenon, where neutron beam hits the nuclei of atoms and the force of impact accelerates the neutron within the nuclei. According to the classical theory of radiation\textsuperscript{32}, this radiation spreads out in all direction from an atom, has the same frequency as the primary beam and is called neutron scattered radiation.
Neutron diffraction technique exploits the scattering of the radiation. Diffraction is an interference effect, which leads to the scattering of strong beams of radiation in specific directions and can be described by Bragg's law.

\[ \lambda = 2d \sin \theta_{hkl} \]  

Eq. 3.1 describes diffraction from crystals where \( \lambda \) is the wavelength of the incident radiation, \( d \) is the spacing between the scattering entities (e.g., planes of atoms in the crystal) and \( \theta \) is the angle of scattering. Neutron, electron and X-ray diffraction are all particularly powerful because their wavelengths are smaller than the typical spacings of the atoms in crystals. Consequently, strong and easily measurable diffraction occurs. The basic principle of diffraction measurements for mechanical characterization involves using the lattice plane spacing of grains as internal strain gauges. These lattice spacings are determined from diffraction spectra under various external loading conditions or at different locations (in the case of residual strain measurements). As neutron diffraction is analogous to X-ray and electron diffraction, the details regarding parameters of diffraction peak have been omitted for brevity and can be found in Ref. [32-34].

Neutron diffraction is advantageous to obtain individual phase information. To obtain phase specific information, a refinement methodology needs to be developed to analyze neutron diffraction spectra on account of texture, volume fraction and strain. In that context, in the following section, single peak analysis and Rietveld refinement methodology is detailed.
3.4 Single Peak Fitting

For diffraction spectra obtained from specimens under mechanical load (or different positions), shifts in positions of individual lattice plane (hkl) reflections can be converted to elastic strains\(^{35}\). For example, strain for a plane (hkl) at a given stress is reported as:

\[
\varepsilon_{hkl} = \frac{d_{hkl}^0 - d_{hkl}^b}{d_{hkl}^b}
\]

where \(d_{hkl}^b\) is the spacing of the plane subjected to stress and \(d_{hkl}^0\) is its spacing in the unloaded condition. Since, the strains are calculated relative to the initial state of the specimen, the presence of pre-existing residual intergranular stresses are ignored.

3.5 Rietveld Refinement

Anisotropy arising from crystal geometry or strain redistribution among individual grains may lead to significantly different elastic responses between lattice planes, thereby limiting the inferences that can be drawn from the analysis of individual peaks. One solution to this problem is to use Rietveld refinement, that utilizes reflections from many lattice planes and can describe the average polycrystalline deformation.

Instead of limiting analysis to single peaks, the Rietveld refinement method provides a mathematical model calculating the intensity, \(Y_c\), at every point in the spectrum:

\[
Y_c = Y_b + \sum_h S K F_h^2 P(h) (\Delta T_h)
\]

… 3.3
where the first term, $Y_b$, is the background intensity and the second term is the Bragg scattering containing a scale factor $S$, a correction factor $K$, a structure factor $F_h$, and a profile function $P(\Delta T_h)$, determined by the displacement $\Delta T_h$ of the profile point from the reflection position. The refining procedure optimizes parameters that include phase volume fractions, atom positions and texture until the calculated spectrum exhibits an optimum least squares fit with the measured spectrum$^{36,37}$.

To formulate texture, a more rigorous generalized spherical harmonics description of the orientation distribution function (the function that maps the probability of each of the possible grain orientations with respect to the exterior dimensions) can be incorporated$^{38}$. The authenticity of this technique is validated using a standard calcite sample$^{39}$.

Some of the other parameters in Rietveld refinement includes background functions, powder absorption factors, isotropic temperature factors and the profile function to describe the peak shape. Figure 3-1 shows the typical diffraction spectra from one of the scattering geometries where the red crosses are the measured data and line through them shows the Rietveld least square fit. The tick marks indicate the reflections from austenite and martensite phases. The difference curve between refinement and measured data is shown at the bottom of the figure. From this curve, three pieces of information, strain (from peak shift), texture (from relative intensity), and phase fraction (from area under the respective phase peaks) can be obtained.
3.6 Figures

Figure 3-1: Representative GSAS Rietveld refinement output from General Structure Analysis System (GSAS) software.
CHAPTER 4: A NEUTRON DIFFRACTION INVESTIGATION OF HYSTERESIS REDUCTION AND INCREASE IN LINEARITY IN THE STRESS-STRAIN RESPONSE OF SUPERELASTIC NITI

The superelastic effect in NiTi occurs due to a reversible stress-induced phase transformation from a cubic austenite phase to a monoclinic martensite phase. In polycrystalline samples, there is usually a hysteresis associated with the forward and reverse transformations which translates to a hysteresis in the stress-strain curve during loading and unloading. This hysteresis is reduced in cold-worked NiTi and the macroscopic stress-strain response is more linear, a phenomenon called linear superelasticity. Here we report on in situ neutron diffraction measurements during loading and unloading in plastically deformed (up to 11%) and cycled NiTi. The experiments relate the macroscopic stress-strain behavior (from an extensometer) with the micro-mechanical changes (from neutron diffraction spectra) in linear superelastic NiTi.

4.1 Introduction

The superelastic effect in near equiatomic NiTi is associated with a thermoelastic martensitic phase transformation on loading, generating strains typically around 8%, and the reverse transformation on unloading, with concomitant recovery of the strains. This reversible stress-induced phase transformation occurs between a cubic B2, so-called austenite phase and a monoclinic B19′, so-called martensite phase. Thermodynamically, the thermoelastic transformation is based on a balance of chemical free energy, elastic strain energy, the energy associated with frictional resistance to interfacial motion and similar dissipative processes. The energy dissipation, e.g., frictional resistance to the interfacial resistance, requires additional stress for the forward transformation while lowering the stress for the reverse transformation.
This hysteresis macroscopically manifests as a loop in the stress-strain response between loading and unloading.

Given their substantial recoverable strains, superelastic NiTi can store greater energy, e.g., in springs. However, mechanical design is encumbered by the non-linear nature of the stress-strain response and the aforementioned hysteresis. One of the ways to reduce the hysteresis and increase linearity in the stress-strain response has been to cold work or plastically deform these alloys. Previous studies\textsuperscript{26,42-45} have documented these changes in the stress-strain response of plastically deformed NiTi. This includes the phenomenon of linear superelasticity for high percentages (above 30%) of plastic deformation\textsuperscript{43}. Theories\textsuperscript{46-49} have been proposed to explain these changes, but no experimental studies have simultaneously examined the micromechanical and microstructural changes associated with the reduction in hysteresis and increase in linearity in the mechanical response of bulk superelastic NiTi. Furthermore, a majority of studies have examined heavily (above 30%) plastic deformed NiTi. TEM studies from such samples have noted the appearance and disappearance of martensite micro-twinning variants\textsuperscript{26,44}.

\textit{In situ} neutron diffraction studies during loading can be used to study the texture, strain and phase fraction evolution in NiTi\textsuperscript{50-52}. The increased penetration of neutrons results in measurements being representative of the bulk polycrystal behavior without free surface effects. By recourse to \textit{in situ} neutron diffraction experiments during loading, this work provides for the first time a connection between atomic-scale phenomena and macroscopic changes in superelastic NiTi with plastic deformation, namely, hysteresis reduction and increase in linearity.
in the stress-strain response. The neutron diffraction measurements also assess the effect of cyclic loading on plastically deformed samples.

4.2 Experimental Procedures

4.2.1 Sample fabrication and characterization

Commercially available NiTi (55.94 wt.% Ni) bars were obtained from Special Metal Corporation, New Hartford, NY. These bars were cold drawn from cast ingots that were produced by vacuum induction melting followed by vacuum arc remelting. The bars were subsequently annealed at 550 °C for 20 min and quenched in water. These bars were then used to fabricate cylindrical compression NiTi specimens (10 mm in diameter and 24 mm in length). The specimens were fabricated by electrical discharge machining, solutionized at 1000 °C for 1 hour in argon and oil quenched to room temperature. Annealing was subsequently done at 400 °C in air for 1 hr followed by ice water quenching. The austenitic finish, austenitic start, martensite start and martensite finish temperatures were determined to be 9.9, -0.5, -30.4 and -59.7 °C, respectively, by differential scanning calorimetry. Two of the aforementioned cylindrical samples were plastically compressed by 8% and 11%, respectively, and remachined to cylindrical specimens 8 mm in diameter and 20 mm in length. The amount of plastic deformation was selected so as to monitor phenomenology responsible for the progression of a non-linear hysteretic load-unload response to one with increased linearity and reduced hysteresis, rather than to examine heavily plastically deformed samples (as in majority of the previously mentioned investigations).
4.2.2 Neutron diffraction and mechanical testing

*In situ* neutron diffraction measurements during compressive loading were performed using the Spectrometer for Materials Research at Temperature and Stress (SMARTS) at the Los Alamos Neutron Science Center. An extensometer was attached to the samples to record macroscopic strain during the experiments. The load was ramped in stroke control at 25 MPa/min and kept constant during hold periods when diffraction spectra were collected. The ramp and hold periods were 4 min and 30-45 min, respectively, depending on the beam intensity (average of 100 $\mu$Ahr). During the experiments, the incident neutrons formed a 45° angle with the loading axis and two detectors 180° apart were used to record the diffraction pattern with scattering vectors parallel and perpendicular to the loading axis. Prior to making measurements in the beam, three samples each with 0%, 8% and 11% residual plastic deformation were deformed up to 1400 MPa (load-unload cycle) eight, six and three times, respectively. The purpose of these mechanical cycles was to homogenize and remove any instabilities associated with the transformation while ensuring that the non-recoverable strain was minimal53.

4.3 Results and Discussion

Figure 4-1 is the macroscopic stress-strain response from extensometry of the samples with 0%, 8% and 11% residual plastic deformation. The solid circles indicate the stresses at which neutron diffraction spectra were obtained. Previously, work has systematically characterized superelastic NiTi using *in situ* neutron diffraction during loading5,22 and hence only a measurement in the unloaded condition was made. Neutron spectra corresponding to 14 stresses up to 1400 MPa were acquired in the case of the sample with 8% residual plastic strain. For the sample with 11%
residual plastic strain, neutron spectra were acquired in the unloaded condition and at 1400 MPa. In these experiments, the amount of plastic deformation and number of neutron spectra acquired was selected so as to monitor fundamental phenomenology responsible for the progression of a non-linear hysteretic load-unload response to one with increased linearity and reduced hysteresis. As evident from Figure 4-1, with increasing plastic deformation the hysteresis and maximum recoverable strain decrease while the linearity in the stress-strain curve increases.

Figure 4-2 compares spectra from the three samples in the unloaded state. The spectra are normalized so that the area under the spectra corresponding to the total number of neutron counts are the same. As expected from the composition and the transformation temperatures, the NiTi sample with no residual plastic deformation is fully austenitic in the unloaded condition. This can be contrasted with samples with residual plastic deformation that show the presence of martensite. Thus the residual plastic strain which is expected to generate various crystallographic defects such as dislocations, among others, and their resulting internal stress field results in the stabilization of martensite in the unloaded condition.

Figure 4-3 shows a section of spectra from the sample with 8% residual plastic strain at various stresses during loading and unloading. This figure represents the progression and reversibility of the stress-induced transformation in the presence of the aforementioned stabilized martensite. Upon loading, the shift to shorter d spacings results from the elastic compressive strain while the decrease in intensity of the 111 austenite peak and concomitant increase in the intensity of 102 martensite peak is due to forward transformation. On unloading, the reverse is true.
As previously mentioned, the samples were cycled to obtain stress-strain curves with no non-recoverable strains. This manifests as a complete load-unload loop in the stress-strain curves presented in Figure 4-1. Figure 4-4 is presented in order to assess the effect of cycling. It includes normalized spectra from the first cycle and sixth cycle of the sample with 8% residual plastic strain in the unloaded condition. Here, the spectra are again normalized so that the area under the spectra corresponding to the total number of neutron counts are the same. The inset shows the corresponding macroscopic stress-strain curve from extensometry. The non-recoverable strain following a load-unload cycle is minimal in the sixth cycle when compared to the first cycle. The ratio of the intensity of the 100 martensite peak to that of the 100 austenite peak increases from 1.11 after the first cycle to 1.48 after the sixth cycle. This is indicative of stabilization of additional martensite with cycling or texture evolution in the martensite with cycling. Previous work has shown experimental evidence of both phenomena occurring for the case of NiTi\textsuperscript{23}. It is not unreasonable to expect the same for the case of NiTi in the presence of residual plastic strain.

The preceding presentation has set the stage for a comparison of the macroscopic behavior of NiTi subjected to residual plastic strains (Figure 4-1) with atomic scale phenomena from neutron diffraction spectra (Figure 4-2 through Figure 4-4). The martensite that is formed due to the application of stress is able to accommodate the mismatch with martensite that is stabilized due to the stresses associated with the residual plastic strain. The mismatch is fully accommodated elastically following cycling as seen in the closed nature of the stress-strain curve or the absence of any non-recoverable strain upon loading. Prior to this elastic accommodation, the initial cycles (six in the case of the sample with 8% residual plastic strain) involve inelastic accommodation.
The inelastic accommodation is associated with phase fraction and texture evolution (through twinning) in the martensite phase. Figure 4-3 is direct evidence of the reversibility of the stress-induced transformation in the bulk enabling it to be considered a reversible thermoelastic martensitic transformation and thereby subject to classic thermodynamic theory\textsuperscript{40,41}. Application of such a theory would associate increased stored elastic strain energy with increase in linearity in the stress-strain response. The increased defect density and accompanying stress field as a result of the plastic deformation can be expected to cause this change in the stored elastic strain energy. The decreased hysteresis would be associated with decreased frictional resistance to interfacial motion and decreased stored elastic strain energy dissipation. Again, the increased defect density and accompanying stress field can be expected to favorably select martensite variants or result in variant coalescence that reduces the overall energy dissipation. The stabilized martensite (and its ability to twin) may also be a contributing factor. The overall reversible strain scales with the volume fraction of transformable martensite which was observed to decrease with residual plastic deformation from the neutron diffraction observations.

**4.4 Conclusions**

The significance of the present work lies in providing for the first time a qualitative connection between microscopic and macroscopic changes associated with the reduction in hysteresis and increase in linearity as a result of residual plastic deformation in the mechanical response of bulk superelastic NiTi. It sets the stage for a quantitative investigation, e.g., using Rietveld analyses of complete spectra while providing valuable insight to phase transformation in composite or heterogeneous systems.
4.5 Figures

Figure 4-1: Applied compressive stress vs. macroscopic compressive strain measured by extensometry for undeformed, 8 % and 11 % plastically deformed NiTi. The symbols represent the stresses at which neutron diffraction spectra were recorded.

Figure 4-2: Section of normalized diffraction spectra for undeformed, 8 % and 11 % plastically deformed NiTi at no load. The scattering vector is parallel to the loading direction. The austenite (A) and martensite (M) peaks are identified.
Figure 4-3: Section of diffraction spectra for 8 % plastically deformed NiTi at various applied stresses. The spectra are normalized and displaced along the Y axis for clarity. The scattering vector is parallel to the loading direction. The austenite (A) and martensite (M) peaks are identified.

Figure 4-4: Section of diffraction spectra from 8 % plastically deformed NiTi with and without cycling at no load. The spectra are normalized and displaced along the Y axis for clarity. The scattering vector is parallel to the loading direction. Inset shows the respective macroscopic stress-strain curves from 8 % plastically deformed NiTi with and without cycling. The austenite (A) and martensite (M) peaks are identified.
CHAPTER 5: DIFFERENCES IN THE TENSILE AND COMPRESSIONAL BEHAVIOR OF SHAPE MEMORY NiTi INVESTIGATED USING NEUTRON DIFFRACTION

Martensitic shape memory NiTi differs in its mechanical response under tension and compression. Neutron diffraction measurements during loading offer a way to obtain in situ texture and strain measurements from bulk, polycrystalline martensitic NiTi samples. Previous work used the in situ neutron diffraction technique to study tension compression asymmetry in shape memory NiTi at UCF (A. L. Little, M.S. Thesis, 2004). That work was mostly limited to single peak analysis. This work started as an extension to the previous study and incorporates the Rietveld technique for texture measurements. Furthermore, based on lattice correspondence theory twinning variant strain calculations are undertaken for both tension and compression cases to link the macromechanical and micromechanical behaviors in tension and compression and examine reasons for the differences.

5.1 Introduction

Deformation phenomena in shape memory alloys involve stress-, temperature-induced phase transformations and crystallographic variant conversion or reorientation, equivalent to a twinning operation. In near equiatomic NiTi, Ti rich compositions can exist near room temperature as a monoclinic B19’ martensitic phase, which when deformed undergoes twining resulting in strains as large as 8%. Upon heating, the martensite transforms to a cubic B2 austenitic phase, thereby recovering the strain and exhibiting the shape memory effect. Ni rich compositions on the other hand can exist near room temperature in the austenitic phase and undergo a reversible martensitic transformation on application of stress. Associated with this reversible martensitic
transformation are macroscopic strains, again as large as 8%, which are also recovered and resulting in superelasticity.

