IN SITU DIFFRACTION INVESTIGATIONS OF MECHANISMS THAT LEAD TO PATH DEPENDENT MECHANICAL BEHAVIOURS OF NICKEL-TITANIUM SHAPE MEMORY ALLOYS

by

Jinesh Dahal
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Golden, Colorado

Date ____________________________

Signed: ____________________________

Jinesh Dahal

Thesis Advisor

Golden, Colorado

Date ____________________________

Signed: ____________________________

Dr. Aaron P. Stebner

Department Head of Mechanical Engineering

Signed: ____________________________

Dr. John Berger

Department Head of Mechanical Engineering
ABSTRACT

Development and characterization of Shape Memory alloys (SMAs) has taken big steps over half a century in understanding the role of alloying components, processing of alloys and microstructural optimization to real life engineering application. This has aided in the growth of application of SMAs to multi-billion-dollar industry but the component design with SMAs still follows that traditional route of prototyping and laboratory testing. Implementation of numerical simulations would help in making component’s design-time more efficient and design-cycle cost effective, but few bottle necks are present to fully implement the numerical models. Out of them, lack of multiaxial experimental data to deconvolute and interpret the role of multiple deformation mechanism has been on the top priority.

Historically, lack of experimental capabilities to study in situ deformation mechanism like phase transformation and reorientation of variants was the main hindrance. But with development of modern diffraction technique, it has been possible to study deformation and correlate them with microstructure evolution. In this current work, we aim to provide some insights quantify evolution of internal state variables (ISVs) like volume fraction under biaxial loading conditions.

The first part of the thesis examines the role of loading history on reorientation mechanics of martensitic NiTi. Deformation under mechanical loads of two sets of specimens with different initial microstructure were compared. Neutron diffraction data were collected at different interval for the texture evolution information. First set of samples with “Preferred Variants” deformed by deformation twins along with transformation twins whereas “Self-Accommodated” samples showed reoriented by transformation twins only. Although, the samples have same processing route, alterations in microstructure caused variation in stress strain response highlighting the influence of loading history.

In the second part, austenitic NiTi are subjected to three loading paths under biaxial loading conditions and diffraction data are collected from neutron diffraction and HEDM experiments at various loads. Three loading paths included both proportional and non-proportional mechanical loads on a cruciform sample and evolution of volume fraction can be studied independently for different paths. Different volume fraction of austenite was obtained upon loading to same strain value as loading path influenced the transformation kinetics. The contribution from transformation kinetics to total strain was higher than the reorientation of
martensitic phase at the current loading levels. The results show volume fraction evolution are path dependent in nature. Change of loading path change the favorability of austenite grains and new set of grains transformed that gave continuation to transformation kinetics.

Thus, from the current analysis, we provide a method to quantify volume fraction analysis during biaxial loading that is first data set of the its kind. The other important outcome of the current project is the ability to deconvolute active mechanism like transformation and reorientation under multiaxial projects. This has huge potential in studying mechanism like plasticity and transformation in TRIP steels under multiaxial loading. Furthermore, the characterization of complex deformation mechanism in SMAs can aid in calibrating and validating material models for implementation in various numerical framework.
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1.1 Motivation

Shape memory alloys (SMAs) are a group of alloys that have the capability to remember the shape after subjected to thermomechanical loads. The capability to remember its shape results in large reversible strain that have been utilized in various engineering application like biomedical self-expanding stents [1]–[3], actuators in aerospace and aviation industry [3-5], dampers in civil structure [7] and micro-devices in robotics [5]. The use of shape memory alloys for these various applications are guided by different functional behaviors in shape memory alloys. During the actuation process, wires of shape memory alloys are heated in a presence of mechanical load that produces displacement for the purpose and this behavior is referred to as shape memory effect as shown in Figure 1.1. But in case of biomedical field, superelastic behaviors are attractive to build various implants that produces large recoverable strain during mechanical loading under isothermal conditions.

![Schematics of different behavior in SMAs. (a) Shape memory effect (b) Superelastic effect.](image)

Figure 1.1 Schematics of different behavior in SMAs. (a) Shape memory effect (b) Superelastic effect.

Shape memory effect and superelastic behavior of SMAs are attributed to thermoelastic phase transformation and can be explained using a temperature-stress graph as shown in figure 1.1. Below the equilibrium temperature ($T_o$), the stable phase is referred to as martensite and when heated converts to high temperature phase called the austenite. Under cooling, the phase transformation is reversed from austenite to martensite phase and the initial state of the material is
obtained (label 1 in Figure 1.2). Since the material is capable to return to its initial condition, this behavior is referred to as shape memory effect under no load. But, from the application view of point, this transformation path is less beneficial as there is no external shape change.

But in the presence of mechanical load (label 2 and label 3 in Figure 1.2), large recoverable strains can be obtained alongside phase transformation. During superelasticity (label 2), the ambient phase austenite is transformed in orientation martensite when mechanical load is applied at isothermal conditions. The orientation martensite is unstable after the loads are removed and is converted back to the austenite during loading. During the shape memory effect (label 3), the ambient phase of oriented martensite is heated in presence of mechanical loads and phase conversion to austenite takes place. When cooled the phase transformation is reversed and the strains are recovered to initial state that is utilized during the actuation.

Similarly, application of mechanical loads converts self-accommodated martensite to oriented martensite during isothermal process (label 4). No phase transformation occurs during the mechanical loading and the strains are recovered (or initial state is obtained) after heating to austenite followed by cooling to self-accommodated martensite. From the application points of view, design parameters from mechanical responses like recoverable strains present from different functional behavior becomes a critical during engineering design.

Figure 1.2 Schematics of Stress-Temperature Diagram for phase transformation in SMAs.
But these mechanical responses are very complex as multiple deformation mechanisms like elastic, transformation, reorientation and plastic occur concurrently that show high asymmetric and anisotropic behavior during mechanical loading. Comparing experimental results from uniaxial tension, compression and multiaxial loadings test have shown that macroscopic parameters like transformation/reorientation stress (critical stress for start of transformation or reorientation), strain hardening, and recoverable strains are unique based on the state of applied stress tensor and loading history during mechanical loading [8]–[11].

All deformation mechanism occurs concurrently during application of mechanical loading, but the current research focuses on the analysis on transformation and reorientation kinetics as these mechanisms are important from the prospective of engineering application. Anisotropy and asymmetry responses from uniaxial and shear experiments points towards directionality of the applied stress tensor in the transformation and reorientation kinetics is seen to be vital in characterization of SMAs. The complexity is elevated as the direction of stress tensor is altered during loading which in most cases represent more realistic application scenario. To study these influences, two types of mechanical loads are applied to study these effects and are collectively referred to as path dependence in literature - combination of tension/torsion loads with varying loading paths [12]–[17] and cyclic loading [18]–[22]. Experimental results from applying tension/torsion loads to superelastic tubes (ambient phase is austenite) under proportional and non-proportional loading paths show different level of equivalent stresses at same equivalent strain [13], [16], [17], [19], [23]. This indicates that progression of transformation and reorientation aren’t characterized perfectly by equivalent stress and strain (as in case of metal plasticity) and the kinetics of deformations mechanism are dependently on history of loading. Another important result observed during non-proportional loading paths is that coupling between tension and shear components done under stress or strain-controlled test. The strain-controlled experiments done in references [13], [23] showed relaxation of axial stresses when the loading path was switched from torsion to tension. For the stress-controlled experiments done with square loading path, Mehrabi at el. [16] showed that axial strain decreased when the nature of load was switch from axial to torsion loading paths but Sittner at el. [12] reported the axial strain to increase for similar loading paths. These results present only macroscopic experimental results are unable to characterize the transformation and reorientation kinetics fully and characterization of deformation at lower length
scales. To understand all the behavior, it becomes necessary to understand the deformation at a scale microstructure and correlate it with the macroscopic loading scenarios.

The behavior of path dependence in SMA present many major challenges in defining constitutive relations in SMAs. Of all the challenges, the identification and contribution of dominant deformation mechanism among elastic, transformation, reorientation and plasticity at multiaxial stress state resulting from various loading path becomes pivotable and incipient in understand other nature of deformation. Similar concerns were expressed by Kelly at el. [24] during development of unified SMAs material model for superelastic and shape memory effect. In the model, phase transformation was initiated during multiaxial loading after a critical stress value was reached defined by a transformation surface. The contribution from transformation strain was modelled as a tensorial quantity with magnitude been represented by the amount of transformation and direction being controlled by the reorientation mechanics. During validation of the superelastic model, the researcher examined the macroscopic stress-strain response from simulations to tension/torsion experiments for two non-proportional loading paths. During the case study, reorientation mechanism was to be dominant mechanism to introduce the influence of loading path and keeping the transformation mechanism constant. But researcher also expressed that similar results could be obtained by switching the dominant mechanism to transformation. Thus, it becomes clear that unique solution couldn’t be obtained with certainty from numerical simulations. Similar difficulty have been reported during comparison of numerical and experimental responses of non-proportional loading of SMAs by other authors [25]–[29].

This problem indicates towards the necessity of multiaxial experimental results that are capable of identifying dominant mechanism under in-situ conditions are needed to understand role of path dependence in SMAs. The current research is aim at answering similar question- “What is the influence of loading path on transformation and reorientation kinetics during mechanical loading of austenite phase in SMAs?” For the purpose, the experimental area needs to fulfill two major criteria:

- Need for experimental setup capable of applying multiaxial loading in controlled manner.
- Capability of obtaining in-situ experimental results on dominant deformation mechanisms.

In the past, most of the experiments performed with the aim to study path dependence has focused on macroscopic responses that can be utilized to calibrated numerical models [12], [19], [29]–[32]. The main hinderance for the researchers was absence of capabilities to characterize in
situ martensite phase evolution during multiaxial loading. But with recent development of high energy diffraction techniques, as presented in references [18], [33]–[37], in-situ observation of transformation strain evolution during loading and unloading is achieved. But these diffraction studies were based on uniaxial loading conditions and lack of multiaxial loading still prevented in studying influences of loading path in SMAs.

In the current work, we aim to perform in-situ high energy diffraction experiments under biaxial loading conditions to create distinction between phase transformation and reorientation mechanism that contributes to the transformation strain in total. For the purpose of biaxial loading, custom made biaxial machine from “The Beam Team” lab was used that has capabilities of loading in various proportional and non-proportional loading paths [38]. Neutron diffraction techniques are used to examine bulk behavior in samples and hard x-rays (HEDM) experiments are used to examine individual grains behavior complementary to the bulk behavior. Thus, experimental results from the current work will provides insights in transformation and reorientation kinetics during biaxial loading that would assist in development of material models.

1.2 Background to Deformation Mechanisms in SMAs

In this section, basic of deformation mechanisms along with the influence of stress state on individual mechanism in SMAs is presented. This will be followed by effect on these mechanisms when the loading path is altered as in non-proportional loading and cyclic loadings. The initial deformation in SMAs under any mechanical loads is elastic in nature. As the load (stress) increases, transformation and reorientation mechanisms followed by plastic deformation. The strains produced by transformation and reorientation are recoverable but plastic deformation due to slip in austenite and martensite phase are not and led to residual strain during unloading. Although, some form of plasticity due to dislocation activities during transformation and reorientation have been reported [39]–[42], it is not the dominant mechanism contributing to the strain and very less residual strain are observed at the strain level performed during the current work. Thus, our discussion will limit to characterization of transformation and reorientation mechanism that are responsible for in SMAs and particularly on Nickel-Titanium (NiTi) as the experiments performed during the research work are based on the alloy.

Both phase transformation and reorientation are crystallography-based mechanisms that depend upon altering phase and orientation based on lattice structure of two phases. In NiTi two
crystal lattice play primary role during various SMAs behavior - the austenite phase (high temperature phase) is the simple cubic structure (B2) and the martensite phase (lower temperature phase) has monoclinic lattice (B19’) as shown in the Figure 1.3. The cubic lattice has a, b and c are equal to 3.015 Å with all angle $\alpha = \beta = \gamma = 90^\circ$. But for the monoclinic lattice, the lengths of lattice parameters are unique and approximated to $a = 2.89$ Å, $b = 4.12$ Å and $c = 4.62$ Å and the angles $\alpha = \gamma = 90^\circ$ and $\beta = 97^\circ$.

During solidification of martensitic NiTi forms multiple domains with lathe morphologies are formed. These domains are connected by twin relation and individual domains are called “variant”. The microstructure formed by internal twinning of multiple variants are referred to as “self-accommodated martensite” as shown in Figure 1.4. On applications of stress or due to local internal stress, the variants arrange themselves into a single orientation and the microstructure is referred to “Oriented” or “Preferred martensite”. Various (0 1 1) and (1 1 1) Type I, [0 1 1] Type II and (1 0 0) and (0 0 1) compound twin interfaces of have reported have been reported in literature [42]–[47]. Although, these twin planes are interfaces between the variants of B19’ but have shown to have unique relationship with the austenite phase and will be discussed below alongside phase transformation in NiTi.
1.2.1 Phase Transformation in NiTi Alloys

Martensitic transformation in NiTi is obtained by displacive movement (characterized by shear) of atoms causing a change in lattice form cubic to monoclinic lattice. The impetus for the change in crystal lattice is thermal or mechanical loading and the shear involved during transformation is manifested as external strain during superelasticity. From the prospect of crystallography, the transformation is defined by change in lattice direction form its initial state in B2 to final state B19′ phases defined by orientation relationship between them. A deformation matrix (U) can be defined in the cubic lattice system to quantify the deformation as

\[
U = \begin{bmatrix}
\gamma_T & \varepsilon_T & \varepsilon_T \\
\varepsilon_T & \alpha_T & \delta_T \\
\varepsilon_T & \delta_T & \alpha_T
\end{bmatrix}
\] (1.1)

In equation 1.1, parameters \(\gamma_T, \varepsilon_T, \alpha_T\) and \(\delta_T\) in the deformation are sole function of lattice parameter of B2 (a, for cubic lattice) and B19′ (a, b, c and \(\beta\) for monoclinic lattice). The calculated values for the parameters in NiTi are \(\gamma_T = 0.9563\), \(\varepsilon_T = -0.04266\), \(\alpha_T = 1.023\), \(\delta_T = 0.05803\) are presented in references [44, 45]. The diagonal term shows that the extension \(\alpha_T\) and the contribution from off diagonal term from \(\delta_T\) and \(\varepsilon_T\) makes the monoclinic lattice sides longer than the cubic lattice that contributes to the strain observed during the mechanical loading.

The other point to make here is that B19′ lattice is low symmetry comparing to the parent B2 lattice and this leads to possibility of having multiple uniquely orientated B19′ form a single B2 lattice and are referred to as corresponding variant (CV). This concept of uniqueness in variants can be explained with 2D example of cube being converted into a parallelogram. Square A can be converted into two parallelogram B1 and B2 by shearing the top surface in two opposite direction
as shown in Figure 1.5. The formed parallelogram B1 and B2 are unique as no pure rotation can be applied to one of the variants to overlap with the other. Extrapolating this to 3D, the B2 structure can be converted into twelve B19' variants. Crystallography, unique U from cubic to monoclinic transformation can be obtained by applying symmetry operator ($R_c$) of cubic lattice for individual twelve variants.

Figure 1.5 Schematics of square A being transformed into two unique parallelogram B1 and B2.

Figure 1.6 Schematics of transformation between B2 to B19'. $U_i$ and $U_j$ are deformation matrix are two variants that satisfy the interface compatibility. The width of the variants showing the different volume fraction for individual variants.
The capability of forming multiple variants in NiTi has implications in defining twin microstructure of B19’ during superelastic transformation. During transformation, deformation occurring across interface formed between the phases (refer to as habit plane) must be continuously to maintain the compatibility of the material but calculations have shown that a single variant cannot satisfy the condition [4–6]. To maintain the compatibility multiple variants is formed as shown in Figure 1.6 schematically. By forming multiple variants, additional interfaces are created between the CVs that have to be compatibility in similar sense to above and are referred to as twin plane. From mechanistic point of view, the compatibility conditions places constraint on the formation of variants during transformation as the strains produced locally must be accommodated. There are 8 possible habit plane solutions that stratify the interface between B2 and B19’ and 144 combinations of twin interfaces is possible with 12 CVs in B19’ but the constraints provides solution to 192 possible habit planes with 66 different combinations of CVs [48].

With basic understanding of transformation nature in NiTi, we will proceed with the discussion regarding the role of mechanical loading as driving force for phase transformation. The strain contribution from the transformation is defined by the ability to change phase from B2 to B19’ or vice versa and the measure of volume fraction $V_f$ evolution can be used to quantify to quantify the transformation strain. To understand the role of path dependence from mechanical loading the influence of stress state on $V_f$ must be understood in terms of favorability of variant formation (nucleation) and growth of the variants during transformation. During mechanical loading, two factors play vital role in variant selection during transformation. Firstly, the CVs formed must be able to maintain compatibility across the interface (habit plane) as discussed above. Secondly, the additional constraint is placed by direction of loading as the shape strain output during transformation must be maximize towards the external loading direction must be satisfied. For simplest case of uniaxial loading, nucleation of variants in B2 single crystal is possible when the shearing stress in the habit planes exceeds the critical stress ($\tau_{cr}$). In order words, the nucleation is guided by Schmid’s factor in the grain relating to the habit plane satisfying the combability conditions to form favorable variants. The Schmid’s factor for a certain habit plane is different in case tension and compression and thus transformation process influences the criterion for variant selection. For example, the Schmid’s factor for all possible variants in tension and compression for NiTi single crystal with different orientations were calculated by various
The conclusion from all the researchers led to during tension loading, the direction of stress had potential to form more favorable variants as Schmid’s factor was higher whereas Schmid’s factor for compression was lower and higher transformation stresses were required to initiate transformation.