Previous studies have documented differences between the tensile and compressive mechanical response in these alloys\(^{54-60}\). There is both theoretical and commercial interest in understanding the reasons for this stress-strain asymmetry. The theoretical interest is driven by continuing attempts to model and predict the mechanical behavior of polycrystalline shape memory alloys incorporating crystallographic phenomenology [e.g., Ref.61,62]. The commercial interest lies in engineering their use under multi-axial loading conditions [e.g., Ref. 5].

The approaches used to study the stress-strain tension-compression asymmetry have been both experimental and computational. For example, TEM studies have even reported that early stages of martensite deformation under tension may be related to the interfacial migration between two adjacent martensite plates, while under compression it is mainly related to the generation and migration of dislocations\(^{55,56,58,59}\). The computational approaches have included variant selection criteria and crystallographic level self-consistent micro-mechanical models, among others \(^{61,62}\). However, none of the investigations have connected atomic-scale texture, phase or twin volume fraction and strain measurements with the macroscopic stress-strain response in bulk, polycrystalline samples with no starting texture or preferred orientation of grains. We emphasis the bulk nature of this investigation (owing to the use of neutrons as described in the following paragraph), contrasting it with previous TEM studies which may be influenced by sample preparation and free surface effects. Furthermore, we have used polycrystalline samples fabricated by hot isostatic processing and shown to be texture-free. This has eliminated the role
of starting texture, a variable recognized to significantly influence the subsequent mechanical response e.g., Ref. 60,62.

The study outlined in this work was carried out on martensitic samples and was undertaken at the neutron powder diffractometer (NPD) at Los Alamos National Laboratory. The diffractometer, facilitated the acquisition of neutron diffraction spectra while simultaneously loading samples separately in tension and compression. Such in situ neutron diffraction measurements have previously studied micromechanical and microstructural changes associated with the stress-induced transformation in superelastic NiTi. A methodology was established to analyze neutron diffraction data from stress-induced transformations in NiTi\textsuperscript{20} and to obtain quantitative phase fraction, texture and strain information. This methodology was applied to superelastic NiTi-TiC composites deformed during single cycles\textsuperscript{21,22} and to NiTi during multiple cycles\textsuperscript{23}. In situ neutron diffraction was also used to investigate twinning ahead of a crack tip in a mechanically loaded compact-tension (CT) shape memory NiTi specimen\textsuperscript{63} and martensitic NiTi-TiC composites\textsuperscript{51}.

5.2 Experimental Procedures

Hot Isostatic Pressing (HIP) was used to produce homogeneous, dense and non-textured NiTi samples. Cylindrical billets of NiTi approximately 9.1 cm X 16.5 cm were fabricated from pre-alloyed powders of 49.4 atomic percent nickel. The pre-alloyed NiTi powders (size between 44 and 177 µm, from Special Metals Corp., NY) were packed in a low-carbon steel container (thickness 0.318 cm, internal diameter 2.5 cm, length 12 cm, lined with a boron-nitride-coated
nickel foil to prevent carbon contamination) and were subjected to HIP at 1065°C and 1000 atm for 3 hours. For compression measurements, a cylindrical specimen 8 mm in diameter and 20 mm in length was electrical discharge machined while for tension measurements, a tensile dog-bone shape specimen with a rectangular gauge cross-section of 7 mm by 4 mm and gauge length of 25 mm was similarly machined. Both samples were solutionized at 930°C for 1 hour and furnace cooled to room temperature in titanium-gettered flowing argon. A PERKIN ELMER* DSC-7 calorimeter was used at a rate of 1 K.min⁻¹ under nitrogen cover gas to determine the transformation temperatures. The austenite start (Aₛ), austenite finish (Aᶠ), martensite start (Mₛ), martensite finish (Mᶠ) were determined to be 66, 86, 49 and 35±2 °C, respectively. Density measurements by water displacement showed the samples to above 99.9% of the theoretical density. Neutron diffraction measurements were performed in ‘time of flight’ mode using the Neutron Powder Diffractometer (NPD) at the pulsed neutron source at Los Alamos National Laboratory (LANL). Detailed information on the experimental setup can be found elsewhere⁶⁴ and is only summarized here. The sample was mechanically loaded in uniaxial direction while neutron diffraction spectra were simultaneously acquired in three scattering geometries. The loading axis formed an angle of 45° with the incident neutron beam, allowing measurements in opposing 90° detectors for which the scattering vectors were parallel and perpendicular to the loading axis. A schematic of the experimental set-up showing the scattering vectors Q and its relationship with the loading axis is shown in Figure 5-1. A third detector was used in back-scattering geometry for which the scattering vector was 61° from the loading axis (not shown in the figure). A 5 x 10 mm pulsed white neutron incident beam of standard collimation was used to analyze the sample that was placed between detector banks (each comprising of 31 ³He 30-cm tubes) that are placed symmetrically about the sample position at ±90°, covering a d spacing
range of 0.25 to 4 Å. An extensometer was placed on the sample to record macroscopic stress-strain data.

The tension and compression loading was done separately on the samples at ambient temperature, each between 0 to 3.7 % strains, with diffraction data obtained at various applied stress levels. The diffraction spectra were recorded at nine tensile stress (5, 33, 75, 125, 150, 180, 200, 220 and 240 MPa) levels and six compressive stress (5, 33, 66, 100, 200, and 300 MPa) levels. The load was ramped in stroke control (0.1 mm/min) and kept constant during hold periods. The neutron count times were about 2-4 h depending on the beam intensity (average beam current 60 µAhr).

5.3 Neutron Spectra Analysis

An established methodology to analyze neutron diffraction data from stress induced transformation in NiTi has previously been described by Vaidyanathan et al.\textsuperscript{21}. In the following both single peak and Rietveld peak fitting approaches are used to determine the evolving elastic strain and texture during loading.

5.3.1 Single peak analysis

Strains for specific grain orientations were determined by fitting individual lattice peaks with respect to the unloaded state using the RAWPLOT program in the General Structure Analysis System (GSAS) Software\textsuperscript{65} developed at Los Alamos National Laboratory. The RAWPLOT allows for the fitting of peak positions, intensity, and profile shape coefficients for a set of
individual reflections. A small nominal stress of 5 MPa and −5MPa for tension and compression respectively (this was needed to hold the specimen horizontally in loading frame) was used as the “zero stress or no stress” unloaded condition. The strain is determined from Eq. 3.2 as described previously.

To follow the texture evolution, intensities of individual peaks were examined. RAWPLOT was again used to fit best-fit curves through individual peaks and determine peak intensities. Normalized intensities were calculated from:

\[
NI = \frac{I_{hkl}^{\text{TOT}}}{I_{hkl}^{\text{TOT}}} \cdot \frac{I_{0}^{\text{TOT}}}{I_{0}^{\text{TOT}}} \quad \ldots 5.1
\]

where \(I_{hkl}\) is the peak intensity for a given plane, hkl, at a given stress, \(I_{hkl}^{0}\) is the corresponding peak intensity for the plane in the “zero stress” condition, \(I_{0}^{\text{TOT}}\) is the integrated peak intensity of the spectrum at the corresponding stress and \(I_{0}^{\text{TOT}}\) is the integrated peak intensity of the spectrum in the “zero stress” condition. Eq. 5.1 essentially corrects for different count times while determining whether the number of diffracting grains in the diffracting volume are increasing or decreasing, for a given grain orientation. It is therefore indicative of the texture evolution.

5.3.2 Rietveld refinement

The Rietveld refinement procedure has previously been described in section 3.5. To analyze the data, the Rietveld code GSAS was used. The profile which fitted best the data was a combination
of two functions: the first is the result of convoluting two back-to-back exponentials with a Gaussian and the second is a linear combination of a Lorentzian and a Gaussian (pseudo-Voigt).

To formulate texture, an eighth order generalized spherical-harmonic description of the orientation distribution function (which maps the probability of each of the possible grain orientations with respect to the external sample dimensions) was used. Using two sets of neutron time-of-flight data from a standard calcite sample, previously used for a round-robin study, von Dreele showed that the technique gives texture results identical with those obtained from individual reflection pole figures. Here the texture results are represented as axial distribution function (ADF) plots from two sets of neutron time-of-flight data. These plots are identical to a slice of a pole figure because of the symmetry in the sample. In an ADF, the dependent axis is a measure of the number of crystals (relative to a randomly oriented polycrystal) that are oriented at an angle \( \phi \) (independent axis) between the normal to the chosen plane and the loading axis. Thus the ADF plots for randomly oriented polycrystal would be represented by a horizontal line at unity.

5.4 Results

Macroscopic stress-strain curves corresponding to tensile and compressive loading for which neutron diffraction spectra were acquired are shown in Figure 5-2. The loading portion of the curve consists of an initial region where martensite deforms elastically with an elastic modulus of 68 ± 5 GPa. In this elastic region, no differences were seen between tensile and compression loading. Subsequently, in compression, a region with a stress-strain slope of 5 GPa follows the
elastic region, while in tension the elastic region precedes a stress-strain region with a slope of 1.25 GPa (i.e., 4 times less compared to compression). The dotted horizontal lines in Figures 5-2 at an applied load of 124.8 MPa in tension and 100.2 MPa in compression, marks the onset of macroscopic inelastic deformation. Here an assumption is made similar to plasticity yield criteria (0.2% strain offset) in metals.

Figures 5-3a and 5-3b illustrate selected portion of normalized spectra (with the scattering vector parallel to the loading direction) with applied stress corresponding to tension and compression loading. The spectra were normalized so that diffraction spectra at all stresses have the same area under the peaks which essentially corrects for differences in neutron diffraction counts. Upon loading, the shift to larger and shorter d spacing results from elastic strains during tensile and compressive loading, respectively, while corresponding differences in relative peak intensities indicates inelastic deformation in both tension and compression.

Figures 5-4a and 5-4b show the microscopic stress-strain plot (by fitting single peaks, Eq. 5.1) for individual planes. The plots show the applied stress vs. strain responses for 011, 100, 111, and -110 martensite planes in tension and compression, respectively. In both cases, it has been seen that the initial portion of the microscopic stress-strain curve comprises of elastic deformation followed by strain redistribution. Similar to Figure 5-2, the onset of inelasticity as determined by the 0.2 \% offset criteria is also indicated in Figure 5-4a and 5-4b.

Following equation 5.1, Figures 5-5a and 5-5b show the normalized intensity vs. applied stress for the 100 martensitic peak from both banks of the detector. For no load diffraction spectra, the
Rietveld refinement was performed without incorporating texture for both tensile and compressive samples. Good agreement between the Rietveld fit and diffraction data indicates the absence of texture in both samples. Figures 5-6a and 5-6b show a representative GSAS Rietveld refinements from detector banks 180 degrees (+90° and -90° banks) apart for the compression sample. The Rietveld refinement of spectra obtained from the unloaded condition gives the best fit for a p 1 1 21/m martensite structure\textsuperscript{66,67}. The lattice parameters for martensite were thus obtained from spectra in the unloaded condition during both tensile and compressive loading. The differences in lattice parameters obtained for both (tensile and compressive) samples were negligible and were within experimental error. The lattice parameters determined were $a = 2.8984 \pm 0.0001$ Å, $b = 4.6474 \pm 0.0002$ Å, $c = 4.1251 \pm 0.0002$ Å, and $\beta = 97.460^\circ \pm 0.004^\circ$.

Figures 5-7a and 5-7b represent the axial distribution plots, respectively, for various planes (100, 011, 110, 211) as a function of stress under tension and compression loading in martensitic NiTi. The ADFs show that the specimen starts from a horizontal line at one time random in the unloaded condition. The horizontal line represents a random polycrystalline sample as described previously thereby validating the refinement procedure.

Figures 5-8a and 5-8b compare neutron diffraction spectra at 33 MPa for both tensile and compressive loading. The spectra indicate the presence of 100 austenite peak reflection during tensile loading and absence during compression loading. Figure 5-9 shows the normalized full-width-half-maximum (FWHM) for 100, 011 and 111 planes vs. macroscopic strain in the samples for both tensile and compressive loading. Here RAWPLOT peak-fits were used to
determine the normalized peak width values in terms of FWHM at a given macroscopic strain with respect to the FWHM in the unstrained condition. In both graphs, normalized FWHM reflects the general trends in the evolution of peak width as a function of strain.

5.5 Discussion

One of the major differences between this study and previous studies is the utilization of bulk and non-textured samples fabricated by HIP. A drawing or rolling procedure would have been expected to induce a starting texture. The HIP route was selected since a starting texture-less sample was desired. The starting texture would have significant effect on shape-memory phenomenology and the objective was to remove that parameter. The fact that convergence was achieved in Figure 5-6 with no texture formulation being used validated the lack of texture in the samples.

The differences in the macroscopic stress-strain response of martensitic NiTi between tension and compression loading have been pointed out in the earlier section, namely a higher stress for the onset of inelastic deformation and a lower stress-strain gradient for the case of tension when compared to compression (Figure 5-2). This sets the stage for a comparison between the macroscopic response and neutron data as done in the following.

A qualitative examination of the 011 and 100 peaks in Figures 5-3a and 5-3b illustrate the differences between tensile and compressive loading response of martensitic NiTi. With increasing stress, the 011 peak become more intense at the expense of 100 peak in tensile loading
and vice versa in compressive loading. This indicates the different variants active in tensile and compressive loading. The differences in strain distribution (for 011, 100, 111 and 110 reflections) in tension and compression can be seen in Figures 5-4a and 5-4b. In tension, 011, 100 and 111 planes respond more linearly up to higher stresses than in compression. There appears to be greater strain distribution among the lattice planes in compression than in tension.

Figures 5-5a and 5-5b illustrate with increasing compressive stress, there is an increase in the number of 100 planes perpendicular to the loading direction. The corresponding normalized peak intensity plots show intensity decreases in the +90° detector bank and increases in the -90° detector bank indicating development of 100 texture. The comparisons were made with corresponding ADF plots (from Rietveld refinement) for 100 plane reflection (Figure 5-7b), thereby validating the refinement procedure. Similar consistent comparisons between single peak analysis and Rietveld refinement were obtained for the other plane reflections and have been omitted for brevity.

Figures 5-7a and 5-7b represent the axial distribution function (ADF) for various (100), (0 1 1), (110), (2 1 1) planes in tensile and compressive loading. With increasing tensile and compressive stress, it is seen that almost all planes align themselves parallel or perpendicular to the loading axis, indicating that the main deformation mechanism is martensite variant conversion or reorientation thereby validating the previous results obtained in literature51,55. This variant coalescence mechanism in Ref. [51], is equivalent to a twinning operation. However, in NiTi martensite, twins exist at the no stress condition, and with increasing stress these twins
disappear hence in some references\textsuperscript{55,58,59} this mechanism is also called as detwinning mechanism. Though in the literature, there is confusion in using these terms, planes we adopt the term twinning. In this work, with increasing tensile stress the 100, 110 and (2 1 1) planes decrease in the number while the (0 1 1) planes grow in the number oriented perpendicular to the loading axis. In compressive loading, the opposite behavior is observed. The tensile deformation ADF (Figure 5-7a) indicate that twinning results in increasing the number of (0 1 1) planes perpendicular to the applied load at the expense of (100), (110), and (2 1 1) planes and vice versa with compressive deformation ADF (Figure 5-7b). While the onset of twinning on the macroscopic stress-strain curve happens at stresses at around 125 MPa and 100 MPa (in tension and compression respectively), neutron diffraction results indicate otherwise. This fact is strengthened from a recent study\textsuperscript{51}, which measured the elastic modulus with three different techniques. It determined elastic modulus from the response of lattice planes measured using neutron diffraction during loading, instrumented indentation using a spherical indenter and macroscopic extensometry. In tension and compression, Young's modulus from extensometry is determined as 68±5 GPa (estimated error) in both cases. The neutron diffraction result also showed that the elastic modulus for martensitic NiTi in both tension and compression is 109±5 GPa (obtained from lattice plane averages of 100, 011 and 111 planes). It is not straightforward to account for elastic anisotropy and obtain an elastic modulus from lattice plane specific modulus due to the low symmetry of the monoclinic NiTi. However, the average plane specific moduli reflects the average bulk polycrystalline response as reported previously for the case of cubic NiTi\textsuperscript{20}. The lattice plane specific elastic moduli for planes 011, 100 and 111 during tensile and compressive loading were calculated to be 113, 92, 130 and 122, 91, 108 GPa respectively.
The error associated with these elastic modulus calculations is ±5 GPa. Thus this validates the similar elastic behavior of martensitic NiTi in both tension and compression loading. However, the disparity in elastic modulus values from the extensometry (68 ±5 GPa) and neutron diffraction (109 ±5 GPa) and indentation (101 ±7 GPa) is due to small amounts of twinning at low loads.