Similarly, biaxial stress state has been reported to form different CVs compared to the uniaxial test in NiTi. Most reported experimental results under biaxial loading are torsional test in NiTi thin tubes [13], [14], [16], [19], [30], [53] and macroscopic stress and strain are measured for the comparison with uniaxial test based on torque applied and the angle of rotation respectively. The general consensus from the experiments were macroscopic transformation stress in shear were higher than in tension but lesser than compression indicating anisotropic nature of transformation with the hypothesis that the variation was due to formation of different CVs. This hypothesis was verified Niendrof at el. [54] by comparing the experimental results from a notched and unnotched dog bone NiTi sample. They reported multiple pair of CVs present in a notched dog bone NiTi sample whereas single pair of CV and growth was seen in un-notched sample by correlating with deformation using Digital Image Correlation (DIC).

1.2.2 Reorientation in NiTi Alloys

When external loads are applied in the multivariant B19′ microstructure, a single variant is favorable based on the external loading. The favorable variant is defined by the capability of having the largest strain output to accommodate the external strain i.e. having the largest lattice parameter aligned to the loading axis in the single crystal. The mechanism is dominant during loading of self-accommodation B19′ and have been observed concurrently with transformation during loading of B2 [21], [47], [55]–[58]. In both cases, neutron diffraction experiments have shown that most of the variant formed during tensile loading have their longest lattice side aligned towards and shortest lattice side aligned to compression loading axis. In general, reorientation mechanism describes formation of most favorable variant to maximize the shape strain to accommodate external loading by reconfiguration or rearrangement from existing multivariant B19′ microstructure.

Reorientation in NiTi occurs via two processes of detwinning and twin nucleation. Detwinning is growth of favorable variant with reduction of another variant by the movement of twin plane interfaces. When the mechanical load is increased, the driving force for deformation
overcomes the elastic energy of the twin interface and frictional force for its movement and leads to the growth of favorable variants.

In contrast, twin nucleation describes nucleation and growth of new variant alongside the existing variant that satisfy the interface combability condition. Very few researches are reported in literature relating the study of twin nucleation in NiTi as these domains are small and advanced in-situ experimental method are needed to study the evolution of individual in general [55], [59]. More recently, Bucsek at el [55] used far-field and near-field HEDM experiments to track the $V_f$ and orientation of all variants formed during tensile loading in NiTi single crystal. The increase in volume fraction of the preferred variants was contribution of various other variants that formed initially during loading, but the work also pointed out intermediate variants are formed during reorientation to form compatible interfaces between the variants.

As both the mechanism leads to formation of preferred variants from the multivariant arrangement, the reversible strain from both detwinning and twin nucleation will be collectively addressed as contribution to reorientation strain. Quantification of the reorientation strain is modelled by the direction of the transformation strain tensor whose magnitude was discussed previously as volume fraction of all CVs. More explicitly, the volume fraction of overall CVs are used to quantify transformation kinetics and change in $V_f$ of individual CV relates to reorientation with overall $V_f$ of CVs being constants. Since the transformation (formation and growth of new CVs) and reorientation kinetics (rearrangement of CVs) can be difficult, most of the researchers have study the reorientation mechanism in isolation with ambient material being self-accommodated B19' phase as differentiation of [35], [42], [47], [58]. Similar to transformation mechanisms, tension-compression asymmetry have been observed affirming the role of nature of stress during reorientation [60]. The asymmetry behavior is attributed to the nature of twin nature and resolved stress that facilitates the movement for detwinning. If the stresses for detwinning are available, higher constraints provided to interfaces by need to accommodate strains during detwinning can be overcome plastic deformation along the interfaces but also can lead to twin nucleation to facilitate more reorientation.

### 1.2.3 Role of Loading Path in NiTi Deformation

Path dependence of deformation in NiTi has been studied by changing of loading direction during the experiment. Form the mechanics point of view, the change in loading path alters the
direction of the principle stress values and that leads to the change in direction and magnitude of driving forces for the active mechanism (either transformation or reorientation). Various multiaxial loading profiles like of square [12], [13], [16], [29], [61], butterfly [23], [29] and circular [19], [23], [29], [62] have been applied to superelastic NiTi. The results from macroscopic observations indicated that transformation strain tensor is not aligned to the deviatoric stress tensor as in the case of plasticity and conclusion has been derived from variation observed in plots of axial and shear components in individual stress and strain space. The observation becomes clearer in equivalent stress-strain plots as the loading direction changes. Microscopically, multiple possibilities have been hypothesized as habit plane can move to grow old CVs, new CVs can be generated with change in loading direction and interface movements between the variants can cause reorientation. But very little evidence has been provided experimentally to correlate parameters of volume fraction and CVs identification and change in loading path in NiTi. Recently, Hsu at el. [61] presented in-situ diffraction analysis during multiaxial loading indicating that new CVs formed as a result of loading path change and evidence of reverse transformation but the connecting to reorientation mechanism was still lacking.

1.3 Outline of work

In Chapter 2, description of samples preparation and characterization and diffraction experiments used in the current work are presented. Basics for understanding neutron diffraction and HEDM experimental setup and data analysis for both the experiments are described. This is followed by the interpretation of results regarding deformations in NiTi.

The study of path dependence nature of NiTi is divided into two parts relating to two mechanisms and is presented in individual chapter. In chapter 3, in-situ neutron diffraction results from uniaxial loading in B19’ is presented between two samples with self-accommodated variant microstructure and preferred variants microstructure. The experiments provide us with information to understand the reorientation (detwinning) mechanism in isolation based on the initial microstructure. Results from neutron diffraction present texture evolution at various loading stages and identifies the CVs involved into detwinning in each specimen. This analysis also provides background of detwinning and reorientation mechanism to analysis data in superelastic material during biaxial loading.
Chapter 4 examines the results of neutron diffraction and HEDM experiments under biaxial loading jointly to provide bulk and grain scale results. Experiments with both proportional and non-proportional loading are performed alongside neutron diffraction and HEDM experiments. Similar to chapter 2 texture analysis of both B2 and B19’ phases are analyzed to examine volume fraction evolution and reorientation in superelastic NiTi. Results from HEDM experiments provide orientation and strain information for individual grains in B2 phase.

Finally, chapter 5 mentioned the highlights and observations using high energy diffraction experiments to understanding recoverable deformation in NiTi. This section also provides some recommendation for future applications of diffraction techniques to study SMAs and other experiments that may contribute for development of SMAs.

Three appendix section are placed at the end of the thesis and includes work performed during my PhD research at Colorado School of Mines and my internship at Los Alamos National Laboratory. Appendix A presents results of solidification of weld drop of finite element analysis to obtain temperature profile. Appendix B includes discussion of finite element analysis of large deformation during coining. Appendix C discusses role of plastic deformation during transformation in TRIP steel and the possibility of using HEDM experiments for characterization of slip system in individual grains.
CHAPTER 2
MATERIALS AND METHODS

This chapter will present methods samples preparation used for both neutron and x-ray diffraction experiments. This will be followed by brief discussion on diffraction methods, both neutron and HEDM experiments, data obtained from the experiments and interpretation of results to identify mechanism and quantify parameters.

2.1 Sample Characterization and Preparation

Two types of specimens are used for the current research project – martensitic tensile dog-bone specimen for the study reorientation mechanics and austenitic biaxial specimen for the study transformation and reorientation under multiaxial loading.

As received material for martensitic material was prepared from hot extruded and hot straightened NiTi rods with atomic composition of 49.9 % of Ni from SAES. The Mf of the material was reported to be 46 °C indicating the material was martensite at room temperature. Dog-bone tensile sample were prepared from EDM with gage section of 5 mm diameter and 15.25 mm long for the mechanical testing. From purpose of comparison, a set of specimens are subjected to thermomechanical loading to induced preferred variant texture. Thermomechanical loading

Figure 2.1 (a) Martensitic dog bone samples used for neutron diffraction. (b) Thermomechanical sample applied to virgin specimen to create preferred variant martensite.
consists of two thermal cycles between 37 and 180 °C under constant stress of 100 MPa as shown in Figure 2.1. Tensile strain of around 4 % was observed during the thermal cycling.

NiTi plates were received from ATI metals with dimensions 110mm X 110 mm X 6mm thick. The as-received specimen was hot rolled in steel cans and reported As was -5 °C with no prior heat treatment. For the determination of grain size distribution, the samples were etched with solution of 40% hydrofluoric acid, 40% nitric acid and 20% water by volume. Micrographs were taken using Keyence VHX-5000 optical microscope for three sample tokens from different section of same as shown in Figure 2.2.

![Figure 2.2 Optical scans for grain size measurement for NiTi.](image)

Grain size measurement were done by line intercept method where the average grain size is obtained by dividing the length of line intercept to the number of grains counted along the same line intercept. ImageJ software was used to visualizing the micrographs obtained and counting the grains for line intercept method. The average grain size along the rolling and transverse direction was measured to be 108.33 microns and 74.23 microns from the three-sample token and measurement form individual token are presented in Table 1.
Table 2. 1 Grain Size Measurement for 3 sample tokens.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Avg. Grain Size (microns) along Rolling Direction</th>
<th>Avg. Grain Size (microns) along Transverse Direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Token 1</td>
<td>118.17</td>
<td>70.44</td>
</tr>
<tr>
<td>Token 2</td>
<td>98.30</td>
<td>76.52</td>
</tr>
<tr>
<td>Token 3</td>
<td>108.53</td>
<td>75.75</td>
</tr>
<tr>
<td></td>
<td>Average Grain Size = 108.33 microns</td>
<td>Average Grain Size = 74.23 microns</td>
</tr>
</tbody>
</table>

Since no initial cold working was performed on the NiTi plates, two stage heat treatment of solutioning and ageing was performed to add strengthen the matrix by precipitation. During ageing, nickel-rich coherent Ni₄Ti₃ precipitates are form that act as barrier to the dislocation motion [63]–[66]. The heat treatment was performed in a vacuum furnace with gas quench with the maximum rate of at rate of 20 °C/min. Counterweights were place on the top of the plates to prevent any wrapping during the heat and cooling of the plates. The solutioning was done at 925 °C for 25 minutes and gas quenched to around 200 °C. This was followed by ageing heat treatment for 10 hours at 300 °C and air cooled to room temperature. The ambient phase was confirmed to be B2 using diffraction experiments. The heat treated plated were EDM into the cruciform samples that are suitable for custom-made MTS biaxial frame. The dimensions of cruciform samples are designed so that the load transfer to the gage section is not influenced by sample geometry and uniform elastic deformation is obtained. The verification of the sample geometry for the cruciform specimens used in the current work is being discussed in reference [67] in detail.
2.2 High Energy Diffraction Basics

Diffraction experiments have been vital tool in studying microstructure and their evolution as they provide in-situ measurements in non-destructive manner at microscale length. The characterization of microstructure parameters lattice parameter, phase fraction of different phases and precipitates in alloys, texture of individual phases and residual stresses like in crystalline solid can be quantified very accurately [68]. The heart of the diffraction process lies in understanding the scattering incident neutrons or electromagnetic radiations (x-rays, electron beam) after their interaction with atoms that have periodic repetitions in metals. In general, interaction of electromagnetic waves or particles (x-rays, electrons and neutrons) with crystalline materials causes deviation from its initial trajectory along with absorption and transmission. When the energy of wave remains constants (i.e. wavelength constant) before and after the interaction, the scattering is referred to as elastic scattering and any loss of energy by absorption during interaction causes inelastic scattering. The scattered in-phase waves cause constructive interferences– the amplitude (or intensity) of the wave is increased with the wavelength of the wave being constant. When the scattered waves from all atoms in periodic lattice is considered, constructive interferences are observed in certain conditions defined by Bragg's law:

\[ n \lambda = 2 d_{hkl} \sin \theta \]  

(2.1)
In equation 2.1, \( n \) is the diffraction order, \( \lambda \) is the wavelength of the incoming and outcoming waves, \( d \) is the interplanar distance and \( \theta \) is the angle between the incident wave to the plane normal. Figure 2.1 (a) and (b) shows schematics of diffraction process through planes (100) and (111) respectively in the simple cubic lattice.

Another extraction from Bragg's law is that the range of \( \sin \theta \) bounded between -1 and 1 and thus only the planes with interplanar distance \( d \) satisfying,

\[
\frac{1}{d_{\text{hkl}}} = \left(0, \frac{2}{\lambda}\right)
\]

(2.2)
can be diffracted during the experimental setup. With this knowledge we will be able to define the HEDM and neutron diffraction techniques and how they have been used to study various deformation in SMAs.

### 2.2.1 High Energy Diffraction Methodology (HEDM)

Traditionally, x-ray diffraction experiments are performed utilizing “soft” x-rays (<10KeV) produced by lab diffraction apparatus. These experiments have played a great role in identifying crystal structure but with the intensity provided, it becomes very difficult to probe micron-scale microstructural features and their evolution during in-situ experiments. HEDM experiments, although a novice technique, utilizes hard x-rays (50-115 keV) from synchrotron sources that can
penetrate the through the materials and have been used to study various metal alloys over the past two decade [69]–[72]. HEDM experiments are very novice in field of NiTi research and very few work have been published [73]–[75]. Sedmák at el. [73] studied the orientation-based transformation and stress strain evolution in individual B2 grains during transformation. Paranjape at el [74] studied the constraints presented by grain neighborhood during transformation and stated that unfavorable variants based on orientation were produced. These experiments presented were done in polycrystal and identifying individual variants of B19’ were difficult as the length scale of these variants forming can be of length in nanometers. Bucsek at el [55] performed experiments in single crystal NiTi and were able to identify variants and their volume fraction using the forward models. Thus, HEDM experiments show potential for giving grain level information during transformation that can be used to study transformation in NiTi and overall in study of deformation mechanics in SMAs.

The experiments presented in this research work is performed as line 1-ID at Advance Photon Source (APS). Thus, the discussion herein will only focus on understanding the HEDM experiments and the obtaining grain level information i.e. center of mass, lattice parameters, orientation and elastic strain tensor for individual grain. During the HEDM experiments, x-rays beam are passed through the sample (along $e^i_1 = k_{in} = [0 0 1]$) in a loading frame that has the capability to rotate 360 degrees ($\omega$) along vertical direction (along $e^j_1 = [0 1 0]$) as shown in Figure 2.5.

![Figure 2.5](image)

**Figure 2.5** HEDM experimental setup. $K_{in}$ and $K_{out}$ represents the incoming direction and diffracted beam respectively. The diffracting plane is shown as $G_{hkl}$ and the diffracted spot for the plane is observed at $P (X_d, Y_d)$. 


The diffraction spots (reflection of individual hkl) are collected in the detector (CCD cameras) at small interval of rotation ($\Delta \omega$) that satisfy the Bragg's conditions i.e. the scattering vector is equal to the plane normal:

$$Q = G_{hkl} \quad (2.3)$$

$Q$ is the scattering vector that bisects the incoming beam $k_{in}$ and the diffraction beam $k_{out}$ that is observed at the detector position at position $P (X_d,Y_d)$. Each diffraction spot collected at position can be characterized completely by three experimental parameters ($2\theta$, $\omega$, $\eta$) where $2\theta$ describe the hkl planes for in Bragg condition, $\omega$ is the rotation of the diffraction stage that diffracts the hkl plane onto the detector and $\eta$ describes the position of the spot in the detector. Another important parameter to be mentioned is the distance of the sample to detector distance ($L_{sd}$) as this dictates the observed position of diffraction spot on detector based on the influence of orientation and position of the grain in the sample. If the detector is placed further than 800 mm, the diffraction spots are influenced by orientation and is referred to as far field (ff-HEDM) experiments. When the detector is placed less than 50 mm, the diffracted beam is influenced by position and intragranular features and is called near field (nf-HEDM) experiments. The main objective of ff-HEDM experiments to assign collected diffraction spots to individual grains (referred to as indexing) based on their orientation, center of mass and elastic strains given that Bravais lattice of material is known. Generally, two method are presented in the literature for this purpose:

(a) Forward model: The forward model is based on simulation of plane normal $G_{hkl}$ in terms lab coordinates $G_l$ for each of the diffracting plane with all possible orientation in the entire orientation space[76], [77]. The plane normal $G_{hkl}$ is the plane normal vector can be calculated using the geometry of the diffraction setup in the lab co-ordinate:

$$G_l = R^l_s R^s_c B^* G_{hkl} \quad (2.4)$$

Equation (1.29) is a collection of transformation and rotation of the vector where $B^*$ converts $G_{hkl}$ into the real space, $R^s_c$ is the orientation of the grain with respect to grain and $R^l_s$ is the rotation that relates $\omega$ to the illuminated $G_{hkl}$. The calculated vector components are compared with the diffraction spots in the detector and error is minimized to get the orientation $R^s_c$ along with tolerances for experimental variables ($\Delta 2\theta, \eta, \omega$).
(b) Backward model: Backward model uses the observed the diffraction spots for the analysis directly for more computationally efficient method [78]–[80]. In general, the $G_{hkl}$ are calculated for the Bravais lattice to be analyzed with assumption that grains are perfectly aligned with the sample orientation and grains are positioned as center of the sample- i.e. $(0, 0, 0)_{lab}$. Rotation are calculated based for all the diffraction spots that would take the $G_{hkl}$ to the observed Q vector (based on diffraction spots) in the diffraction process [81]. With the orientation obtained, COM and strain components are obtained by optimizing the position of spots in the detector along with the lattice parameters. The sensitivity of these parameters depends upon the distance between the sample position and detector and as $L$ increases the accuracy of parameters decreases. Thus, during the experiment calibration done with a standard material (usually CeO$_2$) becomes very vital as the position of the detector have to be accurately predicted. Confidence level (C.L.) and errors in position ($X_d$, $Y_d$) and angles ($\theta$, $\omega$, $\eta$) parameters are used to measure accuracy during indexing grains. C.L. measures the ratio of hkl's observed at detector for a grain of certain orientation to total number of hkl's calculated using diffraction principle for experimental setup. This is used as initial criterion for number of hkl's needed to identify as a grain. The error parameters are used to assigning spot centers during reading of the spots and can also be used as post processing parameters to obtain better results.