Previously, two types of twinning are discussed for martensitic NiTi. Type I twinning results in a mirror reflection about the twinning plane \( K_1 = (1 \bar{1} 1) \) and Type II twinning results in 180 degree rotation about the twinning plane \( K_2 = (0.7205 \bar{1} 1) \) around the shear direction \( \eta = [0 \bar{1} 1] \). Ref. [72] has identified a \((0.7205 \bar{1} 1)\) type II twinning to be prevalent in both tension and compression. However, Ref [51] has identified \((1 \bar{1} 1)\) Type I twinning in compression case. In this work, we have used the similar method as discussed in Ref. [51] to identify the type of twinning. Figure 5-11 shows the [011] stereographic projection of monoclinic NiTi for the tension case (using the same notation from Ref. [51]), indicating the effect of \((1 \bar{1} 1)\) twinning and subsequent reorientation for \((0 \bar{1} 1)\) and \((1 0 0)\) planes. In the monoclinic structure, the \((1 \bar{1} 1)\) plane is a close bisector for near orthogonal planes \((0 \bar{1} 1)\) and \((1 0 0)\). In \((1 \bar{1} 1)\) type I twinning, variants with \((0 \bar{1} 1)\) planes parallel to the loading axis (in Bragg condition for the +90 deg detector) twin in such a way that their \((0 \bar{1} 1)\) plane align perpendicular to the loading axis (in Bragg condition for the -90 deg detector). Concomitantly, variants with \((1 0 0)\) planes perpendicular to loading axis (in Bragg condition for the -90 deg detector) twin in such a way that their \((1 0 0)\) planes line up parallel to the loading axis (in Bragg
condition for the +90 deg detector). Thus with increasing tensile stress, an increase in intensity for the (1 0 0) planes in the +90 deg detector (respective decrease in intensity in -90 deg detector) and associated opposite behavior for (0 1 1) planes indicates that type I twinning is prevalent in the tensile case. However, with type II twinning, observed behavior can not be justified where (1 0 0) and (0 1 1) planes, which are perpendicular to [0 1 1], should be rotated by 180 deg giving an equivalent diffraction orientation.

For compressive loading, Ref. [51] give a symmetric situation in their paper where the (1 0 0) planes tend to align perpendicular to the stress axis. Similar stereographic projection and a detailed discussion for compression case can be found in Ref. [51]. The results for compressive loading in this work are consistent with Ref. [51] and hence will not be repeated here. Thus as outlined and justified in the above discussion, this work has observed (1 1 1) type I twinning to be prevalent in both tension and compression.

Another interesting observation is that for tensile loading, the direction normal to the loading axis experiences a Poisson contraction. The behavior in this direction is identical to that was observed for the compressive case parallel to the loading axis. Similar observation is seen in compressive loading. Thus this observation additionally validates (1 1 1) type I twinning occurs in tension and compression.

To calculate the variant-variant conversion strain (hereafter designated as twinning strain) in martensitic NiTi, the lattice parameter values were obtained from Rietveld refinement. As
described in a previous section, GSAS Rietveld refinement was used to fit the diffraction spectra for martensite, which gives the best fit with \( P 1 1 2_1/m \) structure. In GSAS, \( P 1 1 2_1/m \) or monoclinic structure lattice parameter output has non-orthogonal angle (\( \gamma \)) in between h and k axis of hkl plane (or \( b>c>a \) in \( a,b,c \) lattice parameter value of monoclinic structure). However, incorporating the phenomenological theory of martensite, the twinning strain calculations were done by considering the non-orthogonal angle (\( \beta \)) in between h and l axis of the hkl plane (or \( c>b>a \) in \( a,b,c \) lattice parameter value of monoclinic structure). Hence, the lattice parameters were rearranged from GSAS output to use in the procedure for twinning strain calculation.

The lattice parameter values used for martensite to calculate twinning strain, were \( a = 2.898 \pm 0.0001 \) Å, \( b = 4.125 \pm 0.00013 \) Å, \( c = 4.647 \pm 0.0002 \) Å and \( \beta = 97.46^\circ \pm 0.004^\circ \). For austenite d spacing, no load lattice parameter was used from previous work\(^1\) to be \( 3.009 \pm 0.0002 \) Å and was consistent with same thermomechanical history for these samples. Thus using the above lattice parameter values, the approach illustrated in the following can be used to determine the strains associated with variant-variant conversions.

In NiTi, it is well known that the transformation associated with austenite to martensite variant take place with unique lattice correspondences\(^5\). These unique correspondences can be used to calculate the associated transformation strain from parent austenite variant to a given martensite variant. To calculate the transformation strain, the method suggested by Saburi and Nenno\(^7\) is followed. Crystallographically, the transformation from austenite to martensite (here the cubic to monoclinic phase) involves rotation, distortion and shear. In tensorial notation it is represented as \( R, D \) and \( S \). The rotational variable, \( R \), aligns the principal axes of a martensite variant with the
principle axes of the austenite phase according to relationship given by the lattice correspondence. The distortion variable, D equals the length of these axes, while the shear, S initiates the necessary amount of displacement. These three geometric processes work together to form a monoclinic cell. Here the product of DS is referred to as the deformation gradient tensor, $G^{74}$. The components of the deformation gradient tensor can thus be easily determined from geometrical considerations as

$$G_{ij} = \begin{bmatrix} \frac{a}{d_{100,B2}} & 0 & -c\sin\theta \\ 0 & \frac{b}{2d_{110,B2}} & 0 \\ 0 & 0 & \frac{c\cos\theta}{2d_{110,B2}} \end{bmatrix} \quad \text{...5.2}$$

where a, b and c are the lattice parameters of the monoclinic (θ being the deviation from 90° of the unique axis) and $d_{100,B2}$ and $d_{110,B2}$ are the lattice spacings in the <100> and <110> directions in the parent austenite phase. For the rotation variable, a normalized R tensor for each variant can be calculated from the given lattice correspondence, e.g., for variant 12.

$$R = \begin{bmatrix} 0 & -0.707 & -0.707 \\ 0 & -0.707 & -0.707 \\ -1 & 0 & 0 \end{bmatrix} \quad \text{...5.3}$$

Thus, the transformation strain along <hkl> (parent basis) can be evaluated as
\[ \varepsilon_{\text{var}} = \frac{|R . G . R^{-1} \cdot v|}{|v|} - 1 \]

where \( v = \begin{bmatrix} h \\ k \\ l \end{bmatrix} \)

...5.4

Irrespective of the type of twinning, the variant combination for each direction within 12 unique lattice correspondences will be

\[ _{12} \text{C}_2 = \frac{12!}{2!(12-2)!} = 66 \]

...5.5

In martensitic NiTi, strains can be calculated relative to the parent vector basis in three directions \((100)_{B2}, (110)_{B2}\) and \((111)_{B2}\). The strain upon twinning (twinning strain) from variant \(x_1\) to \(x_2\) (Table 1) can be thought as the difference between the strain from austenite A to \(x_1\) and the strain from A to \(x_2\). For all three directions, the total variant combinations will be 198 (66 x 3) twinning variants. Irrespective of type of twinning, in this case, a graphical representation (see Figure 5-10) illustrates the twinning strain in all 198 possible variant combinations and Table 5-1 provides the twinning strains for \((1 1 1)\) type I twinning.

The above method considers the phenomenological crystallographic theory of martensitic transformations. In NiTi, \(<111>_{B2}, <110>_{B2}, <100>_{B2}\) are three major directions and shows maximum and minimum stress induced martensite strain range either in tension or compression.
In this work, the same directions were used to determine strains associated with variant-variant conversions. As far as shape deformation and crystallography of martensite plate are concerned (for example, the case of single crystal), this theory is useful. However, in polycrystals or particularly in fine-grained samples, a martensite plate is blocked by a grain boundary and cannot extend to sufficient length and internal stresses accumulate and influence further transformation. The phenomenological theory can not provide a method to calculate these internal stresses, hence requires another additional method to evaluate and incorporate twinning strain calculations of polycrystals. In the current work, calculation of twinning strain ignores the internal stresses. But nevertheless this work is still useful to understand strain magnitudes in tension and compression.

Irrespective of the type of twinning and following lattice variant correspondence, it is seen that a total of 198 possible combinations exist to determine the twinning strain in NiTi. Out of these, 44 combinations result in positive stain, 85 in negative strain and 69 in no strain. Figure 5-10 is a graphical representation of the magnitude of the various strains. This suggests that compressive loading offers more number of variant conversions resulting in negative strain than the analogous case of tensile loading and positive strains. This study has observed (1 1 1) type I twinning in both tension and compression. The strains projected for all variant combinations for (1 1 1) type I twinning are given in Table 5-1. In this case the total number of variant reduces to 36 possible combinations, which subsequently contribute to the twinning strain. Out of these, 7 combinations result in positive strain, 15 in negative strain and 14 in no strain. Again, in case of type I
twinning, compressive loading offers more number of variant conversions resulting in negative strain to variant conversions in tensile loading resulting in positive strain.

According to Ref. [54] the differences in twinning strain occur because of the different variant being selected in tension and compression. However, to be more specific this study has determined 44 variant combinations in tension that result in positive strain and 85 variant combinations that result in negative strain in compression. Thus, according to the external stress state, these variants work together to define the total macroscopic strain in a stress-strain plot.

In compressive loading, availability of more combinations of variants that result in negative strain is expected to induce more mismatch compared to tension due to the increased variant interface area. The more competition of variants in compression and the associated mismatch hinders migration of variant interfaces. This phenomenon can be expected to result in steeper stress-strain gradient in the stress-strain curve. This hypothesis is consistent and can be connected to TEM study of Ref. [55], which showed the presence of high dislocation density in compression compared to tension.

Figures 5-8a and 5-8b show neutron diffraction spectra with indexed planes under tensile and compressive loading respectively. The peak located at 3.017 Å in tensile loading was the reflection for the (001) plane for austenite, (designated as 001 A in Figure 5-8a) and was not present during compressive loading. Analysis of neutron diffraction spectrum for the tensile sample shows that as the stress increases, the (001) peak reflection began to diminish at approximately 75 MPa and was indistinguishable at higher stresses. The fact that residual
austenite was observed at 33 MPa during tensile loading and not compressive loading shows that the higher local stresses or internal stresses are responsible for diminishing the peak appearance of 001 A in compression than in tension. This indicates that, at a particular stress, higher stress / strain fields are observed in compression over that of tension. This result is consistent with recent TEM observation of high density of dislocation, i.e., higher strain field in compression compared to tension.

In the current study, Figure 5-9 represents the normalized FWHM for 100, 011 and 111 planes in the sample during both tensile and compressive loading. It appears that variant reorientation and coalescence results in a spread of the interplanar spacings. A size scale effect due to variants growing at the expense of less favorably oriented grains can not be ruled out, but it appears that the broadening still increases in most cases due to strain redistribution following twinning. This effect is consistent with the significant peak broadening of 100 and 011 peaks at higher stresses in both tensile and compressive loading respectively. However, from current measurements, determination of effect of internal stress on peak broadening is not trivial.

5.6 Conclusions

To the best of our knowledge, this is the first time that single peak analysis and Rietveld method have been applied to investigate twinning in martensitic NiTi, during tensile and compressive loading, using an in situ neutron diffraction technique. The following conclusions were made and explained.
i. The macroscopic stress-strain response in tensile and compression differ in that a lower stress-strain gradient was observed in the tensile response but the compressive response exhibited a steeper gradient.

ii. The elastic moduli of most individual hkl planes determined from neutron spectra and elastic modulus values from extensometry for both tension and compression shown similar elastic behavior as opposed to the region where twinning dominates.

iii. In compressive loading, crystals having a (100) grain orientation with their normals lying close to the load axis are the dominant variants. In contrast, in tensile loading crystals having a (011) grain orientation with their normals lying close to the load axis are the dominant variants. The observed texture was consistent with (1 1 1) type I twinning for both compressive and tensile loading.

iv. It has been seen that there are total 198 possible twinning strain combinations. Out of which 44 combinations result in positive strain, 85 in negative strain and 69 in zero strain. Thus compressive loading offers more number (85+69) of variant conversions in oppose to tensile loading (44+69).

v. The variant conversion strains dictate the choice of various variants, satisfying strain and stress compatibility. For the case of compression compared to tension, more orientations appear that are compatible with compressive strains and this increased choice results in a steeper stress-strain gradient as the variant interfaces interact with each other during reorientation and coalescence.

vi. Compressive loading measurements suggested higher internal stresses in specimen in comparison with tensile loading.
vii. Strain redistribution following variant reorientation and coalescence results in a spread of the interplanar spacing, which manifested as increased peak broadening with increasing stress.
5.7 Figures

Figure 5-1: Schematic of experimental set up showing the principle of neutron diffraction for mechanical characterization on the Neutron Powder Diffractometer (NPD) at Los Alamos National Laboratory.
Figure 5-2: Macroscopic stress-strain response of NiTi (from extensometer) for compressive and tensile loading, showing stresses at which loading was interrupted and neutron spectra were recorded (dots). The ramp rate was 0.1 mm/min.
Figure 5-3: Section of diffraction spectra for various applied stresses for (a) tensile and (b) compressive loading. The spectra are normalized and displaced along the y axis for clarity. The scattering vector is parallel to the loading axis.
Figure 5-4: The stress strain response of 011, 100, 111, -110 individual lattice plane reflections in NiTi during loading in (a) tension and (b) compression. The horizontal line in the graph represents macroscopic onset of twinning at 0.2% offset strain.
Figure 5-5: Representative normalized peak intensities the (100) peak with stress for detector banks 180 degrees apart i.e., (a) +90° bank and (b) –90° bank during compressive loading.
Figure 5-6: Representative GSAS Rietveld refinements from detector banks 180 degrees apart i.e., (a) $+90^\circ$ bank and (b) $-90^\circ$ bank from the compressive sample in the unloaded condition.
Figure 5-7: Axial distribution plot for 100, 01-1, 110 and 21-1 planes as a function of stress during (a) tensile and (b) compressive loading.
Figure 5-8: Neutron diffraction spectra for NiTi under (a) tensile and (b) compressive load of 33 MPa. The scattering vector is perpendicular to the loading direction.
Figure 5-9: Relative broadening of 100, 011 and 111 peaks from -90 degree detector bank during tensile and compressive loading.
Figure 5-10: Number of possible variant combinations resulting in tensile and compressive strains.
Figure 5-11: Stereographic projection along [011]_M indicating the positions of (0-11)\textsubscript{M} and (100)\textsubscript{M} before (represented as full line) and after (represented as dotted line) type I twinning. The twinned (0-11) are in diffracting position. Poles are indicated in bold type and plane position after twinning with the subscript T.
## 5.8 Tables

Table 5-1: Variant conversion strain (percent) calculated along the three main directions of the parent phase

<table>
<thead>
<tr>
<th>Variant Combination</th>
<th>(100)$_{\text{B2}}$</th>
<th>(110)$_{\text{B2}}$</th>
<th>(111)$_{\text{B2}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3’G 1</td>
<td>-6.9</td>
<td>0.0</td>
<td>-14.3</td>
</tr>
<tr>
<td>6’G 1</td>
<td>-6.9</td>
<td>7.6</td>
<td>0.0</td>
</tr>
<tr>
<td>5’G 1’</td>
<td>-6.9</td>
<td>-14.3</td>
<td>-14.3</td>
</tr>
<tr>
<td>4G 1’</td>
<td>-6.9</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>6G 2</td>
<td>-6.9</td>
<td>7.6</td>
<td>14.3</td>
</tr>
<tr>
<td>4’G 2</td>
<td>-6.9</td>
<td>0.0</td>
<td>14.3</td>
</tr>
<tr>
<td>3G 2’</td>
<td>-6.9</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>5G 2’</td>
<td>-6.9</td>
<td>-14.3</td>
<td>0.0</td>
</tr>
<tr>
<td>5G 3</td>
<td>0.0</td>
<td>-14.3</td>
<td>0.0</td>
</tr>
<tr>
<td>6’G 3’</td>
<td>0.0</td>
<td>7.6</td>
<td>14.3</td>
</tr>
<tr>
<td>5’G 4</td>
<td>0.0</td>
<td>-14.3</td>
<td>-14.3</td>
</tr>
<tr>
<td>6G 4’</td>
<td>0.0</td>
<td>7.6</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Previous work has reported on the use of neutron diffraction to probe predominantly homogeneous stress-induced transformations in NiTi associated with uniaxial stress states\textsuperscript{21}. This chapter discusses neutron diffraction measurements from a NiTi disk specimen loaded laterally in compression and associated with a macroscopically heterogeneous stress state. Measurements were performed on the Spectrometer for MAterials Research at Temperature and Stress (SMARTS) at Los Alamos National Laboratory in a spatially resolved mode. Neutron spectra confirm the presence of both monoclinic and cubic phases of NiTi, with the respective volume fractions depending on the location of the measurements (and the corresponding stress state). The neutron diffraction measurements of the strain, texture and phase volume fraction offer insight in to accommodation mechanisms as the cubic and monoclinic phases co-exist in a macroscopically heterogeneous stress state.