During analysis using MIDAS, thresholding of the image must be done prior to the indexing as noise from the detector and grain overlapping can cause indexing false grains. Example of thresholding image for indexing B2 phase with intensity value of 200 is shown in Figure 2.6. Form the thresholding operation, spottiness (degree of separation of individual spots) of the diffraction spots in detector is increased that is advantageous during the indexing process. Secondly, it also helps to remove the secondary phases that are non-essential to indexing of the major phases. For example, various precipitates Ni$_5$Ti$_4$ and B19' have potential spots very close to B2 spots and can be removed to prepare a clean data set for indexing as shown in Figure 2.6. Some post analysis is done after the indexing of grains with two error measure of difference in spot position (‘DiffPos’) and difference in omega (‘DiffOme’). The error measure is calculated as difference between the measured quantity during the experiment and the forward model of the individual spot for the grain with the orientation obtained during indexing. Grains with DiffPos of
300 microns and DiffOme of 0.25 degrees are excluded for the current analysis. In-built TrackGrain module is MIDAS is used to track the grains between the load steps and misorientation between the tracked grains are checked for the accuracy of the data.

Figure 2. 6 Thresholding of detector images. (a) Raw image obtained during the HEDM experiment. (b) Thresholding image

2.2.2 Neutron Diffraction Experiments

Neutron diffraction experiments have been utilized to understand elastic strains and modulus evolution [82]–[84], quantifying phase fraction[21], [34], [85], [86] and texture evolution [36], [56], [87] of both phases during transformation in NiTi. The quantification of modulus and phase fraction evolution are vital in calibration of ISVs during the numerical implemental of the material models and reduces the number of variables to be optimized. The hkl based modulus provide accurate anisotropic modulus and volume fraction calibrates the evolution of transformation strain during superelastic transformation. Particularly, the texture analysis has been used to understand different variants evolution during the uniaxial transformation and observed that preferred variants with maximum strain along the loading axis were verified. In our study, we perform neutron diffraction experiments on tensile dogbane samples and cruciform samples to obtain bulk texture changes and volume fraction IPF to understand the nature of CVs formation and evolution of their orientation.

The neutron experiments presented in the current research are performed at LANSCE facility using SMARTS instrument in Los Alamos is a spallation source that has a pulse length of 0.27 μs. Schematics of the neutron diffraction setup is shown in Figure 2.7 where Bank 1 and Bank
2 are the detectors collection the diffracted beam. During the uniaxial test, the diffracted beam to Bank 2 are obtained from the planes that are parallel to the loading direction and satisfy the Braggs condition. Similarly, diffracted beam to the Bank 1 are off the planes normal to the loading direction and stratifying the Braggs condition. For the biaxial samples, Bank 2 is used to collect the diffraction data from the planes normal to the ND and satisfy Braggs conditions. The detailed technical specification of the SMARTS instrument described in detail in reference [88].

Figure 2. 7 Top view of neutron diffraction setup layout. Bank 1 and Bank 2 represent the two detectors for collection of diffraction data.

Rietveld refinement is used to analyze the observed experimental intensities ($I_o$) by comparing the it with the calculated ($I_{calc}$). Although various program is present for rietveld refinement in literature, GSAS is used for analysis of all neutron diffraction and power diffraction data in the current research. During the refinement, a profile for entire neutron spectra is fitted using equation 1.34 and the difference between $I_o$ and $I_{calc}$ is reduced by using least square method [89], [90].

$$I_{calc} = I_b + S_h \sum_{hkl} S_{ph} K F_{hkl}^2 P (T - T_{ph})$$  \hspace{1cm} (2.5)

In equation (2.5), $I_b$ is the background intensity and contribution from diffused diffraction. $S_h$ is the histogram scale factor that is added to every reflection equally whereas $S_{ph}$ is added to reflection from individual phases to get the phase fraction. Similar to the $F_{hkl}$ for x-ray experiments, the structural factor corresponds to the atomic position and can be analyzed as intensity contribution.
to each reflection. \( P (T - T^{\text{ph}}) \) is the profile function defines the position and shape for reflection from each phase. The position is an outcome of lattice parameters and elastic strains in individual phase. The shape of peaks profile (also referred to as peak broadening) is consequences crystal size and plastic deformation present in material. The parameter \( K_{\text{ph}} \) for each phase provides the information of the is the correction parameter that is described as:

\[
K_{\text{ph}} = E_{\text{ph}} A_{\text{h}} O_{\text{ph}} M_{\text{p}} \frac{L}{V_{\text{p}}}
\]  

(2.6)

The correction factor includes contribution extinction correction \( (E_{\text{ph}}) \), absorption correction \( (A_{\text{h}}) \), preferred orientation correction \( (O_{\text{ph}}) \), multiplicity for the particular hkl \( (M_{\text{p}}) \) and Lorentz-polarization correction per unit volume \( \left( \frac{L}{V_{\text{p}}} \right) \). During the rietveld refinement, most of the parameters \( (F_{\text{hkl}}, M_{\text{p}}, E_{\text{ph}}, V_{\text{p}}, A_{\text{h}}) \) for known crystal and \( L \) from experimental calibration) are given for experiments and thus only \( I_{\text{b}}, S_{\text{ph}} \) and \( O_{\text{ph}} \) and strain parameters are refined to reduce the errors.

### 2.2.3 Twinning studies from Inverse Pole Figure (IPF) plots

The identification of deformation mechanism is performed with the help if inverse pole figure (IPF) obtained from neutron diffraction experiments. During the Rietveld analysis, intensity of individual hkl for both B2 and B19' is obtained and the area under the curve for individual hkls is directional proportional to the amount of crystal orientated towards that direction. Thus, texture calculation is defined by fitting the discrete intensity values of all hkls using continuous distribution functions (also called orientation distribution functions (ODF)). The density of individual hkls from ODF are normalized based of structure factor and volume fraction and these normalized hkls are represented Multiple of random distribution (MRD) values. Example of an IPF of B19’ with m.r.d values are shown in Figure 2. 8 (a).
The information about the deformation is based on the evolution of the texture with in-situ loading condition. Below, we will discuss the observation of twinning mechanism based on evolution texture as presented in reference [91]. Initially, IPF plots with continuous values is discretized in 1-degree grid each as IPF plots are based on equiangular projection rather than equidistance projection. Following the discretization, difference plot is made with the reference, usually taking the reference as load 0 condition, as shown in Figure 2. 8. Regions in the difference plot with increased value show that crystals orientated towards the direction have increased due to twinning. With the known twin system (shear direction (s) and plane normal(b)) in the material, a correspondence matrix that consist of shear and rotation (or reflection) operation can used define twinning mechanism as[92], [93]:

\[ \mathbf{v} = \mathbf{L} \mathbf{S} \mathbf{u} \]  

In equation, \( \mathbf{v} \) and \( \mathbf{u} \) defines the lattice vector in parent and twin structure and in comparing to IPF \( \mathbf{u} \) is the decreasing hkl that have twinned into lattice \( \mathbf{v} \) due to twinning in the material. \( \mathbf{S} \) can be obtained by magnitude of shear (s) and the plane normal (b) for the known twinning system. The matrix \( \mathbf{L} \) is the changes in bases of the crystal lattice described by rotation matrix and is defined differently for Type I, Type II and compound twin. For Type I twin, \( \mathbf{L} \) is defined as reflection along plain normal K and for Type II twin the rotation matrix is defined by a rotation of 180 across the shear direction. In our current work, the increasing hkl value is used (defined by \( \mathbf{v} \)) to calculate ‘\( \mathbf{u} \)’ using the known twin system. Thus, the activity of the twin system can be verified by relative decrease of m.r.d values in difference plots for the hkl pole in the IPF plots. For multiple twinning system present as in the case of B19’ criterion of maximum work can be used and explanation is provided during the data analysis in Chapter 3.
3.1 Introduction

NiTi alloys have been applied to various applications in fields of aerospace, medical, automotive, and building materials for their shape memory and superelastic phenomena [4], [5], [7], [94]. The occurrence of these phenomena is attributed to the solid-solid phase transformation between cubic and monoclinic phases on the application of temperature and load. The shape memory effect is induced as transformation of martensite phase (B19' monoclinic lattice) in NiTi is deformed mechanically up to the limit of recoverable strain and are reverted back to its original shape by heating it to the austenite phase (B2 cubic lattice) followed by cooling [95]–[97]. This intrinsic property comes from the ability of the austenite phase to retain (or remember) its structure at high temperature and is commonly referred to as Shape Memory Effect (SME). The total displacement obtained by deformation of B19' phase that can be obtained without any residual after cooling to original shape is termed as recovery strain.

The microstructure of B19' in NiTi consists of multiple domains with alternating plates that are internally twinned, and this structure provides self-accommodation of the elastic strain for energy minimization in the interfaces. The characteristics of twins formed in the B19' are calculated using nonlinear geometrically theory based on energy minimization and strain compatibility across the interfaces [48]–[50]. Experimentally, various twin systems like {-11 1} type I, {011} type I, (0 0 1) and (1 0 0) compound, [0 11] type II have been reported that satisfy the nonlinear geometrically theory by various authors summarized in reference [46], [49], [98]. Each plate is referred to as a variant having a unique orientation relationship with the B2 phase, and alternating plates that are compatible to each other are called corresponding variant (CV). When the B19' is heated, the monoclinic crystal lattice transforms into a more ordered cubic lattice at the high temperature, and conversion of self-accommodated B19' to B2 phase does not involve any shape change. But during tensile loading of B19', the self-accommodated variants tend to coalesce into a single variant that is favored (preferred variants) based on the loading direction—the orientation of the selected B19' has the largest lattice parameter along the loading direction, thus maximum strain is obtained along it [99]. Based on the observation of from tensile tests in
references [33], [35], [47], the deformation during tensile loading of B19’ has been categorized in four regimes (labelled as I, II, III and IV). The change in the modulus in stress-strain has been considered as markers or indicators for regime change that have been associated to different twinning mechanisms. The correlation of these mechanisms to these regimes has been mostly based on Transmission Electron Microscope (TEM) and diffraction experiments (both synchrotron and neutron). TEM experiments have provided the morphology and twin systems present in undeformed (self-accommodated) and deformed samples at various regimes and neutron diffraction have been used to characterize the bulk response of the material [34], [44], [91].

The initial microstructure of solution-annealed martensite has been characterized as predominately self-accommodated variants with <011> type II twins [44], [46], [60], [98], [100] along with {1 1 -1} type I twins that were described as spear like morphology in reference [44]. Some observation of fine-scale (001) compound twins have also been reported in aged solutioned samples [101]. During the regime I, the stress strain response is linear, and the deformation is considered to be elastic. Lui at el [47] used three extensometers on different length of the tensile bar sample and showed that strain was uniform through specimen. However, the results from the neutron diffraction indicated that texture evolution has started in this regime by the movement of twinning interfaces [82], [91]. With further loading in regime II, identified by drop of stress and deviation of linearity, the poles (reflections from hkl planes) of the preferred variant are observed to get stronger in intensity during the neutron diffraction [33], [82], [87] and x-ray synchrotron diffraction [102]. TEM studies showed that migration of <011> type II interfaces to increase the thickness of the preferred variants along with dislocation structure in twins [44], [47], [98], [100], [101]. Growth of new twins (1 0 0) compounds twin [22] after 6% strain and {1 1 -1} type I twins after 4% [25] have been reported. Regime III is defined by the increase in strain hardening in the stress strain response additional poles appear to increase in sharpness of additional poles that have been observed indicating additional twin system present [33], [35], [102].

During the regime III, presence of large network of dislocation have been observed in TEM experiments [42], [100], [103] the additional twins system were verified to be (-2 1 0) compound twins (referred as deformation twins) in TEM studies [44], [100]. The calculated shear for deformation twinning was larger in comparison to plastic slip and thus deformation twins are thought to be major deformation contribution to large deformation in B19’ at high strain loadings.
Regime IV is characterized by plastic deformation that was verified by lowering of the intensity of poles during the diffraction experiment [102].

The reorientation of twins to achieve a single variant of B19’ from self-accommodated microstructure has been broadly classified into two mechanism:

(a) Detwinning: Detwinning occurs inside a single plate of B19’ and one variant that is more favorable grows in expense of its pair. The growth happens with the movement of twin interfaces until the entire domain is turned into single variants. Miyazaki at el. [99] [30] reported that triangular shape three variants with (001) type I and <011> type II twinning system (named as 1’(+), 1(−) and 2’(−) in the reference) all detwinned to single variant (2’(+)) under the optical microscope. Similarly, TEM results from post experiment have shown formation of single variant in comparison to the initial microstructure.

(b) Twin Nucleation and Growth: New twin system are nucleated in the existing twin and grow to replace the older variants that are supposed to the preferred variants during particular loading conditions. At intermediate loading stages, the CVs formed initially to accommodate cannot be converted to the preferred or favorable variant as the interface between them may not be compatible. Thus, this leads to formation of new twined domains that have compatible interfaces with both existing twins and favorable variants. Gao at el. [104] has presented the calculations for compatible variants in NiTi and have called it ‘transformation pathway’. Bucsek at el [55] indicated intermediate variants (numbered as variant 4 and variant 11 in the paper) formed in between the existing variants and preferred variants (numbered 3 in the reference) to maintain strain compatibility across the interfaces during the detwinning process.

The deformation of self-accommodated B19’ to preferred variant martensite has a significant role in both superelastic effect and shape memory effect in terms understanding the dominant mechanism for material development and direct application. Sehitoglu at el. [105] experimentally obtained total recoverable strain for B2 NiTi single crystal with different orientation and stated that overestimate of recoverable strain from theoretical transformation strain calculation was due to contribution from both detwinning and reorientation of B19’ CVs. During the shape memory behavior, the objective of the training procedure is to induce biasness to form (nucleate) preferred variants when cooling from the B2 structure instead of the self-accommodated structure that lacks any shape change [33], [95], [106]. Thus, precise characterization of formation
of preferred variants due to reorientation mechanics can determine working strain limits and reduce functional fatigues design application.

Previous work in this area has been focused on understanding the effect of thermomechanical effect [60], [82], [107], texture from processing [102], [108], stress levels for variant orientation during mechanical loading [109], [110] and changes in hysteresis during cyclic loading. But, very few studies have considered influence of loading history during the reorientation process in NiTi [58], [107]. In these studies, author focused on single cyclic to study the nature CVs reorientation but the difference in response of self-accommodated and preferred variant B19′ is absent form literature. The need to study reorientation of preferred variant B19′ as the mechanisms is present during the superelastic behavior and understanding active mechanisms during extended to characterization transformation strain in whole. With the aim of expand the research on this topic, we examine the evolution of texture in B19′ NiTi specimens with variants that are self-accommodated and have preferred orientations using neutron during different stages of tensile and compressive loading. These experiments will aid us in understanding:

- Differences in strain-strain responses during loading and unloading for B19′ martensite polycrystal sample with self-accommodated variants and preferred variants.
- Understanding the strain hardening between first and second cycle for previously mentioned specimens.

### 3.2 Methods and Materials

The NiTi rods (nominal composition of 49.9% at Ni) produced by Special Metals, NY with martensite finish temperature ($M_f = 46\pm2 ^\circ C$) were used for mechanical testing for the current work. Since the $M_f$ temperature is higher than the experiment temperature of $30^\circ C$, the obtained material was fully martensitic at the room temperature that was confirmed with the diffraction experiments of as received materials.

Neutron diffraction experiments were performed at the Los Alamos National Laboratories using Spectrometer for Materials Research at Temperature and Stress (SMARTS) instrument. The details of the experimental setup can be found in the reference [88] and only major experimental parameters are presented here. Two detectors (referred as Bank 1 and Bank 2) are placed on either side of the sample to collect diffraction vectors from crystal planes (referred to as hkl) parallel (Bank1) and perpendicular to the loading direction (Bank2). Diffraction spectra (0.6 – 3.5 Å) were
recorded for 40 minutes at different loading stages as shown in Table 1 that accounted for diffraction vectors in the span of 0 to 11 degrees.

Four specimens (labelled as S1, S2, S3 and S4) with two different texture (labelled as T1 and T2) were used for the current work. As received texture of the virgin sample (T1) consists of self-accommodated variants of B19’ as shown in Figure 2(a) and Figure 3(a). As discussed earlier, the sample received with T1 texture was cycled twice between 35°C and 170°C under constant stress of 100 MPa to obtained T2 to eliminate any role of composition and processing while comparing mechanical responses. The details for mechanical loading and the strains levels for diffraction data collection are presented Table 3.1 below.

Table 3.1 Details of Mechanical Experiments for four samples S1, S2, S3 and S4. Column 4 in the table mentioned the strain levels at which the diffraction data were collected.

<table>
<thead>
<tr>
<th>Sample Name (Texture label)</th>
<th>Mechanical Loading</th>
<th>Number of Cycles</th>
<th>Strains (%) level for diffraction data collected</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1 (T1)</td>
<td>Max Tensile: 3 %</td>
<td>2</td>
<td>Cycle 1: 0, 1, 2, 3, 2,1,0, -0.8,0</td>
</tr>
<tr>
<td></td>
<td>Max Compression: -0.8%</td>
<td></td>
<td>Cycle 2: 0,1,2,3,2,1,0, -0.8,0</td>
</tr>
<tr>
<td>S2 (T1)</td>
<td>Max Tensile: 5%</td>
<td>2</td>
<td>Cycle 1: 0, 5, -1,0</td>
</tr>
<tr>
<td></td>
<td>Max Compression: -1%</td>
<td></td>
<td>Cycle 2: 0, 2,5, 0, -1, 0</td>
</tr>
<tr>
<td>S3 (T2)</td>
<td>Max Tensile: 3 %</td>
<td>2</td>
<td>Cycle 1: 0, 1, 2, 3, 2,1,0, -0.8,0</td>
</tr>
<tr>
<td></td>
<td>Max Compression: -0.8%</td>
<td></td>
<td>Cycle 2: 0,1,2,3,2,1,0, -0.8,0</td>
</tr>
<tr>
<td>S4 (T2)</td>
<td>Max Tensile: 5%</td>
<td>1</td>
<td>Cycle 1: 0, 1, 2, 3, 5, 3, 2</td>
</tr>
<tr>
<td></td>
<td>Max Compression: -1%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.3 Results and Discussion

The stress-strain for all four samples loaded to 3% and 5% maximum strain are presented in Figure 3.1 respectively. The initial deviation from the elastic loading (end of regime I) for all the curves is around 200 MPa that indicates start of the detwinning (reorientation) of B19’ variants. S1 and S2 samples (solids lines) have a constant stress plateau during detwinning whereas S3 and S4 (broken lines) have strain hardening is observed. Although, the peak stresses for different samples are different as shown in Table 3.2 but the stress strain curves for similar initial texture
samples overlapped (refer to Figure 3.1) indicating the reorientation mechanisms are similar with same initial conditions.