6.1 Introduction

Equiatomic NiTi Shape-memory alloys (SMAs) are known to exhibit stress- or temperature induced transformations between high symmetry cubic (B2 - austenite) and low symmetry monoclinic (B19\textsuperscript{-} martensite) crystal structures. These reversible and thermoelastic transformations facilitate these materials to exhibit special properties called superelastic and shape memory effects\textsuperscript{24,29}. The superelastic effect occurs in superelastic NiTi (B2 - austenite), wherein large and completely recoverable strains are generated and recovered mechanically through stress-induced phase transformation from cubic austenite to monoclinic martensite.
phase. Shape-memory NiTi (B19' - martensite), on the other hand, when deformed undergoes
twinning to produce tensile strain as large as 8%. Heating results in phase transformation
(B19' $\rightarrow$ B2) and associated recovery of all strain, a phenomenon known as shape memory effect.
The phase transformations from cubic austenite to monoclinic martensite phase in these alloys
are time independent or athermal in nature, indicating that the fraction of martensite transformed
is only a function of the transformation temperature or stress. An \textit{in situ} neutron diffraction study
can be used to study such stress- or temperature-induced transformation. Previously \textit{in situ}
neutron diffraction studies of shape memory and superelastic NiTi during uniaxial loading have
been reported. However, previous work was limited to homogeneous stress-induced
transformations in bulk NiTi associated with a uniaxial stress state$^{20-22,52,75-78}$.

This study makes use of a novel geometry, that of a thin US quarter sized NiTi disc loaded in
compression coupled with spatially resolved neutron diffraction measurements. The present
work focuses on the heterogeneous stress-induced transformation in superelastic NiTi under
plane stress condition where the out of plane normal stress is negligible (or biaxial stress
distribution). Resulting heterogeneous stress distribution across subjects various regions of the
disc to a range of stress levels (high stress region to no stress region) with reference to point of
loading. The regions in the vicinity of loading, bear high stresses (above phase transformation
stresses) resulting in phase transformation of parent austenite to product martensite phase. On the
other hand, regions far from loading, bear low stresses (below phase transformation stresses).
The gradual transformation of the parent phase (under low stress) in the presence of spatial
constraints introduced by the product phase (under high stress) exists in practice where interfaces
between parent phase and neighboring product phase play an important role in the mechanical
response of NiTi alloys under multiaxial loading conditions. The response to heterogeneous stress distribution in NiTi alloys may include variant selection / variant coalescence / twinning or preferential transformation. In the literature\textsuperscript{79-80}, theories have been proposed to explain intergranular interactions and behavior of grain in SMAs, but no experimental studies have examined the micromechanical changes in terms of strain, texture and phase fraction associated with mixed load deformation mechanism. Thus, the objective of this study is to obtain insight into load partitioning / transfer as austenite and martensite phases coexist. X-ray and neutron diffraction studies in spatial resolved mode can be used to study these parameters during transformation in these alloys. Neutrons are more advantageous compared to X-ray due to their superior penetration power (several millimeters, compared to a few micrometers for X-rays from a conventional source)\textsuperscript{35}, which results in measurements being representative of the bulk polycrystal behavior without free surface effects.

The implication of the measurements lies in validating the available computational models to understand NiTi deformation behavior under heterogeneous stress state. Currently, most of the phenomenological constitutive models are based on uniaxial data, oftentimes extended to understand mixed load deformation mechanisms\textsuperscript{62,81-83}. In this context, some recent work in the literature reported several tension–torsion experiments and their modeling efforts to understand the behavior of NiTi under mixed load conditions\textsuperscript{84-87}. However, there is still uncertainty in predicting the material response under mixed or heterogeneous loading in NiTi alloys. Very little information exists for biomedical critical devices such as endovascular stents where there is a need for understanding the mechanical response of NiTi for its fabrication and use under mixed loading conditions. The difficulty of understanding mixed load deformation mechanism lies in
local variations of stress distributions (internal or intergranular stresses) across the surface which subsequently results in multi phase microstructure, consisting typically of austenite (B2), martensite (B19\(^\prime\)) and reoriented martensite.

6.2 Experimental Procedures

6.2.1 Sample fabrication

Commercially available NiTi (56.05 wt.% Ni) bars were obtained from Special Metals Corporation, New Hartford, NY. These bars were cold drawn from cast ingots that were produced via vacuum induction melting followed by vacuum arc remelting. Subsequently, bars were annealed at 550 °C for 20 min and quenched in water. These bars were then used to fabricate NiTi thin disc specimens (with 28.10 mm in diameter and 2.75 mm in thickness). The diameter to thickness ratio of the disc was intentionally kept above 10:1 to have negligible out of plane normal stresses during compression loading. These specimens were fabricated by electrical discharge machining, solutionized at 874 °C for 1 hour 45 mins in argon and oil quenched to room temperature. Subsequently annealing was done at 400 °C in air for 1 hr followed by ice water quenching.

6.2.2 Neutron diffraction and mechanical testing

Neutron diffraction measurements were performed using the Spectrometer for MAterials Research at Temperature and Stress (SMARTS) at the pulsed neutron source at Los Alamos
Neutron Science Center (LANSCE). Measurements were performed in a spatially resolved mode with the NiTi disc loaded in compression across its diameter. Aluminum spacers were designed to hold the disc throughout compression loading. The spacers were designed for two purposes, one to avoid the damage to the loading platen and two to have minimum surface contact with the platens. Figure 6-1a is the schematic of the experimental set up with disc loaded in compression. The load was ramped in stroke control at 400 N/min and kept constant for hold periods (30 - 45 mins, depending on beam intensity) where neutron diffraction spectra were collected at the center of disc for loads of 400 N (disc holding force), 6 kN, 9 kN and 12 kN. The loading was limited to 12 kN when neutron diffraction spectra at center of the disc showed coexistence of austenite and martensite phases. Neutron beam with a cross section of 1 x 1 (spatial resolution 1 mm) and 2 x 2 (spatial resolution 2 mm) mm was used in a spatially resolved mode throughout this experiment. During the experiments, the incident neutrons formed 45° angle to the loading axis and two detectors 180° apart were used to record the diffraction pattern with scattering vector parallel and perpendicular to the loading axis. The disc was thus loaded in compression, while, simultaneous neutron diffraction spectra were acquired in spatially resolved mode in two scattering geometries.

6.3 Results and Discussion

The analytical solution for elastic stress distribution in a thin disc specimen loaded in compression is given as: 88:
where $\sigma_x$ and $\sigma_y$ are the normal stresses, $\tau_{xy}$ is the shear stress and P, B, R are the compressive load, disc thickness and disc radius respectively. x and y are the cartesian co-ordinates of a given location where the center co-ordinates of the disc are (0,0). Figure 6-1b illustrates the elastic stress distribution (MATLAB polar plot) for a disc specimen under P= 12 kN force loaded in the Y direction. The stress distribution in the other direction was negligible (maximum stress was - 250MPa in X and XY direction) and hence is not represented. For a force of 12 kN, a corresponding maximum stress of 2000 MPa was generated in the disc, close to the loading point proximity of loading and decreases gradually to approx 400 MPa at the center of the disc. This stress again decreases to being stress free towards the edge of the disc, in the regions far from the loading axis. As the stress distribution is symmetric across the disc surface, neutron diffraction measurements were performed in a quarter of the disc represented as solid black circles in Figure 6-1b. As expected, preliminary analysis showed the variation in volume fraction of stress-induced martensite with stress distribution in the sample.

For compression loading of the disc, determination of elastic stress distribution from the analytical solution showed the presence of shear stresses (in addition to normal stresses) all over the regions of disc excluding the regions such as horizontal (Y axis) and vertical axes (X axis). In Figure 6-2, influence of shear stresses is qualitatively illustrated through normalized neutron
diffraction spectra at four locations A, B, C and D. Normalization is performed so that spectra from all locations have the same total intensity (neutron counts). With similar normal stresses, off-axis measurements (shear stress region, location A and C) indicate increased volume fraction of martensite compared to on-axis measurements (no shear stress region, location B and D). This is direct evidence that shear stress assists in formation of martensite with comparable normal stresses.

From the acquired neutron diffraction spectra, strains for specific grain orientation were obtained by fitting individual lattice peaks with respect to the unloaded state using RAWPLOT program in the General Structure Analysis Software (GSAS). Strains were considered from diffraction pattern with scattering vector parallel to the loading axis (Y axis). A nominal holding force of 400 N (equivalent to stress 10 MPa at center of disc) was used as “zero stress” unloaded condition. The strain, \( \varepsilon_{y}^{hkl} \), for a plane, hkl, at a given location was calculated as:

\[
\varepsilon_{y}^{hkl} = \frac{d_{hkl} - d_{0}^{hkl}}{d_{0}^{hkl}},
\]

...3.2

where \( d_{hkl} \) was the spacing of the plane at a given location and \( d_{0}^{hkl} \) was taken as corresponding lattice spacing at center of disc in unloaded condition. Since strains were relative, presence of pre-existing residual intergranular stresses was ignored. For the case of no transformation occurring in the parent phase during compression loading, analytical strains were also calculated from the austenite single crystal compliance tensor. Analytical strains, for biaxial stress distribution in the loading direction, \( \varepsilon_{y}^{hkl} \), was determined as:
\[ \varepsilon_y^{\text{hkl}} = s_{12} \sigma_{xx} + s_{11} \sigma_{yy}, \]

where \( s_{ij} \) is the single crystal compliance tensor in collapsed matrix notation and \( \sigma_{xx} \) and \( \sigma_{yy} \) are the analytical elastic stresses in \( x \) and \( y \) direction, respectively. As the texture of the sample was not known analytical strains were calculated for both [111] (stiffest) and [100] (most compliant) directions. In addition to individual directions, analytical strains were also obtained from average polycrystalline response (elastic modulus = 74.5 and Poisson’s ratio = 0.39). Considering the martensite as a heterogeneous phase present in the parent phase, the strains were also predicted in the high stress regions (above phase transformation stress) by applying Eshelby theory. Values obtained from single crystal averaging methods for austenite (elastic modulus = 74.5 and Poisson’s ratio = 0.39) were used to represent the matrix in the Eshelby predictions. Recently higher elastic constants were reported in Ref. [68] for monoclinic martensite, hence elastic modulus 101 GPa and Poisson’s ratio 0.3590 were used for martensite phase. During Eshelby analysis, inclusion (here martensite) phase fractions were estimated from neutron diffraction spectra (from Rietveld least square fit) where relative intensities of martensite peaks were compared with austenite peaks. No significant sensitivity of Eshelby strain was seen with estimated phase fraction of inclusion (with ±10 % phase fraction error results into 0.002% strain error for every 100 MPa stress). Details of Eshelby calculation are given in Appendix. Figure 6-3 compares the spatial strain measurements (on the vertical scan of \( Y = 8 \) mm) with three methods; measured elastic strain from neutron, predicted elastic strain using analytical method and
Eshelby theory with von Mises effective stress at given location. The von Mises effective stress was calculated as:

\[
\sigma_{\text{eff}} = \sqrt{0.5 \left( (\sigma_{xx} - \sigma_{yy})^2 + \left( \sigma_{yy} \right)^2 + \left( \sigma_{xx} \right)^2 + 6(\tau_{xy})^2 \right)}
\]

From Figure 6-3, strain measurement approaches are validated as the measured neutron strain falls in the region between the predicted elastic strain from most compliant [100] and stiffest [111] direction of NiTi. In low stress regions, good agreement is observed between the measured neutron strain and the predicted elastic strain from compliant [100] direction. Possible explanation for this agreement may be [100] preferred orientation of grains in loading direction of the disc. The raw neutron diffraction spectra obtained from the planes parallel to loading axis indicated absence of (111) austenite planes thereby validating absence of [111] preferred orientation of grains in loading direction of the disc. At low stresses, agreement between the measured neutron strain and the predicted strain in the [100] direction is expected as the low stress is borne by the parent phase without transforming to martensite. This is consistent with our analytical assumption. In regions corresponding to higher stresses in Figure 6-3, the increase in slope of the measured strains (i.e., austenite strains) indicates that the load is transferred from austenite to the martensite phase. It is interesting to note the reasonable agreement between measured strain and Eshelby theory where transformed martensite phase is assumed to be the inclusion in the austenite matrix. Since, Eshelby theory considers only the elastic mismatch, this indicates that the allotropic (shape change) mismatch is accommodated. This is consistent with previous observations in shape memory and superelastic NiTi. 21
In the context of the aforementioned accommodative nature, Figure 6-4 is represented to establish the heterogeneous and preferential (from austenite to martensite phase) transformation under a mixed loading condition. Figure 6-4 represents overlay of normalized spectra (from a vertical scan at $Y = 7.5$ mm) with decreasing stress from -470 MPa to -11 MPa (i.e., $X = 0$ mm to $X = 11$ mm, see Figure 6-1b for stress distribution). From this figure, it is observed that, with decreasing stress, there is an increase in volume fraction of austenite and decrease in volume fraction of martensite facilitating accommodation of mismatch stresses (internal or intergranular stresses). Macroscopically, this effect results in a heterogeneous stress-induced transformation in the disc. After $X = 8$ mm (below $\sigma_{yy} = 70$ MPa), the decrease in austenite intensity indicates the unfavorable orientation of austenite, thereby making conditions less favorable for phase transformation.

6.4 Conclusions

In summary, the significance of the present work lies in potential use of novel specimen geometry (thin disc under compression) to relate qualitatively and quantitatively the thermoelastic deformation behavior in the presence of an heterogeneous stress state. The data is of immense value to validate available computational models to understand NiTi deformation behavior under heterogeneous stress state. Furthermore, it produces valuable mechanical insight of multiphase microstructure in SMAs during heterogeneous loading. The result also offers information on load transfer / partition and strain evolution in high symmetry and lower symmetry phases which give insight into martensite-austenite interfaces in NiTi alloys.
6.5 Figures

Figure 6-1: (a) Schematic of the experimental setup with disc loaded in compression. (b) Polar plot of analytical elastic stress distribution in the loading direction (Y direction). Solid black dots illustrate the location of neutron diffraction measurements. The stress distribution in other directions was negligible (below 250 MPa).
Figure 6-2: Section of diffraction spectra from locations A, B, C and D of the disc. Schematic of quarter part of the disc illustrate locations A, B, C and D from where the diffraction spectra were obtained. Accompanying table reports the normal and shear stress values for regions A, B, C and D.

<table>
<thead>
<tr>
<th>region</th>
<th>normal stress (MPa)</th>
<th>shear stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-249</td>
<td>129</td>
</tr>
<tr>
<td>B</td>
<td>-247</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>-131</td>
<td>88</td>
</tr>
<tr>
<td>D</td>
<td>-130</td>
<td>0</td>
</tr>
</tbody>
</table>
Figure 6-3: Comparison of spatial strain measurements with three methods. The corresponding stresses were obtained from analytical solution\textsuperscript{88} for vertical scan of $Y = 8$ mm.
Figure 6-4: Overlay of normalized diffraction spectra from a vertical scan at \( Y = 7.5 \) mm. Diffraction spectra show increase in volume fraction of austenite and decrease in volume fraction of martensite with decreasing stress. Preferential transformation from austenite to martensite is seen at \( X = 8 \) mm (with \( \sigma_{yy} = 70 \) MPa).
CHAPTER 7: ANALYSIS OF SYNCHROTRON DIFFRACTION SPECTRA OBTAINED DURING STRESS-INDUCED TRANSFORMATIONS IN A SUPERELASTIC NITI WIRE

Previous studies by the author included use of the synchrotron diffraction technique for mechanical characterization of shape memory alloys (SMAs). For example, in situ synchrotron X-ray diffraction (at Argonne National Laboratory) has been used to study stress-induced transformations in NiTi (C.R. Rathod, M.S. Thesis, 2003). These measurements were carried out in situ, by recording diffraction spectra during mechanical loading. A methodology was established to analyze synchrotron diffraction data from stress-induced transformations in NiTi and to obtain quantitative phase fraction, texture and strain information. As part of his Ph.D. dissertation, the author has performed refinements in the analysis methodology and that work is presented here in the form of chapter.

7.1 Introduction

NiTi alloys are of commercial and theoretical interest due to the shape memory and superelastic phenomena they exhibit. These phenomena are the result of a thermoelastic martensitic transformation from the parent cubic austenite (B2) phase. The shape memory effect is associated with the deformation of a monoclinic martensite phase (B19’) followed by its reversion to the parent phase upon heating. On the other hand the superelastic effect, is associated with a stress-induced austenite to martensite transformation and its reversion to the parent phase upon releasing the stress. The superelastic effect in NiTi is typically associated with recoverable strains up to 8%. This impressive amount of strain is produced due to stress-
induced transformation in NiTi alloys. Hence, mechanical characterization study is of obvious interest in these alloys.

Diffraction techniques for mechanical characterization have long been used to study deformation behavior in crystalline materials\textsuperscript{35,91}. Neutrons, synchrotron, conventional x-ray and electron are all various sources for diffraction techniques. Use of all these techniques for diffraction spectra for mechanical characterization relies on the use of atomic planes as internal strain gauges\textsuperscript{35}. The distances between the atomic planes, directly obtained from diffraction spectra, are used to compute strains. In addition to strain information, the integrated intensity of diffraction peaks in spectra can be used to determine the volume fraction of the scattering phase. Furthermore, the relative intensity of diffraction peaks in a particular phase can be used to determine the amount of texture or preferred orientation in that phase. In the case of superelastic NiTi wire, performing such diffraction measurements \textit{in situ}, i.e., by simultaneously recording diffraction spectra from samples that are subjected to external stresses or temperature changes, can provide quantitative, phase specific information on the evolution of strains, texture and phase volume fractions. Previously, techniques like neutron diffraction were applied to study deformation in bulk samples (where the size scale is between 100 microns to few centimeters)\textsuperscript{35}. However, these techniques are limited to standard geometries and longer measurement times, and require large diffraction volumes because of the small neutron flux available at existing neutron sources. Consequently, less spatial resolution (1-10 mm) is associated with neutrons. On the other hand, third generation high energy or synchrotron X-rays offer great advantages in probing bulk materials with greater spatial resolution (0.1-10 mm). This method has shown remarkable success in investigations of bulk and intricate geometries (where the size scale is between few
microns to several millimeters). Previously *in situ* synchrotron diffraction technique was used to study the deformation behavior in crystalline materials \(^5\text{,}^{92\text{-}95}\), but no quantitative study involving phase transformations has been represented before. Here we use the *in situ* synchrotron diffraction technique to quantitatively study the phase specific strain, volume fraction and texture evolution during stress-induced transformation in shape memory alloys. Here, we demonstrate for the first time the use of synchrotron diffraction measurements to quantitatively observe the stress-induced transformation in polycrystalline superelastic NiTi wire. The implication of these measurements lies in understanding the deformation behavior in medical device geometries such as stent, orthodontic and guide wire geometries. Such experimental measurements can be extended to ascertain the discrete phase strain, phase volume fraction, and texture evolution during stress-induced transformations in stents (an application where doctors use them to control occlusions in human arteries) and is also useful in assessing the microstructural and micromechanical changes due to pulsatile fatigue. Thus, objectives of this study are

- To establish an analysis methodology from synchrotron diffraction data to determine strain, phase fraction and texture in NiTi alloys;
- To study nature of phase transformation in a NiTi wire; and
- To determine the internal strain, phase volume fraction and texture evolution during a stress induced phase transformation in NiTi in the presence of tensile loading.
7.2 Experimental Procedures

7.2.1 Sample fabrication and characterization

All the diffraction experiments were performed on the Dupont-Northwestern-Dow Collaborative Access Team (DND-CAT) bending magnet beam line at the advanced photon source, Argonne National Laboratory (ANL), Argonne, IL. Commercial NiTi wires of 0.9 mm wide and 0.25 mm thick (with various lengths 3-5 cm, from Memory Inc., Brookfield, CT) were used for the experimental study. Differential scanning calorimetry with a PERKIN-ELMER* DSC-Diamond calorimeter at a rate of 20 K-min$^{-1}$ under nitrogen cover gas was used to determine the transformation temperatures.

7.2.2 Synchrotron diffraction and mechanical testing

The schematic experimental setup for the synchrotron transmission technique is shown in Figure 7-1. The NiTi wire was irradiated with a monochromatic, parallel beam of 65 KeV photons (wavelength of about 0.19 Å) with 0.5 mm X 0.5 mm square cross section, placed in the center of the gauge section and parallel to the sample thickness. Uniaxial *in situ* tensile tests were performed at room temperature using a miniature, screw-driven tensile device described by Noyan and Cohen$^{96}$. The tensile strain was increased stepwise and held constant for 600 seconds during X-ray exposure time. During this test, the strain was accounted from laser extensometry data, obtained in multiple steps (26 different stress levels) of loading and unloading of the NiTi.

* PERKIN-ELMER is a trademark of Perkin-Elmer Physical Electronics, Eden Prairie, MN.
Two samples having the same cross sectional area were used for data collection. Both the samples were uniaxially stressed to 375 MPa and unloaded. Diffraction data for both samples showed similar spectra. The objective of sample 1 (designated hereafter as S1) was to track strain, texture and phase fraction in a sample. Fe powder was used as a reference ring for accurate strain quantification and error correction purposes in S1. The iron powder was filled in a small polyethylene container fixed directly to the specimen gauge section using rubber bands. Sample 2 (designated hereafter as S2) was used to track the nature of the phase transformation in NiTi wire. To observe the nature of phase transformation at higher stress, the sample was moved vertically 2mm up and down from the mean position (original position) and additional diffraction patterns were recorded. The charge couple device (CCD) camera was used to capture the complete ring shaped diffraction patterns from the specimen. It was manufactured by MAR, Inc. (Evanston, IL) providing 16 bit intensity readings on 132 mm screen consisting an orthogonal array of 2048 x 2048 pixels. The distance L (Figure 1b) between the CCD camera and specimen was 377 mm that provided simultaneous recordings of all rings with diffraction angles $\theta \geq 3.72$ deg. The previously reported $^{95,97}$ details and precautions to minimize errors while performing synchrotron X-ray diffraction experiments were followed throughout the experiment. The path length of the incident beam inside the specimen was 0.25 mm thick and the diffraction volume over which the average strain results measured was about 0.0625 mm$^3$.

7.3 Data Analysis Methodology

The raw diffraction pattern images were obtained at 26 different stress levels during loading and unloading of the NiTi wire. In the ideal case, diffraction patterns are composed of perfect and
concentric circles. These perfect rings take the shape of ellipses with increasing stress on the sample. As the semi-axes of these ellipses are oriented parallel and perpendicular to the direction of loading, the simplest approach to evaluate data is to determine the diameter in horizontal and vertical directions. Though this approach is fairly applicable to extremely smooth diffraction rings obtained from a fine-grained diffracting specimen, it is not accepted universally. Here, an algorithm has been developed similar in some aspects to that proposed by Korsunsky et al. 97 and Wanner and Dunand 95. This algorithm consists of using the whole diffraction ring for data analysis and also it considers maximum intensity (along the radial direction) as the key factor in determining the center of the pattern. The algorithm has been implemented in the MATLAB 6.0 software package and consists of the following steps (see Figure 7-2). Details of this methodology are available in Ref. [4].

### 7.3.1 Raw image

Figure 7-2a shows a typical diffraction pattern, obtained from CCD camera representing the austenite phase. These raw diffraction images were saved in 16-bit Tiff format.

### 7.3.2 Identification of center of pattern

This step differs from other algorithms detailed elsewhere, in that the center of a diffraction pattern is determined with greater accuracy. The method essentially consists of locating the center of the pattern image (pixel-wise (1024, 1024)) and then using this center to determine the center of the brightest ring (ring with maximum intensity). This was accomplished by analyzing Fe (110) ring for S1 and (110) austenite ring for S2 respectively. Figure 7-2b show the procedure
for identification of center, where in the first step the X coordinate was varied until the same d spacing values (or same radius in pixels) were observed at 0 and 180 degrees (azimuth angle, see MATLAB simulated diffraction pattern). Center coordinates changed from center (1024, 1024) to center (1034, 1024) for the pattern shown. In the second step, the X coordinate was fixed (X=1034) and the Y coordinate was varied until the same d spacing values were obtained at 90 and 270 degrees. Subsequently, this procedure was validated by obtaining d-spacing vs. azimuth angle distribution to a best-fit straight-line graph (see Figure 7-2b). The center coordinates for the diffraction pattern shown here were obtained as center (1034, 994). Our new way of identification of pattern center suggests most appropriate center location, as well as it provides extra advantage in programming (here it is MATLAB) to do the peak fitting and integration of peak area, with no additional peak shift (i.e., comprising only peak shift due to strain) over azimuth angle in radial direction.

7.3.3 Simulation of diffraction pattern in MATLAB

After the center identification procedure, simulation of diffraction pattern was followed. The complete diffraction pattern was divided into 72 \( \phi \) steps (5-degrees for each step) and each 5-degree step was divided into 30 sub-steps of 0.166 degree. The idea behind dividing the pattern in two stages was to facilitate Gaussian fitting over 5 degrees. However, extraction of intensities from the pattern was separated by 0.166 degree. For all 2160 radial slices, the intensity was extracted. Rebinning was performed for the whole pattern and data was saved in a long row matrix for the subsequent step. Figures 7-2c show the simulated diffraction pattern (MATLAB polar plot) at no load. The polar plot is designated with 0,30,60,90 to 360 degrees in \( \Delta \theta \) direction.
represented as azimuth angle and radius with 20, 40 and 60 mm (approx. 310, 620 and 930 in pixels) in $\Delta r$ direction. Similar designations were used for all diffraction patterns.

### 7.3.4 Gaussian peak fitting for radial slices

During the analysis methodology Gaussian peak fitting (due to the monochromatic nature of the synchrotron x-ray beam) was performed to determine strain, phase fraction and texture evolution from the diffraction rings. Gaussian peak fitting was used to capture the amplitude, center, and width of a diffraction peak. The radial slices consist of various diffraction peaks. Each diffraction peak was fitted to a Gaussian curve using MFIT$^{98}$ program implemented in MATLAB. During Gaussian fitting, 30 radial line slices within 5 degrees were integrated. Thus a complete ring comprised of 72 such Gaussian fits. Failure of the fitting algorithm due to reasons such as graininess of the ring and noise in diffraction data at some locations were handled individually. The representative Gaussian peak fit is shown in Figure 7-2d.

### 7.3.5 Strain analysis

As the loading progresses from zero stress to higher stress levels, the circular diffraction ring takes the shape of ellipses in the diffraction pattern. Earlier work$^{94,95,99}$ showed that the use of ring diameter in strain analysis is independent of the choice of the pattern center and doesn’t affect the strain results. Hence, here the change in diameter of the diffraction rings is accounted for strain in the sample. The ring diameter is obtained from the diffraction spectrum comprising of plane reflections present in diametrically opposite locations. Figure 7-2e represents a slice of the diffraction ring in the $\Delta r$ direction. The strain in the longitudinal and transverse direction is
ascribed from the ring diameter obtained from the diffraction spectra in the corresponding longitudinal (line connecting 90 degrees to 270 degrees, in azimuth angle) and transverse direction (line connecting 0 degrees to 180 degrees, azimuth angle) respectively. Subsequently, the strain in all directions is calculated by the following methodology.

For small Bragg angles, diameter $D$ of the diffraction ring on the camera screen is inversely proportional to lattice spacing $d$ as

$$d \approx \frac{2\lambda L}{D}$$  \hspace{1cm} \text{...7.1}

where $\lambda$ is the wavelength of the synchrotron beam and $L$ is the specimen to camera distance.

From the $d$-spacing, the lattice strain $\varepsilon_{hkl}$ in a sample can be calculated as:

$$\varepsilon_{hkl} = \frac{d_{hkl} - d_0}{d_0} = \frac{D_0 - D}{D_0}$$  \hspace{1cm} \text{...7.2}

where $d_{hkl}$ is the spacing of the plane (hkl) subjected to stress and $d_0$ represents the spacing of plane (hkl) obtained from the initial state or unloaded stress state of the sample. Similar formulation is applied to diameter $D$. Eq. 7.2. has wide acceptability in strain measurements and it tacitly assumes that $\lambda L$ remains constant throughout the experiment. In many practical cases, this assumption is not completely justified. The specimen to camera distance $L$ may change due to small positioning errors as the specimen is kept perpendicular to the beam. In addition, the specimen position is manipulated due to the applied external load on it. With the nominal specimen to camera distance used in our study, an unintentional specimen displacement of only 0.1 mm in the direction of beam would cause a spurious lattice strain of about $2 \times 10^{-4}$. Also, the stability of the beam, especially its wavelength, is an important variable that affects the strain
measurements. If the wavelength and distance $L$ change occurs during the experiment, erroneous results might occur. Eq. 7.2 is thus modified and details can be found in Ref.[95]. The modified equation considers the iron powder reference ring diameter to remove the spurious lattice strain in the sample. The strain analysis equation can then be given as

$$
\varepsilon_s = 1 - \left[ \frac{D_s}{D_0s} \right] \times \left[ \frac{D_{0c}}{D_c} \right] \quad \ldots 7.3
$$

where $s$ and $c$ subscripts represent the quantities related to the specimen and the calibration iron powder, respectively. In this case, the strains are calculated relative to the initial state of the specimen. The presence of pre-existing residual intergranular stresses is ignored.

### 7.3.6 Phase fraction analysis

Phase fraction information can be obtained by integrating indexed rings corresponding to the austenite and martensite phases respectively. The simplest approach is to determine the volume fraction of martensite ($V_{mar}$) is from the integrated intensity of the austenite rings:

$$
V_{mar} = 1 - V_{aus} = 1 - \left( \frac{I_{hkl}}{I_{hkl}^0} \right) \quad \ldots 7.4
$$

where the volume fraction of austenite ($V_{aus}$) at a particular stress level is determined from $I_{hkl}$ and $I_{hkl}^0$, the integrated normalized (hkl) intensities at that stress and zero stress respectively. Intensity normalization is performed by making the number of counts equal in each diffraction pattern. Intensity normalization is performed to compensate for changes in the intensity of synchrotron beam and unavoidable changes (like slight rotation of sample due to loading etc.) occurring during deformation.
In an ideal case, if the orientation of all austenite grains throughout the deformation remains the same as the orientation in the no load condition of the sample and also if the transformation from austenite to martensite phase takes place in such a manner that the intensity of austenite peaks decreases at the same rate giving $V_{mar}$ values independent of $(hkl)$ from Eq.4, then all the austenite peak reflections will give the same volume fraction of martensite. However, if the texture changes, then the corresponding change in the peak intensities would result in different volume fractions of martensite from the different $(hkl)$ intensities. Figure 7-2f shows a representative radial slices obtained from the phase fraction analysis. The normalized integrated intensities from the individual peaks (from the radial slice) corresponding to austenite and martensite phases were used to calculate the phase fraction in the sample at the corresponding stress level. In this case, the integrated intensity for a particular plane utilized the 2160 radial slices of diffraction pattern. 72 Gaussian peak fits were used to calculate the area under peak.

7.3.7 Texture analysis

The thermomechanical extrusion process to fabricate the wire specimen results in texture or preferred orientation among grains. The texture manifests in the diffraction pattern as non-uniform intensity of various plane reflections (diffraction rings) or incompleteness of diffraction ring over azimuth angle. One-way to do the texture analysis in such a case is to unfold the diffraction ring and determine the non-uniform intensity spread over the azimuth angle. The texture index values obtained from diffraction ring intensities were used as a measure to assess texture in the sample. Here, we define the texture index (TI) as the ratio of 360 degrees to the
non-uniform intensity spread (no transmitted intensity region or incomplete region) in terms of full width half maximum (FWHM in degrees).

\[
\text{Texture index (TI)} = \frac{360^\circ}{\text{non-uniform spread of ring in terms of FWHM} \text{ (degrees)}} \quad \ldots7.5
\]

For example, TI value 1.0 shows random orientation of grains and TI value greater than 1.0 shows preferred orientation in the sample. Thus variation of TI value from 1 to \( \infty \) indicates random polycrystalline to single crystal specimen respectively. In previous deformation studies of equiatomic NiTi system, strong texture evolution in austenite (preferential transformation) was seen during stress induced phase transformation from parent phase to product phase\(^{23,52}\). Hence, texture evolution was expected in the present case with loading.

Although, only pole figure incorporating results from at least three orthogonal directions can provide a complete description of preferred orientation\(^{100}\), fiber texture can be gauged from the rotational spread of rings around the fiber axis. In this case, the initial fiber texture is determined with following methodology given below. The general relation which is used to calculate the angle between the diffracting plane and fiber axis is given as\(^{33}\):

\[
\cos(\phi) = \cos(\theta) \times \cos(\delta) \quad \ldots7.6
\]

where \( \phi \) is the angle between the fiber axis and the general position \( N \) for any plane under consideration (in this case, 200A and 110A lattice planes), \( \theta \) represents the Bragg angle and \( \delta \) is the azimuth angle from the fiber axis to the nearest fold of the diffraction ring under consideration. Comparison between the interplanar angles of planes with fiber axis and
determined φ angles were used to determine the fiber texture. Figure 7-2g shows unfolding of the diffraction ring in the Δθ direction during texture analysis. Thus, texture evolution was accounted by comparing the non-uniform intensity spread at various strains.

7.4 Results

Differential scanning calorimetry determined the austenitic start (Aₜ) and austenitic finish (Aᵣ) temperature as -3.81 °C and 18.55 °C, and martensitic start (Mₜ) and martensitic finish (Mᵣ) temperature as 7.94 °C and -142.08 °C, respectively. DSC thus confirmed the stability of austenite at room temperature.

Figure 7-3 shows the macroscopic stress-strain curves of superelastic NiTi samples (S1 and S2) tested in the synchrotron beam. The markers on the curves depict the 26 different stresses at which the diffraction spectra were recorded during loading and unloading of the sample. This stress-strain response of superelastic NiTi is associated with a stress-induced phase transformation, where the initial high symmetry austenite phase transforms to low symmetry martensite phase with the increase in the stress. At maximum stress, both samples showed fully transformed martensite phase. On unloading, the stress-induced martensite becomes unstable and transforms back to parent phase with full strain recovery (concomitant elastic recovery).