Figure 3.1 Stress Strain response. (a) S1 and S3 are loaded up to 3% strain and unload to -0.8% for 2 cycles. (b) S2 is cycled twice between 5% in tensile and -1% in compression. S4 is loaded up to 5% and unload to 2% tensile strain.

In comparing with first and second cycle, both texture T1 (shown in solids lines) and T2 (shown in broken lines for S3) showed drop in stress for the initiation of detwinning but strain hardening was more that lead to higher stress values in second cycle. This phenomenon of strain hardening is more distinct in sample with texture T2 (samples S3 and S4) than with texture T1 (samples S1 and S2) as shown in Figure 2.1 (a) and (b). During the unloading, remnant strain (S1= 2.3%; S2= 4.1%; S3=1.8%; S4=3.5%) is present at the zero-stress level and is attributed to hysteresis present in loading and unloading.

Rietveld Analysis were performed on diffraction pattern collected during the experiments using SMARTSware routine [111] that utilizes GSAS software [112], [113] for peak fitting and texture models. The constants used for analysis are:

(i) Space Group: P 11 21/m
(ii) Lattice parameters: a=2.8931 Å; b=4.6302 Å; c=4.111 Å; gamma=97.30°
(iii) Atomic Position: Nickel x=0.96610; y=0.5718; z=1/4; Titanium x=0.5718; y=0.2804; z=1/4
Table 3. 2 Peak Strain level for specimen with corresponding stress level

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Peak Load Strain</th>
<th>Peak Load Stress</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>3 %</td>
<td>Cycle 1: 236 MPa</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cycle 2: 282 MPa</td>
</tr>
<tr>
<td></td>
<td>-0.8%</td>
<td>Cycle 1: -301 MPa</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cycle 2: -355 MPa</td>
</tr>
<tr>
<td>S2</td>
<td>5%</td>
<td>Cycle 1: 313 MPa</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cycle 2: 374 MPa</td>
</tr>
<tr>
<td></td>
<td>-1 %</td>
<td>Cycle 1: -356 MPa</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cycle 2: -393 MPa</td>
</tr>
<tr>
<td>S3</td>
<td>3%</td>
<td>Cycle 1: 470 MPa</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cycle 2: 491 MPa</td>
</tr>
<tr>
<td></td>
<td>-0.8%</td>
<td>Cycle 1: -280 MPa</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cycle 2: -291 MPa</td>
</tr>
<tr>
<td>S4</td>
<td>5%</td>
<td>Cycle 1: 644 MPa</td>
</tr>
</tbody>
</table>

Texture components are obtained using Spherical harmonics functions that is inbuilt in GSAS software during rietveld analysis and the initial texture for S1 and S3 are shown in Figure(a) and (aa) respectively and for S2 and S4 are shown in Figure 3(a) and (aa) respectively. The as received or virgin material (S1 and S2) consists of self-accommodated microstructure with slightly peak intensities around poles (130) and (001) as shown in Figure2(a) and 3(a). For sample S3 and S4 two thermal cycles produced preferred variants along the (-1 5 0) pole as in figure 2(aa) and 3(aa) respectively.

3.3.1 Detwinning in B19’ attains to preferred texture based on applied strain with multiple detwinning systems.

The Inverse Pole Figure (IPF) plots are obtained from analysis of neutron diffraction data using spherical harmonics as shown in reference[9], [90] and the intensity of the certain poles are described in terms of Multiple of Random Distribution (MRD) values as discussed in Chapter 2. The change in MRDs at different hkl's in an IPFs can be indicator of twinning and detwinning.
mechanism and similar analysis have been used to study variants reorientation in Uranium Niobium alloys [114], NiTi [9] and Magnesium alloys [115]. The difference plot presented during the entire analysis is generated by subtraction the intensity (MRD values) in each grid point between two IPFs - for example subtraction current loading from reference plot identification the poles that have increased and decreased due to mechanical loading. Identification of twinning system can be made from the difference plot by correlation the regions (area around certain hkls) that have decreasing and increasing intensity and are able to satisfy the twinning relationship in the direction of diffracted vectors. The region around the twinning planes do not change in MRDs values as there are not altered during the twin deformation and are the borders between the twinned and parent crystals. In simpler sense, when any twinning (or detwinning) activity occurred during the mechanical loading, the diffraction vectors (representing certain hkl planes in crystals) would increase in intensity proportional to the amount of new crystals (either from twinning or detwinning) being orientated in that direction.

In combination to this, Stebner al el. [35], [91] calculated the deformation for all possible twins system (8 transformation twins and 4 deformation twins) and presented the axial strain in the loading direction when any of these twinning (or detwinning) system were dominant. The generated axial strain was plotted for all orientation in monoclinic orientation space and plotted as IPFs. For example, if (100) compound twin system was activate, the B19’ crystal having orientation (1 2 0) towards loading will result in producing least axial strain whereas crystals with (-1 2 0) will produce the maximum axial strain. Thus, to accommodate the external strain, the crystal in the former orientation (1 2 0) will twins towards the later orientation and the increase and decrease of material in certain orientation can be observed in the difference plot as discussed above. The entire deformation is presented in reference [91] and reader are directed to the dissertation document for details. As in the documents, the backward strategy is utilized in analyzing the detwinning - difference plots were made and the (h k l) that have increased in MRD values are noted. With the all the possible twinning relationship in monoclinic NiTi known, the possible hkls in the parent crystal is calculated for the hkl in twinned that have increased in MRD values and matched to regions in difference plots with decreased regions. Reverse criterion can be used for the detwinning mechanism. These deformation maps that can accommodation external strains efficiently are used as look up reference and compared to the difference plot obtained from experiment in the current work to identify the mechanism occurring during the mechanical loading.
Figure 3.2 and 3.3 show IPFs with MRD values and the difference plots for all samples at strain level mentioned in Table 2.1. The reference figure is taken to be initial zero load condition at the beginning of the sample and the range for the MRD values have been presented in the scale of [0,6] for measured values and [-6, +6] for the difference plots. For the samples S1(also for S2), (-1 5 0) pole increased in intensities while the poles around (-1 1 3), (1 1 2), (-2 0 2) and (1 3 0) are decreasing as shown in Figure 3.3 (a-q) and Figure3.4 (a-i) respectively. Individual twinning system are very difficult to be identified in the difference plot as multiple twinning system seems to be activate with four poles are decreasing. Comparison with the deformation maps indicate that (0 1 1) type I and [0 -1 1] type II detwinning may be activated as crystallite orientated with poles around (1 1 2), (-2 0 2) and (-1 1 3) are detwinning to (-1 5 0) to provide maximum strain. Intensity decreasing around (1 3 0) also can contribute (-1 5 0) poles via (1 0 0) and (0 1 0) compound twinning but this is very difficult to deduce from single orientation data. For example, increase of (1 -5 0) pole can be traced back (1 7 0), (1 4 0) and itself for (100) ad (010) compounds twins. But that regions around (1 7 0) have increased during the experiments as other poles contribute to the same pole simultaneously.

During the unloading to zero strain and further loading into compression (-0.8%) strain (Figure 3.2(e-f) and Figure 3.3 (b-d)), MRD values around (3 1 0) increases that corresponds to similarly observation made by Stebner at el [91] around the poles (3 2 2) during pure compression testing. The corresponding twinning mechanism was deduced to be (1 1 -1) type I twinning during the compression. In general, (-1 5 0) pole is the preferred pole during tensile and corresponds to (0 1 1) type I and [0 -1 1] type II detwinning that also corresponding to the longest lattice parameters in these IPF. The direction in IPFs are calculated based on longest side of monoclinic crystal to be parallel to [010] and shortest side aligned to [100] and in monoclinic lattice indicates that the [0 1 0] direction and (0 1 0) are not parallel as in cubic lattice. Thus, crystals in B19’ align the longest side [0 1 0] align along (-1 5 0) pole that increase in MRD values during reorientation and detwinning. Similarly, for compressive stress, the preferred variant on shortest lattice parameter along [1 0 0] must be favored that provides that maximum strains for accommodation. From the experimental results in S1, we observed the increased of intensity around (3 1 0) when loaded to compressive strain of -0.8% (figure 2(h)) that are very close to [1 0 0] direction. The deviation
may be present as in polycrystals elastic strain has to be accommodated from its neighboring grains and constraints are present.