Figure 7-4a illustrates diffraction patterns from the NiTi wire at zero and 375 MPa. Both patterns were indexed and subsequently used to study the deformation behavior of the wire with loading.
The reversible transformation of austenite phase to martensite phase with stress is represented in Figure 7-4b.

The diffraction pattern obtained from synchrotron diffraction is similar to that of transmission electron microscopy i.e., smaller Bragg angles for low index planes from the perspective that the wavelength of synchrotron X-rays is considerably smaller than the d spacing of low index lattice planes of highly symmetric crystals. This means that low index lattice planes are mostly oriented parallel to the synchrotron beam when they diffract. In addition, most of the planes of austenite are present in both, longitudinal and transverse direction (in diffraction pattern) enabling the calculation of strain in both the direction and Poisson’s ratio. Figure 7-5 illustrates the absolute lattice strain calculated from 110A diffraction ring in the longitudinal direction where the E-modulus is reported by taking the slope of stress-strain curve. Figure 7-6 illustrates 110A lattice strains vs. azimuth angle. From the figure, the two different regions, tensile and compressive nature of stress state can be seen during tensile loading. In addition, it shows the strain reversion extracted from the diffraction pattern. Furthermore, in the fully loaded state, the ratio of strain in the transverse direction to the strain in the longitudinal direction accounted for determining the Poisson’s ratio. The Poisson’s ratio obtained was 0.427 and is compared with previous work\textsuperscript{101} in a subsequent section.

Figure 7-7 shows the volume fraction of martensite determined from the normalized integrated intensities of individual plane reflections (110A, 200A, 211A and 002 M) (see Eq.4) and plotted as a function of the superelastic strain. Here superelastic strain is reported as the difference
between the total strain and the elastic strain during loading, A represents the austenite phase and M represents the martensite phase.

Figure 7-8 shows the ratio of integrated intensities for lattice planes for both austenite and martensite phases with superelastic strain. The intensity ratio was intentionally taken for similar d-spacing planes (austenite lattice plane d-spacing and corresponding or closer martensite lattice plane d-spacing) to confirm the lattice correspondence between austenite and martensite phases in NiTi wire. The following lattice planes (d spacing in brackets) were chosen for integrated intensity ratios. For the austenite phase, the integrated intensity ratio of the 200A lattice plane (1.49 Å) to the 110A plane (2.11 Å) is reported. For martensite phase, integrated intensity ratio of the 002M lattice plane (2.28 Å) to the 022M plane (1.51 Å) is reported. However, the 020M (2.08 Å) and -111M (2.14 Å) martensite lattice planes have closer d-spacing to the 110A lattice plane d-spacing of the austenite phase. The overlapping or convoluted nature of 020M and -111M rings in the diffraction pattern make the analysis impossible. Hence, the 002M lattice plane was selected for the integrated ratio analyses. Nevertheless from a crystallographic point of view, the 110A lattice plane is involved in the formation of the 002M lattice plane during phase transformation.

Figure 7-9 shows the texture evolution for planes 110A, 200A and 002M, where the Y-axis and X-axis are plotted with texture index and superelastic strain respectively. The 200 A shows an increase and decrease of the texture index (measure of texture evolution) with loading and unloading. For the martensite phase, decrease is seen. Figure 7-10 is presented to examine the sensitivity of our texture index analysis methodology. Figure 7-11 is illustrated to examine the
heterogeneous transformation in the thin wire during tensile loading. Table 7-1 gives the results from the calculation involved to determine the fiber texture in wire from fold symmetries (diffraction arcs) present in the diffraction pattern.

7.5 Discussion

With loading, the initial high symmetry austenite phase transforms to a low symmetry martensite phase. Figure 7-4a shows the corresponding diffraction pattern at zero stress (austenite phase) and high stress (martensite phase). Figure 7-4b shows the progression and reversibility of the stress-induced transformation in the longitudinal direction where a short section of the diffraction spectra is represented at each stress level. Upon loading, the shift of peaks to greater d-spacings results from increasing elastic tensile strains while, the decrease in intensity of sharp peaks (austenite) and the simultaneous increase in the intensity of broad peaks (martensite) is due to the transformation from the austenite parent phase to the martensite product phase. The product phase shows the broad nature of peaks, which is due to diffraction of the low symmetry martensite phase.

The corrected lattice strains in the longitudinal direction from 110A lattice planes are shown in Figure 7-5. The longitudinal and transverse strains showed similar nature in the load-unload cycle. The slope of the stress vs. absolute strain curve or elastic modulus shows variation in three different regions, from 41 GPa to 78 GPa. The initial moduli is expected to be influenced by settling of the wire.
Here, the strains from individual lattice reflections are reported only for the austenite phase. As martensite peaks could not be used to characterize strains because a $d_0$ value for the nascent martensite cannot be determined easily. In addition, the low-symmetry martensite has several overlapping peaks which are difficult to separate. It is seen that the 110A elastic modulus calculated from the linear region is $78 \pm 5$ GPa which is in good agreement with the elastic modulus ($74.7 \pm 5$ GPa) calculated for the 110A lattice plane from neutron diffraction studies\textsuperscript{101}. In addition, the elastic modulus for polycrystalline NiTi calculated from single crystal elastic constants measured from acoustic studies by Brill et al.\textsuperscript{90} results in 78.1 (Voigt average)\textsuperscript{102}. Thus \textit{in situ} synchrotron x-ray diffraction under load can be used as an alternative to neutron diffraction to accurately determine the elastic modulus and Poisson’s ratio of crystalline materials. Figure 7-6 plots the 110A lattice strain with azimuth angle. It shows a clear distinction between the tensile and compressive regions in the sample. It is seen that the strain reversion points follow the line that make ~60 degrees to fiber axis. In addition, it is observed that the calculated Poisson’s ratio of NiTi for cubic austenite is 0.427 and is in very good agreement with previous results\textsuperscript{102}. In addition, Figure 7-6 shows the 110A lattice strain evolution with azimuth angle with each step of loading. It is suggested that the fitting of 110A single crystal NiTi deformation model\textsuperscript{62,103} to 110A lattice strain evolution in this polycrystalline wire might provide some information on the constraints of grains to study the load transfer mechanics in NiTi wires.

As described previously, a calculation of the volume fraction change from the austenite parent phase to the martensite product phase was done using the integrated intensities from the diffraction rings. Overall, an increasing relationship of the phase fraction change with superelastic strain is found for the peaks examined during tensile loading of the NiTi sample (see
Figure 7-7). The volume fraction of martensite predicted by 110A planes is higher than the 200A and 211A planes. This volume fraction inequality predicted by all three austenite planes can be understood from the preferable formation of martensite lattice variants from 110A planes in comparison with 200A and 211A planes. The relationship between the recoverable superelastic strain with phase fraction and texture can be given by 102

\[ \varepsilon_{hkl}^* = 2 \cdot V_m \sum_i F_i \cdot \varepsilon_{hkl}^i \]

where \( \varepsilon_{hkl}^* \) = superelastic strain along \(<hkl>\), \( V_m \) = volume fraction of martensite and \( F_i \) = a texture function, that is indicative of the fraction of variants that are of type \( i \). The factor 2 is introduced, considering 24 habit plane variants. In the case of compression, Ref. [102] describes the total superelastic strain, which depends on the texture of the sample. Here it is noted that the phase fraction evolution is determined from examining individual peaks, which may not be completely representative of the transformation due to texture. The deconvolution of these effects will be addressed systematically in future work (possibly by integrating multiple rings). Nevertheless, the trends offered by examining single peaks are of value.

To investigate texture changes, the integrated intensity ratios of 110A peaks to the 200A peaks and 001M peaks to the 022M peaks are presented. These ratios show the increase and decrease with loading and unloading respectively (see Figure 7-8). This suggests that austenite grains in the (110) orientations are transforming before the (200) oriented grains during deformation. In addition, the decreasing ratio of 001M to the 022M with unloading shows that the preferential
disappearance of (002) oriented martensite variants over (011) oriented martensite variants. Thus the established single crystal lattice correspondence relationship 110 A || 002 M is observed in the NiTi wire. The curve also shows the disappearance of (110) oriented austenite grains at a faster rate than (100) oriented austenite grains, which is consistent with established NiTi lattice correspondence theory. Though detailed work is not done on martensite rings, early appearance of (00l) oriented martensite variants are qualitatively confirmed during the transformation from austenite to martensite. In the present case, 110A are transforming preferentially to 002 M. This suggests that in this case the 6th lattice correspondent variant is dominant during deformation of the textured NiTi sample. However, after the formation of 002M, other martensite variants such as -111M must be formed from 110A grains. The resolution and overlapping nature of these diffraction rings in the martensite phase make it impossible to verify the lattice correspondence. The established lattice correspondence between the parent phase and martensite, is validated where possible from Ref.[104].

The texture evolution in NiTi wire with loading and unloading is illustrated in Figure 7-9. From this figure, it is evident that texture index (defined previously) for austenite (lattice plane 110A and 200A) doesn’t change due to superelastic phase transformation in NiTi. However, the difference between texture index in initial condition (e.g., for lattice plane 200A, as received is 1.08) and final condition (after load-unload cycle is 1.04) is attributed to error.

Our texture analysis methodology showed that the 110A lattice plane texture index doesn’t change significantly with superelastic strain. This is very unlikely as the 110A lattice plane takes part in formation of 002M lattice plane during phase transformation. To examine the sensitivity
of texture index methodology and establish the texture evolution in 110A lattice plane Figure 7-10 is represented. It shows that the section of unfolded 110A diffraction ring in $\Delta \theta$ direction (between 140 degrees to 220 degrees in azimuth angle) with increasing and decreasing strain. As the strain increases, reduction of intensity for 110A diffraction ring results in formation of diffraction arcs over azimuth angle. The nature of diffraction arcs over azimuth angle shows six-fold symmetry (For clarity, Figure 7-10 shows only one-fold) consistent with the multiplicity of 110 A diffraction ring. Thus the transformation of diffraction ring (with uniform intensity) into diffraction arcs validates the texture evolution in the sample. This indicates that the sensitivity of our texture index methodology is very low and can not be applied to every case.

The non-uniform intensity of rings in unstressed condition shows the presence of initial fiber texture in a sample. It is observed that the angle between the fiber axis and the nearest 200A fold is 36.28º and the nearest 110A fold is 30.1º. The indices [uvw] of the fiber axis are determined from the interplanar angles. The calculated interplanar angles agree with the values of $\phi$ (interplanar angles given in tabular form, see Table 7-1) for the [211] direction for these planes and are within experimental error. Hence, the [211] strong initial fiber texture is accounted in the sample. In addition, it is understood that the diffraction pattern shows weak fold symmetries (weak intensity arcs) in other direction which shows the weak fiber texture nature in sample in other direction. Thus, the presence of weak and strong texture direction validates the multiple fiber texture in a sample. It is understood that these wires were multi-pass extruded hence expect to show the strong and weak fiber texture. This multiple fiber texture in wire is attributed to cutting of the wire from sheet (since wire had a rectangular cross-section).
Figure 7-11 shows the heterogeneous transformation in NiTi wire. Presence of both the parent and product phases in the tensile loaded sample at the same stress level proves that NiTi wire geometries undergo a heterogeneous type of phase transformation under tensile loading. Similar results have been reported in Ref.[77,105]. In that work heterogeneous deformation under tension and homogeneous deformation during torsional loading of NiTi micro tubes was observed.

7.6 Conclusions

Synchrotron diffraction measurements have been used to study the reversible stress-induced austenite to martensite transformations by obtaining diffraction data as superelastic NiTi is subjected to stress. A stress-induced fully reversible austenite to martensite phase transformation was observed in NiTi. Diffraction data were analyzed from both austenite and martensite phases. A data processing routine was implemented in MATLAB to analyze diffraction patterns and used to follow the strain, phase fraction and texture evolution during loading and unloading. Following are the conclusions from this study.

i. For the first time a methodology was established to quantify the strain, phase fraction and texture evolution during loading and unloading in superelastic NiTi using synchrotron X-rays.

ii. Synchrotron diffraction technique was used to calculate lattice strains. The lattice strain measurements were easier and accurate due to the use of reference iron powder during the experiment. A reference ring from the iron powder was used to remove spurious
strains, which arose due to slight movement and rotation of the specimen during the experiment. The lattice strain vs. stress plot was used to calculate the plane specific E-modulus and Poisson’s ratio in NiTi and showed consistency with theoretical and other reported values. The agreement of E-modulus and Poisson’s ratio from literature and experiments in this study shows that synchrotron diffraction under load can be used as alternative method to determine these quantities.

iii. Although this measurement technique does not give insight into the individual variants of NiTi readily, the integrated intensity ratios of 200A to the 110A for austenite and 001M to 022M for the martensite were used to confirm the single crystal lattice correspondence relationship $110 \ A || 002 \ M$ in polycrystalline NiTi using synchrotron diffraction.

iv. The phase fraction and texture evolution involve convoluted effects. Nevertheless general trends were observed and reported. Limitations of using the degree of folds in the rings as a gauge of texture are presented.

v. This is for the first time a synchrotron X-ray diffraction technique has been applied to identify heterogeneous aspects of the transformation in NiTi during tensile loading.

Thus, this work has established a methodology and emphasis will be placed on *in situ* diffraction measurements. This methodology can be extended to ascertain the discrete phase strain, phase volume fraction, and texture evolution during stress-induced transformations in NiTi wire geometries and can be used to assess the microstructural and micromechanical changes due to
pulsatile fatigue. In addition, this work can be used in future investigations of the mechanics of load transfer and stress cycling in superelastic NiTi. The results presented in this study have direct implications for NiTi thin geometries such as stents, guide and orthodontic wires.

### 7.7 Figures

![Diagram of synchrotron diffraction](image)

**Figure 7-1:** (a) Principle of *in situ* synchrotron diffraction for mechanical characterization on the Dupont-Northwestern-Dow Collaborative Access Team (DND-CAT) bending magnet beam line at Argonne National Laboratory. (b) Schematic of experimental setup in terms of trigonometric geometry.
Figure 7-2: (a) CCD image of austenite diffraction pattern. (b) Center identification procedure. (c) Simulation of raw image in MATLAB code. (d) Gaussian peak fitting with the help of Mfit program. (e) Principle of strain measurement from peak shift. (f) Principle of phase fraction measurement where normalized integrated intensities of diffraction peaks in radial slices over azimuth angle are utilized to measure the phase fraction in the sample. (g) Principle of texture measurement from non-uniform intensities of diffraction ring over azimuth angle.
Figure 7-3: Applied tensile stress vs. macroscopic tensile stress measured by laser extensometry for NiTi. The symbols indicate the stresses at which synchrotron diffraction spectra were obtained.

Figure 7-4: (a) Images show indexed austenite (at zero stress) and martensite (at 375 MPa stress) diffraction patterns (b) The reversible transformation from cubic austenite phase to monoclinic martensite phase is captured from slices in (a).
Figure 7-5: Applied tensile stress vs. longitudinal microscopic lattice strain from the 110A diffraction ring. 110A lattice plane elastic modulus was determined to be 78 GPa.

Figure 7-6: Austenite lattice strains (from 110 plane) as a function of the azimuth angle. Poisson’s ratio for NiTi wire determined to be 0.427. The compressive and tensile regions were shown as a function of azimuth angle. At 60° from fiber axis, strain reversion points are seen.
Figure 7-7: Volume fraction change vs. superelastic strain determined from normalized integrated intensities of austenite (A) and martensite (M) diffraction rings.

Figure 7-8: Plots of integrated intensity ratios of 200A to the 110A and 001M to the 022M vs. superelastic strain in the sample.
Figure 7-9: Variation of texture index (for lattice planes 110A, 200A and 002M) with superelastic strain during loading and unloading of NiTi wire.

Figure 7-10: 110A texture evolution with strain. 110A shows six-fold symmetry in diffraction ring but for clarity only one-fold is shown.
Figure 7-11: Presence of austenite and martensite diffraction peaks from two different regions of a wire separated by 2 mm on fiber axis at the same stress. Heterogeneous transformation is captured in NiTi wire under tensile stress.

### 7.8 Tables

Table 7-1: Determination of fiber axis from the fold symmetries.

<table>
<thead>
<tr>
<th>hkl</th>
<th>δ (90-α°)</th>
<th>θ</th>
<th>φ</th>
<th>Interplanar angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>{200} A</td>
<td>36.11°</td>
<td>3.8266°</td>
<td>36.28°</td>
<td>35.3° with [211] direction</td>
</tr>
<tr>
<td>{110} A</td>
<td>30°</td>
<td>2.7149°</td>
<td>30.11°</td>
<td>30° with [211] direction</td>
</tr>
</tbody>
</table>
CHAPTER 8: USE OF NEUTRON DIFFRACTION TO CHARACTERIZE RESIDUAL STRAINS IN INDUSTRIAL ENGINEERING COMPONENTS

This chapter presents the use of neutron diffraction methodology to characterize the residual strain fields in other materials systems i) characterization of residual strain fields in welded INCONEL 718 NASA space shuttle flowliners at cryogenic temperatures (135K) and ii) determination of residual stresses in a Ti-6Al-4V turbine blade component.

8.1 Characterization of Residual Strain Fields in Welded INCONEL 718 Flowliner

In 2002, cracks were noted propagating from apertures that were punched in "flow liners" that feed liquid hydrogen to the space shuttle engines. The origin of the cracks is not currently understood but welding was adopted as a repair route. This case study presents results from a study of the residual strain fields in the flow liner and in model coupons prior and post welding, and after subsequent cryogenic quenching. We used neutron diffraction to develop spatially resolved strain maps with a spatial resolution of approximately 1mm³.

8.1.1 Introduction

The space shuttle main propulsion system delivers liquid hydrogen and liquid oxygen through twelve-inch diameter feedlines to the three main engines at roughly 75 Kg/sec and 445 Kg/sec, respectively, during ascent. Each of the six feedlines has three bellowed articulating joints to allow flexing due to thermal transients and flow forces. Two of the three joints are supported internally with a ball strut tie rod assembly, but the joint closest to the engine is supported
externally with a heavier gimbal joint to avoid flow disturbance prior to entering the engine’s low pressure pump impellers. To meet the 100-mission life requirement for these feedlines, flow induced high cycle fatigue of the line bellows must be prevented. That is the purpose of flow liners that shield the bellows on the inside of the line from direct flow. The flow liner consists of an upstream and downstream section, which are independently welded to the inside of the feedline at either side of the bellows to provide independent motion as the line flexes. Both flow liner sections have elongated slots 6.35 mm wide to maintain an equal pressure between the rearside of the liner and the flow stream as well as to aid in cleaning of the bellow area during manufacture. Columbia’s flow liners were made of CRES 321 with 76 slots per section, while the subsequently built Discovery, Atlantis, and Endeavour have INCONEL 718 liners (see Figure 8-1a) with 38 slots per section.

In the summer of 2002, the space shuttle fleet was grounded when cracks were discovered in the liquid hydrogen feedline flow liners nearest the engine interface on all four orbiters. No cracks were seen on any of the liquid oxygen flow liners. All the cracks originated at the high stress areas where the straight portion of the slot transitioned to the semicircular curved area or at the center of the semicircular area itself. On the 4 orbiters there were a total of 11 cracks with 9 on downstream sections and 2 on upstream sections. The longest crack was 8.38 mm long. No cracking issues have been seen on any of the flex joints further upstream.

An intensive effort to understand the cause of these cracks ensued. Part of the problem was in the manufacture of the liners themselves. The slots were punched out with a press and microcracks remained around the slots from this process. Also, the blade pass frequency of the low pressure
fuel turbopump (which is just inches downstream of the flow liner) while running at main stage thrust levels roughly matched the natural frequency of the flow liner. Clearance between the impeller blades and pump housing allowed slight leakage which flowed back upstream along the feedline wall. This in turn excited the flow liner as the frequencies matched. This effect extended upstream for a couple line diameters, but was enough to reach the gimbal joint near the engine interface.

Several repair options were investigated. With a great deal of research and testing, a method was developed to return nearly all of the original strength to the part. It involved a several stage welding process. United Space Alliance (USA) welders processed INCONEL 718 and CRES 321 sample coupons that were supplied with high and low cycle fatigue induced cracks in them. These fabricated coupons were subsequently subjected to gas tungsten arc welding. This type of welding is typically used for oxygen sensitive materials and produces no slag after the weld pass. After welding they were tested to failure. Non-destructive evaluation techniques including x-ray, eddy current, and ultrasound were used to verify acceptable welds. After the certification process was complete, USA applied the same procedure to the cracks in the orbiters. In order to prevent future occurrences of cracks, a process to eliminate the microcracks in the rest of the slots was developed. It involved a hand polishing operation that removed a minimal amount of material. This too was successfully tested. To date these repairs and improvements have been incorporated on all the orbiters. Atlantis and Endeavour have since flown and the flow liners subsequently inspected. No new cracks or damage to the weld repairs were noted.
This work was initiated to quantitatively assess the residual strains and stresses associated with the aforementioned weld repair process. Consequently, the coupons used in this investigation were made of the same INCONEL 718 alloy used for the flow liners and subjected to identical welding and certification procedures that were carried out on the space shuttle (again by the same team of USA welders). Neutron diffraction measurements were carried out at Los Alamos National Laboratory to determine residual strains at selected locations in a welded coupon at ambient and cryogenic temperatures. The neutron diffraction technique uses the atomic planes in specimens as internal strain gauges\textsuperscript{35}. The distances between atomic planes, directly obtained from diffraction spectra at different locations, can then be used to map residual strain profiles (e.g., Ref. [106]). While such measurements are regularly performed in open environments at room temperature, making them at elevated or cryogenic temperatures in vacuum environments require additional engineering. Neutrons have a greater penetration depth than conventional x-rays and allow specimens to be placed in controlled-environment chambers and aligned so that the neutron beam can penetrate through the chamber and diffract from the specimen. Furthermore, the larger penetration depth of neutrons results in measurements being representative of the bulk through-thickness (for the case of these coupons) rather than the surface.

An aluminum vacuum chamber with a copper cold mass cooled by liquid nitrogen was fabricated to cool coupons while allowing for the simultaneous acquisition of neutron diffraction spectra. This chamber was installed in the Spectrometer for Materials Research at Temperature and Stress (SMARTS) at Los Alamos National Laboratory (LANL)\textsuperscript{107}. Neutron diffraction spectra from the coupons were obtained at 135 K. While this temperature was above the coldest
operating temperature of the flow liner (which carry liquid hydrogen at 23 K), it was nevertheless deemed useful to gauge the effect of a 153 K drop in temperature on the residual strain field due to the weld repair procedure.

8.1.2 Experimental

8.1.2.1 Coupon Preparation

Eight INCONEL 718 test coupons were fabricated at NASA Marshall Space Flight Center (MSFC). The same fabrication method that was used for the weld qualification process prior to welding the flight element cracks was used here. The coupons had a section length and width of 152.4 mm by 50.8 mm, respectively, and were approximately 1.27 mm thick. Each coupon had two half slots at the top and bottom, as shown in Figure 8-1b. The coupons were fatigue cycled (at approximately 15 Hz) at NASA MSFC. The test coupons were then shipped to NASA Kennedy Space Center (KSC) for weld repair of the cracks. The coupons were repaired using the same gas tungsten arc welding process that was completed on the flight elements. This weld process was (a) prepare the slots for welding with a cutting tool, (b) weld the crack with INCONEL 718 filler and run a feather pass along the toe of the weld, both sides, (c) grind the weld flush, prepare slot for the autogenous heat pass (no filler material), (d) non-destructive inspection - 10x to 30x visual, eddy current, ultrasonic and x-ray, (e) weld autogenous pass inside of the slot, and (f) polish the weld and slot. Three coupons were selected for this investigation and are described in Table 8-1.
8.1.2.2 Cryogenic Test Chamber

To minimize the temperature gradient across the coupon due to convective heat losses and prevent the accumulation of ice on the sample, the coupon was cooled while in a vacuum. This was accomplished by holding the coupon in a fixture in an aluminum chamber. The fixture was a rectangular frame that held the coupon and was in thermal contact with a “cold mass” at the bottom of the chamber. Care was taken to ensure that By controlling the flow of liquid nitrogen through the “cold mass”, the temperature of the coupon was controlled. Due to a leak from the cold mass, the vacuum fluctuated between 10-500 mTorr. The description of this chamber and the test setup are forthcoming\textsuperscript{108,109}.

8.1.2.3 Neutron Diffraction

Neutron diffraction measurements were performed on SMARTS at Los Alamos Neutron Science Center (LANSCE) at LANL. A “time-of-flight” neutron beam with a cross-section of 2 X 2 mm was used for residual strain measurements at room temperature (293 K) and at 135 K, in a spatially resolved mode. While the room temperature measurements were performed under ambient conditions, the cryogenic measurements were made in the aforementioned cryogenic test chamber. For both cases, the coupon was placed on a computer controlled XYZ-theta stage, so that any desired point on the sample could be examined during the experiment. This was achieved with the aid of two Leica theodolites that, by triangulation, could locate a sample with an accuracy of 0.1 mm.
Figure 8-2a shows how the orientation of the incident neutron beam relative to the coupon dictates the direction of the measured strain. For each orientation, strain information is obtained for two directions (since two banks of detectors that were 180° apart were used). Horizontal placement of the coupon at 45° to the incident beam provided strain information in the in-plane longitudinal or x direction and the through-thickness or z direction. Vertical placement of the coupon at 45° to the incident beam provided strain information in the in-plane transverse or y direction and the through-thickness or z direction. Figure. 8-2b shows the locations of the measurements. The average neutron count time per location was 9 minutes although count times as short as 2 minutes gave adequate results. The cruciform pattern was used to check for any misalignment in the positioning of the coupon relative to the incident beam.

8.1.2.4 Neutron Spectra Analysis

The diffraction spectra were analyzed by fitting the entire spectra in Rietveld refinements. The Rietveld refinement procedure optimizes parameters that include atom fractions and lattice spacings until the calculated spectrum exhibits the best least squares fit to the measured spectrum. The General Structure Analysis System (GSAS) code was used and incorporated reflections from planes with d-spacings between 0.5 to 2.5 Å in the face-centered cubic structure from Ref. [110]. Residual strains were calculated in the x, y and z directions from

\[ \varepsilon_a = \frac{a_s - a_0}{a_0}, \]  

...8.1
where $a_s$ is the Rietveld determined lattice parameter at a distance $s$ from the coupon center and $a_0$ is the corresponding “stress free” lattice parameter. The ends of the welded coupon were assumed to be not influenced by the weld and the “stress free” lattice parameter was determined from an average of the lattice parameter measurements at the ± 70 mm locations, at the coupon ends (see Figure 8-2b). This average lattice parameter for the welded coupon was within error when compared with lattice parameter measurements from the as-received and fatigued coupons, validating the assumption that the ends of the coupon were indeed “stress free”. From the measured residual strains in the $x$, $y$ and $z$ directions, $\varepsilon_x$, $\varepsilon_y$ and $\varepsilon_z$, the corresponding residual stresses, $\sigma_x$, $\sigma_y$ and $\sigma_z$ can be computed using equations for isotropic Hookean elasticity:

$$\sigma_x = \frac{E}{1+\nu} \left[ \varepsilon_x + \frac{\nu}{1-2\nu} (\varepsilon_x + \varepsilon_y + \varepsilon_z) \right], \quad \ldots 8.2$$

$$\sigma_y = \frac{E}{1+\nu} \left[ \varepsilon_y + \frac{\nu}{1-2\nu} (\varepsilon_x + \varepsilon_y + \varepsilon_z) \right], \quad \ldots 8.3$$

$$\sigma_z = \frac{E}{1+\nu} \left[ \varepsilon_z + \frac{\nu}{1-2\nu} (\varepsilon_x + \varepsilon_y + \varepsilon_z) \right], \quad \ldots 8.4$$

where, $E$ and $\nu$ are the Young’s modulus (199 GPa) and Poisson’s ratio (0.28), respectively, of the INCONEL 718 alloy\textsuperscript{111}. The von Mises effective stresses can then be calculated, assuming that stresses in the $x$, $y$ and $z$ directions are the principal stresses, as:

$$\sigma_{\text{eff}} = \sqrt{0.5((\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2)}, \quad \ldots 8.5$$
where, $\sigma_1$, $\sigma_2$, and $\sigma_3$ are the principal stresses.

8.1.3 Results and Discussion

Figure 8-3a shows the in-plane longitudinal strains ($\varepsilon_x$) measured at points along a line between the notches in the welded (RS5), as-received (RS1) and fatigued (RS3) coupons. The measurements were made with the coupons in the horizontal orientation at room temperature. Thus, the x-axis label in the figure indicates the distance from the center of the coupon along a line between the coupon notches (AB in Figure 8-2b). Figure 8-3a shows tensile strains along the welds and compressive strains in the region between the welds in the center of the welded coupon. This distribution is clearly absent in the as-received and fatigued coupons.

To confirm that the strain distribution in the welded coupon was not an artifact of lattice parameter changes due to chemistry (e.g., the introduction of filler material during the welding process or diffusion processes), Figure 8-3b is presented. Figure 8-3b compares the in-plane longitudinal strains ($\varepsilon_x$) and the through-thickness strains ($\varepsilon_z$) at room temperature, at the same locations as in Figure 8-3a. As described previously, recording neutron spectra at a given location determines the strain in both x and z directions since two banks of detectors are used. If there were changes in the lattice parameter, both curves would likely follow similar trends. On the contrary, the strain distribution in the two directions are different indicating a multi-axially distributed strain field due to the weld repair process.
Figure 8-4a shows the temperature of the welded coupon with time during the cooling process in the vacuum test chamber. TC1, TC2, TC3 and TC4 were thermocouples placed on the welded coupon at locations shown in Figure 8-2b. Thermocouple TC5 was placed on the “cold mass” that cooled the coupon fixture. Visual inspection confirmed the absence of ice build-up in the chamber. After the chamber was pumped down, the center of the coupon took about 1.7 hours to cool down from 293 K to 135 K, and the temperature variation in the coupon was within ±2 K during the diffraction measurement. The temperature gradient across the sample length, i.e., from center to either end at ±70 mm varied within ±10-20 K and was within experimental error.

Figure 8-4b compares the in-plane longitudinal strains (εₓ) at points along a line between the notches in the welded coupon at 293 K and 135 K. It is important to recognize that while the cooling process resulted in a thermal contraction and a concomitant decrease in the lattice parameter (not shown), the strains reported at 135 K in this figure represent lattice parameter changes relative to a stress free parameter also at 135 K that takes into account this thermal contraction. The fact that there are no substantial changes in the strain distribution suggests that differences in the coefficient of thermal expansion between the weld and the base material are minimal. This is consistent with the weld repair process that did not introduce any foreign material. Furthermore, this is also consistent with our assessment of Figure 8-3b which indicated the lack of any significant chemistry effects. Such effects have the potential to change the coefficient of thermal expansion thereby introducing mismatch strains during the cooling process.
Figure 8-5a shows the in-plane transverse ($\varepsilon_y$) strains measured at points along a line between the notches in the welded coupon. The coupon was placed in the vertical orientation for this set of measurements. For direct comparison the in-plane longitudinal ($\varepsilon_x$) and through-thickness ($\varepsilon_z$) strains are also included in Figure 8-5a. The in-plane transverse ($\varepsilon_y$), in-plane longitudinal ($\varepsilon_x$) and through-thickness ($\varepsilon_z$) strains were used to determine the corresponding stresses and the Mises effective stress from Equations 8.2-8.5. On average, the Mises effective stresses are around 220 MPa but peak to about 555 MPa at the tip of the lower weld. The error associated with such measurements is typically in the 25 MPa range and is associated with experimental error as well as the statistics of the Rietveld refinement. While the yield stress of the coupon is not exactly known, it is expected to be in the range of typically aged INCONEL 718 alloys, i.e., 1100 - 1250 MPa\textsuperscript{112}. It is not unreasonable to expect these residual stresses to influence crack growth rates in the coupons even though their effects on crack initiation thresholds or lifetime tests may be negligible (such as the weld repair certification process described earlier).

The asymmetry in the Mises stress distribution is not fully understood and may be a result of unequal crack growth at the two notches or differences in the crack and weld path from the neutron measurement profile. Furthermore, the purely tensile nature of the in-plane transverse ($\varepsilon_y$) and through-thickness ($\varepsilon_z$) strains was surprising and may be a result of a misalignment that impacted the “stress free” lattice parameter in the y and z directions. While these issues are currently being examined and accounted for in Ref.[109], using the cruciform profile measurements and other longitudinal scans not reported here, they are not expected to significantly alter the conclusions of this paper.
8.1.4 Conclusions

Neutron diffraction was used to determine residual strains in a spatially resolved mode around welds in an INCONEL 718 coupon at room temperature and at 135 K. The material and weld repair process investigated, duplicated NASA’s weld repair process for cracks on the space shuttle flow liners. The following are the conclusions:

i. By measuring strains in three orthogonal directions, the weld repair process was found to introduce Mises effective residual stresses of up to 555 MPa. These stresses were confirmed to originate due to the weld repair process and are not associated with lattice parameter changes from materials chemistry effects.

ii. On comparing the measurements at 293 K and 135 K, no significant strains were additionally induced due to the 158 K drop in temperature. This is indicative of minimal mismatch in the coefficients of thermal expansion between the base metal and the weld.

iii. The experiments demonstrated the capability of the Spectrometer for Materials Research at Temperature and Stress (SMARTS) at Los Alamos National Laboratory to perform spatially resolved measurements at cryogenic temperatures.
8.1.5 Figures

Figure 8-1: (a) An INCONEL 718 flow liner that is currently used on NASA space shuttles Discovery, Atlantis and Endeavor. (b) A coupon with welds propagating vertically from each notch in an aluminum holder.

Figure 8-2: (a) Orientation of the coupon relative to the incident neutron beam that facilitated measurements of residual strains in the in-plane longitudinal (x), in-plane transverse (y) and through-thickness (z) directions. The irradiated volume is approximately 8 mm3. (b) Location of neutron diffraction measurements (dots) and placement of thermocouples (crosses) on the welded coupon. For clarity, the axes scales are not linear.
Figure 8-3: (a) Strains in the in-plane longitudinal (x) direction in the welded, as-received and fatigued coupons. (b) Strains in the in-plane longitudinal (x) and through-thickness (z) directions in the welded coupon.
Figure 8-4: (a) Temperature of the welded coupon during cooling and neutron diffraction measurements. The locations of the thermocouples are shown in Figure 8-2b with TC5 being placed on the cold mass. The spikes represent change of dewars. (b) Strains in the in-plane longitudinal (x) directions in the welded coupon at 293 K and 135 K.
Figure 8-5: (a) Strains in the in-plane longitudinal (x), in-plane transverse (y) and through-thickness (z) directions. (b) The corresponding stresses and the von Mises effective stress determined from Eq. 8.2-8.5.
8.1.6 Tables

Table 8-1: Specifications of the coupons used in this investigation (fabricated at NASA Marshall Space Flight Center).

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Net section width (mm)</th>
<th>Thickness (mm)</th>
<th>Net section stress (MPa)</th>
<th>Cycles</th>
<th>To final crack length</th>
<th>Final crack length (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RS1</td>
<td>51.03</td>
<td>1.27</td>
<td>control</td>
<td></td>
<td></td>
<td>none</td>
</tr>
<tr>
<td>RS3</td>
<td>50.98</td>
<td>1.27</td>
<td>206.84</td>
<td>100,000</td>
<td></td>
<td>none</td>
</tr>
<tr>
<td>RS5</td>
<td>51.03</td>
<td>1.24</td>
<td>206.84</td>
<td>325,000</td>
<td></td>
<td>10.41</td>
</tr>
</tbody>
</table>
8.2 Determination of Residual Stresses in a Turbine Blade Component

8.2.1 Introduction

Recently, a performance related failure issue arose in a turbine blade component at Siemens Westinghouse Power Corporation. The component was made of Ti-6Al-4V coated with WC-Co. Residual stresses in the component were suspected to be a possible cause for the failure.

8.2.2 Neutron Diffraction Study

A Neutron diffraction technique was used to study preliminary investigation of the residual stresses. The technique of using diffraction spectra for mechanical characterization relies on using atomic planes in specimens as internal strain gauges. The distance between atomic planes, directly obtained from diffraction spectra, are used to compute strains. The difference between the residual strain free lattice spacing (from an equivalent “stress-free” sample) and the measured lattice spacing with elasticity constants, provides a measure of residual stresses. Given the high penetrability of neutrons compared to x-rays, such measurements are expected to correspond to the bulk stress-state.

The experiments were performed on the Spectrometer for Materials Research at Temperature and Stress (SMARTS) at Los Alamos National Laboratory. The measurements were performed in a spatially resolved mode using radial collimators on two samples (see Figure 8-6) – one that
failed (designated # 57) and one that did not (designated # 27), to provide a basis for comparison. The locations of these measurements are shown in Figure 8-7. Since two sets of detectors are used, measurements are representative of stresses in the radial and hoop direction.

8.2.3 Neutron Spectra Analysis

Single peak as well as Rietveld peak fitting approach was used to follow strain evolution in the samples. From the single peak analysis, strain for a plane (hkl) at a given location is reported as:

$$\varepsilon_{hkl} = \frac{d_{hkl} - d_{0}^{hkl}}{d_{0}^{hkl}} \quad ...3.2$$

where $d_{hkl}$ is the spacing of the plane at a given location. Since the strains are relative, $d_{0}^{hkl}$ is taken as corresponding lattice spacing at an arbitrary chosen location. As shown in Figure 8-7, for sample #27, this was run #21707 and for sample #57, this was run #21713. Instead of limiting the analysis to single peaks, the Rietveld refinement method was also used to analyze the data. In Rietveld refinement the entire spectra were fitted to obtain lattice parameters (see Table 8-2). Since Ti-6Al-4V turbine blade exists in the ‘α’ phase with a hexagonal crystal structure, lattice parameters obtained in two different directions, i.e., ‘a’ and ‘c’ were subsequently used to calculate strain. From Rietveld refinement, the strains were reported as:

$$\varepsilon_{hkl} = \frac{a_{s} - a_{0}}{a_{0}} \quad ...8.1$$

where $a_{s}$ is the Rietveld determined lattice parameter at a given location and $a_{0}$ is the corresponding lattice parameter at an arbitrary chosen location. As for the case of Eq. 3.2, the same locations were selected. For the ‘c’ parameter, an equation analogous to Eq. 8.1 was used.
8.2.4 Results and Discussion

Figure 8-8a and 8-8b show the strain distribution in radial direction, from both single peak analysis (for plane 101 and 110) and Rietveld analyses. The diffraction measurements are represented as experimental run number on x axis and strain (in microstrain) on y axis. The single peak analysis showed strain distribution similar to Rietveld method and were within error in both components. The results from this figure highlight the consistency in the analyses between the two approaches.

Figure 8-9 shows the comparison of strains in radial and hoop direction for both components. The failed component i.e., # 57 showed more variation in the strain when compared to # 27.

Generally for Ti-6Al-4V, elastic modulus values are in the range of 100-120 GPa\textsuperscript{113}. For this calculation, the elastic modulus was taken as 115 GPa. Figure 8-10a and 8-10b show the estimate the stresses from aforementioned strains for both components, determined from both ‘a’ and ‘c’ lattice parameters (see Table 8-3). On average, both turbine blades showed negligible stresses at around 15 ± 20 MPa (2 ± 2.9 ksi) in radial direction. While the maximum peak stresses of around 220 ± 88 MPa (32 ± 13 ksi) were seen in hoop direction. The yield strength of turbine blades was not exactly known, but was expected to be in the range of 825-910 MPa (120-132 ksi)\textsuperscript{113} for typical equiaxed alpha morphologies of Ti-6Al-4V alloys.
8.2.5 Conclusions

Measured residual bulk stresses were very low (max. \( \approx 0.25\sigma_{\text{yield}} \)) when compared with yield strength of material.
8.2.6 Figures

Figure 8-6: Sections of turbine blade components made of Ti-6Al-4V coated with WC-Co (for proprietary purposes scale is not shown).

Figure 8-7: Location of neutron diffraction measurements represented as run numbers with crossed circles (a) six measurement in # 27 and (b) five in # 57 were carried out.
Figure 8-8: (a) Strains in # 27 at six different locations and (b) strains in # 57 at five different locations from both Rietveld and single peak approaches.
Figure 8-9: Comparison of strains in radial and hoop direction for both #27 and #57. Strains in #57 (failed component) are larger and more unevenly distributed.
Figure 8-10: Estimated stress distribution in turbine blade components (a) # 27 and (b) # 57
### 8.2.7 Tables

Table 8-2: Lattice parameters determined for Ti-6Al-4V turbine blades from Rietveld refinement.

<table>
<thead>
<tr>
<th>Ti-6Al-4V (hexagonal closed packed crystal structure)</th>
<th>linear parameter</th>
<th>angular parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>b</td>
<td>c</td>
</tr>
<tr>
<td>2.9218 Å</td>
<td>2.9218 Å</td>
<td>4.6700Å</td>
</tr>
</tbody>
</table>

Table 8-3: Estimated stress values from ‘a’ lattice parameter for both Ti-6Al-4V turbine blades in radial and hoop direction.

<table>
<thead>
<tr>
<th>turbine blade designation</th>
<th>experimental run number</th>
<th>estimated stress values in radial direction</th>
<th>estimated stress values in hoop direction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>stress</td>
<td>error</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( in MPa)</td>
<td>( in MPa)</td>
</tr>
<tr>
<td># 27</td>
<td>20705</td>
<td>0.000</td>
<td>17.186</td>
</tr>
<tr>
<td></td>
<td>21707</td>
<td>-21.669</td>
<td>20.951</td>
</tr>
<tr>
<td></td>
<td>21708</td>
<td>-13.844</td>
<td>20.855</td>
</tr>
<tr>
<td></td>
<td>21709</td>
<td>-44.244</td>
<td>20.726</td>
</tr>
<tr>
<td></td>
<td>21710</td>
<td>-2.163</td>
<td>21.533</td>
</tr>
<tr>
<td># 57</td>
<td>21711</td>
<td>0.000</td>
<td>25.984</td>
</tr>
<tr>
<td></td>
<td>21712</td>
<td>43.946</td>
<td>26.721</td>
</tr>
<tr>
<td></td>
<td>21713</td>
<td>-7.947</td>
<td>26.574</td>
</tr>
<tr>
<td></td>
<td>21714</td>
<td>15.501</td>
<td>23.864</td>
</tr>
<tr>
<td></td>
<td>21715</td>
<td>7.593</td>
<td>24.425</td>
</tr>
</tbody>
</table>
Due to individual nature of each chapter in this dissertation, an appropriate conclusion is included at the end of each chapter. Here a table outlining the unique contributions of this work are presented.

### 9.1 Conclusions

<table>
<thead>
<tr>
<th>Previously existing work</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>In situ</em> neutron diffraction measurements on superelastic and shape memory NiTi subjected to external loading.</td>
<td><em>In situ</em> neutron diffraction measurements on superelastic NiTi subjected to loading following plastic deformation. Associated influence of mechanical cycling on plastically deformed NiTi (Chapter 4)</td>
</tr>
<tr>
<td><em>In situ</em> neutron diffraction measurements on shape memory NiTi during tensile and compressive loading with emphasis on single peak data analysis.</td>
<td>Extension of previous thesis work at UCF. Successful comparison between tension-compression asymmetry of shape memory NiTi using Rietveld analysis. Subsequent texture evolution in tension and compression. (Chapter 5)</td>
</tr>
<tr>
<td>X-ray diffraction investigation of NiTi under tensile and torsion loading.</td>
<td>Spatially resolved neutron diffraction measurements in superelastic NiTi during bi-axial loading. Associated comparison of</td>
</tr>
<tr>
<td>Study Focus</td>
<td>Details</td>
</tr>
<tr>
<td>----------------------------------------------------------------------------</td>
<td>-----------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>In situ synchrotron X-ray diffraction study of stress-induced transformations in NiTi wire.</td>
<td>Extension of the author’s previous thesis work. Performed refinement in analysis methodology and established strain, texture and phase fraction evolution from synchrotron X-ray data. (Chapter 7)</td>
</tr>
</tbody>
</table>
APPENDIX
MATHCAD 11.0 DOCUMENT TO DETERMINE STRAINS IN THE MATRIX AND STABILIZED MARTENSITE FROM ESHELBY THEORY FOR AN EXTERNALLY APPLIED STRESS

\[ \begin{align*}
    \text{Em} & := 74.514 \\
    \text{vm} & := 0.39 \\
    \text{Gm} & := 26.8
\end{align*} \]

properties of austenite as determined from various bounds

(Em and Gm are in GPa)

\[ \begin{align*}
    s_{11} & := \frac{1}{\text{Em}} \\
    s_{12} & := \frac{-\text{vm}}{\text{Em}} \\
    s_{44} & := 2(s_{11} - s_{12})
\end{align*} \]

\[ \begin{align*}
    c_{44} & := \frac{1}{s_{44}} \\
    c_{11} & := \frac{s_{11} + s_{12}}{(s_{11} - s_{12})(s_{11} + 2s_{12})} \\
    c_{12} & := \frac{-s_{12}}{(s_{11} - s_{12})(s_{11} + 2s_{12})}
\end{align*} \]

\[ \begin{align*}
    s_{11} & = 0.013 \\
    s_{12} & = -5.234 \times 10^{-3} \\
    s_{44} & = 0.037
\end{align*} \]

\[ \begin{align*}
    c_{11} & = 148.638 \\
    c_{12} & = 95.031 \\
    c_{44} & = 26.804
\end{align*} \]

Eshelby S tensor for spherical inclusion

\[ S := \begin{bmatrix}
    \frac{7 - 5\text{vm}}{15(1 - \text{vm})} & \frac{-1 + 5\text{vm}}{15(1 - \text{vm})} & \frac{-1 + 5\text{vm}}{15(1 - \text{vm})} & 0 & 0 & 0 \\
    \frac{-1 + 5\text{vm}}{15(1 - \text{vm})} & \frac{7 - 5\text{vm}}{15(1 - \text{vm})} & \frac{-1 + 5\text{vm}}{15(1 - \text{vm})} & 0 & 0 & 0 \\
    \frac{-1 + 5\text{vm}}{15(1 - \text{vm})} & \frac{-1 + 5\text{vm}}{15(1 - \text{vm})} & \frac{7 - 5\text{vm}}{15(1 - \text{vm})} & 0 & 0 & 0 \\
    0 & 0 & 0 & \frac{8 - 10\text{vm}}{15(1 - \text{vm})} & 0 & 0 \\
    0 & 0 & 0 & 0 & \frac{8 - 10\text{vm}}{15(1 - \text{vm})} & 0 \\
    0 & 0 & 0 & 0 & 0 & \frac{8 - 10\text{vm}}{15(1 - \text{vm})}
\end{bmatrix} \]
\[
\begin{bmatrix}
c_{11} & c_{12} & 0 & 0 & 0 \\
c_{12} & c_{11} & c_{12} & 0 & 0 \\
c_{12} & c_{12} & c_{11} & 0 & 0 \\
0 & 0 & 0 & c_{44} & 0 \\
0 & 0 & 0 & 0 & c_{44}
\end{bmatrix}
\]

stiffness tensor for matrix

\[
\begin{bmatrix}
1 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 1
\end{bmatrix}
\]

volume fraction of inclusion (here martensite)

\[
\begin{bmatrix}
25.5836 \\
-181.81 \\
0 \\
0 \\
0 \\
0
\end{bmatrix}
\]

applied stress in Pa

\[
\begin{bmatrix}
\frac{E_{100}}{10^6} \\
0 \\
0 \\
0 \\
0
\end{bmatrix}
\]

elastic modulus of martensite in GPa and poisson's ratio

\[
\begin{align*}
F & := 0.1 \\
v & := 0.35 \\
s_{11} & := \frac{1}{E_{100}} \\
s_{12} & := \frac{v}{E_{100}} \\
c_{11m} & := \frac{s_{11} + s_{12}}{(s_{11} - s_{12})(s_{11} + 2s_{12})} \\
c_{12m} & := -\frac{s_{12}}{(s_{11} - s_{12})(s_{11} + 2s_{12})}
\end{align*}
\]

c_{11m} = 162.099

c_{12m} = 87.284

c_{44m} = 20
average strain in inclusion

\[
\begin{pmatrix}
c_{11i} & c_{12i} & c_{12i} & 0 & 0 & 0 \\
c_{12i} & c_{11i} & c_{12i} & 0 & 0 & 0 \\
c_{12i} & c_{12i} & c_{11i} & 0 & 0 & 0 \\
0 & 0 & 0 & c_{44i} & 0 & 0 \\
0 & 0 & 0 & 0 & c_{44i} & 0 \\
0 & 0 & 0 & 0 & 0 & c_{44i}
\end{pmatrix} \cdot 10^9
\]

stiffness tensor for inclusion

\[
\varepsilon_{\text{TEM}} := \left[ -[(C_i - C) \cdot \{ S - F \cdot (S - I) \}^{-1} \cdot C_i - C]^{-1} \cdot \sigma \right] \cdot (C_i - C) \cdot C_i^{-1} \cdot \sigma
\]

equivalent transformation strain from elastic mismatch

\[
\begin{pmatrix}
-4.789 \times 10^{-4} \\
7.975 \times 10^{-4} \\
-3.214 \times 10^{-4} \\
0 \\
0 \\
0
\end{pmatrix}
\]

\[
\sigma_{\text{mm}} := F \cdot C \cdot (S - I) \cdot \varepsilon_{\text{TEM}} \\
\sigma_{\text{mi}} := (1 - F) \cdot C \cdot (S - I) \cdot \varepsilon_{\text{TEM}}
\]

\[
\sigma_{\text{m}} := \sigma_{\text{mm}} + \sigma A \\
\sigma_{\text{i}} := \sigma_{\text{mi}} + \sigma A
\]

\[
\varepsilon_{\text{m}} := C_i^{-1} \cdot \sigma_{\text{m}} \\
\varepsilon_{\text{i}} := C_i^{-1} \cdot \sigma_{\text{i}}
\]

\[
\begin{pmatrix}
27.005 \\
-184.165 \\
0.956 \\
0 \\
0 \\
0
\end{pmatrix} / 10^6 \\
\begin{pmatrix}
38.378 \\
-203.003 \\
8.602 \\
0 \\
0 \\
0
\end{pmatrix}/ 10^6 \\
\begin{pmatrix}
1.321 \times 10^{-3} \\
-2.618 \times 10^{-3} \\
8.354 \times 10^{-4} \\
0 \\
0 \\
0
\end{pmatrix}/ 10^6 \\
\begin{pmatrix}
1.054 \times 10^{-3} \\
-2.173 \times 10^{-3} \\
6.557 \times 10^{-4} \\
0 \\
0 \\
0
\end{pmatrix}/ 10^6
\]

average stress in matrix
average stress in inclusion
average strain in matrix
average strain in inclusion
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