Figure 3. 2 (a) IPF with MRD and Difference plots for experiments up to 3% strain (S1 and S3). First row (labels from (a) to (q) and third row (labels (aa) to (qq)) represents the IPF with MRD values for S1 and S3 respectively. Second row is the difference plot of IPF alongside it in first row and the initial plot in S1 and similar plot are shown for sample S3 in forth row.
Figure 3.3b: Continued

Similar texture evolution is observed around (-1 5 0) pole are observed during tensile loading of S3 (Figure 3.2 (aa)-(qq)) and S4 (Figure 3.3 (aa)-(gg)) with additional increase in MRD values around poles (-2 1 0) and (1 1 0). The increase in intensity around (-2 1 0) can be correlated to (1 1 -1) Type I twinning and that correspondence to reduction of intensity around (1 -5 0). But, (1 -5 0) pole is the preferred orientation during tensile loading and increases continuously from another variant reorientation. Thus, it becomes very difficult to deconvolute the increase of MRD values from (0 1 1) type I and [0 -1 1] type II detwinning and decrease from (1 1 -1) Type I. The
other pole with increasing intensity is around (1 1 0) pole and corresponds to formation of (-2 1 0) deformation twins that have been widely reported in neutron diffraction [16, 20] and TEM experiments [22, 42, 28] during regime III of tensile loading. Two important features observed due to the presence of deformation twins are observed that are discussed below.

Figure 3. 4 IPF with MRD and Difference plots for experiments up to 5% strain (S2 and S4).
When S3 is unloaded from the first cycle (Figure 3.2 (gg)), the intensity around pole (1 1 0) decreases and poles around (-3 2 1) poles increases. This is clearer when two difference plots at unloaded zero strain after first cycle and with initial state is taken as reference plots. Figure 3.4 (a) shows the difference plot between the initial condition and unloaded state at 0% strain after first cycle and figure 3.4 (b) shows the unloading difference plot during first cycle from peak load at 3% strain to unload 0% strain. It can be observed in Figure 3.4 (a) that more B19′ variants with pole around (-2 1 0) are aligned towards loading direction than virgin sample and increase of (1 1 0) are absent that were present during loading initially. This indicates that crystal that twinned by (-2 1 0) deformation twin system during the loading (refer to Figure 2.2 (dd)) have reorientation to other CVs during unloading. Reduction of intensity around (1 1 0) poles and increase in (-3 2 1) poles corresponds to detwinning by (1 0 0) compound twin system that may be activated during unloading. This is further verified by looking at the difference plot between the IPFs at peak load at 3% and unloaded 0% strain as shown in figure 3.4 (b). The region around poles (-1 5 0) and (-2 1 0) poles corresponds to crystal that detwin during unloading but the reduction around the (1 1 0) poles cannot be said the same as the deformation twins are irreversible in nature. The more plausible argument would be formation of (1 0 0) compound twins as the MRD values around (-3 2 1) pole increases.

![Figure 3.5 Difference plot of S3 after first unloading to zero strain from two different reference](image)

Figure 3. 5 Difference plot of S3 after first unloading to zero strain from two different reference (a) Difference plot between the IPF of initial microstructure and unloaded sample (0 % strain) after 1 cycle. (b) Difference plot between IPF at 3% tensile strain and unloaded to 0 % strain.

The deformation twins discussed above are reported [22] to occur higher strain level (regime III) after the detwinning of initial CVs is completed as deformation twins has higher critical stresses to activate [43]. Comparison between the experimental critical stress with theoretical calculation are reported to be 20 MPa for (0 0 1) compound twin, 102 MPa for (1 0
0) compound twins and 180 MPa for (2 0 -1) in reference [22]. These stress level indicate that
detwinning of transformation twins are more dominant mechanism at lower stress level and (2 -
1 0) deformation are high stress mechanism.

The formation of deformation twins at the lower strain in samples S3 and S4 can attributed
to the role of initial texture present in these samples during mechanical loading. The different in
the initial texture between the samples are shown in Figure 3.5 and it is observed the amount of
B19′ crystals having (1 1 2), (-2 0 2) and (-1 1 3) poles are lesser in comparison to sample S1
and S2. The reduction in volume fraction these certain orientation crystallites that are most
favorable for Mode B detwinning or forming (1 0 0) and (0 1 0) compound twins during uniaxial
loading leads alternate mechanism of forming i.e. formation of (-2 1 0) deformation twins that
have been observed in samples S3 and S4. As stated earlier, more critical stress was required to
activate deformation twins, this explains the strain hardening observed during tensile loading in
samples S3 and S4 as compared to S1 and S2 respectively shown in Figure 3.1 (a) and (b).

Secondly, Nicholson et al [26] showed similar texture were obtained from three diffe-
rent experiments (isobaric, isothermal and isostrain) and the preferred variant is control-
d by the nature of the strain (tensile or compressive) rather than the stress of the material. His research
showed that following different routes in thermal and mechanical loads could be done for training
purpose to obtain the desired microstructure for application. In line with the discussion, in
specimen S3 and S4, isobaric thermal loads were applied for two cycles to produced preferred
variants microstructure that accumulated around 4% to 5 % strain during the thermal cycle (thermal
loading experiments are discussed in Chapter 2 and presented in reference [20] for similar sample).
Since the accumulation of strain during thermal loading must correspond to some equivalent
loading scenario during tensile loading.
Thus, for comparison, the initial texture developed in samples S3 and S4 are compared to texture developed in sample during a tensile loading between 3.5% to 6% strain in Figure 3.6. The tensile experiment results used as reference in current work is published in reference [18] and is not discussed in detail in here. The IPF labelled as initial Figure 3.6 (a) and Figure 3.6 (aa) is the initial microstructure for sample S3 and S4 respectively. Figure 3.6 (b-l) and Figure (bb-ll) are the IPFs with MRD values from the tensile experiments along with strain level mentioned alongside it. The difference plots obtained from subtracting the MRD values as discussed in Section 3.3 but contours in difference plots have to scaled down between -2 and +2 to make the plots more sensitive to the changes in MRD values with visual inspection. It can be observed that the sample S4 (figure 3.6 (b) to (e)) and S5 (figure 3.6(bb) to (ee)) have more intensity around pole (-1 5 0) whereas reference tensile sample (figure 3.6(g-l)) has higher intensity around poles (1 7 0) with the increasing strain. Difference plots in figure 3.6 (f) and (ff) have the minimum differences corresponds to 4.5% in tensile test respectively.
Figure 3. 7 Comparison of IPF between Samples S3 and S4 with reference tensile sample.
To further bolster correlation between the texture and deformation, difference plots are made between initial texture for samples S1 and S2 and peak loads 3% for S1 and 5% for S2 with tensile sample for corresponding loadings in Figure 3.7 (a-l). But for samples S3 and S4, initial conditions for sample S3 and S4 is compared 4.5% for tensile sample and peak loads 3% and 5% for S3 and S4 with 7.5% and 9.5% for tensile sample respectively in Figure 3.7 (m)-(y). In general, no major differences can be pointed out from the IPF with MRD values while shuttle differences are present in the difference plot. For example, a more B19′ crystals are aligned towards (1 7 0) pole in samples S1 and S2 analyzed in this paper than the samples used for tensile test. For samples S3 and S4, the MRD values around the poles around (-1 3 0) and (1 2 0) are higher than the tensile samples whereas (0 1 0) has higher values in tensile specimen. The major takeaway looking at these difference plot must be that similar detwinning mechanisms are present when loaded with equivalent strain but may vary in extent to which it is occurring. For example, in S1 (similar for S2), Figure 2.7 (f) shows the difference in MRDs values at 3% strain and the poles around (-1 5 0) has increased in intensity that actually corresponds to the (0 1 1) Type I and [0 -1 1] Type II detwinning mechanism identified previously indicating more detwinning has occurred in S1 than the tensile sample. The rest of region with lower MRD values in S1 are identical to initial condition. Similarly, for sample S3 (similar to S4), the poles around (0 1 0) spread out towards the (1 2 0) formation deformation twins. Thus, we can conclude that initial microstructure in sample S3 and S4 and the deformation incurred during mechanical loads are similar to 4.5 % in tensile loads.

To emphasize on that on the role of initial microstructure in stress-stress response, first cycle loading in samples S1, S2, S3 and S4 along with reference tensile test (truncated to 12 % strain) has been shown in figure 3.8 with additional plot labelled as “Shifted S4” and “Shifted S5”. As the name suggest, the two additional “Shifted” plots shown in broken line are shifted by 4.5% for sample S3 and S4 to compare with the tensile curve. The stress- strain response for S1 and S2 sample follow the regime II deformation present in the tensile test and the slopes for stress-strain response are very similar to the tensile specimen. The original stress-strain response for specimen S4 and S5 have higher slope after the initial elastic loading is completed. But it can be observed that when the stress-strain curves for sample S4 and S5 are shifted by 4.5% strain (dashed lines) the hardening (slope of stress-strain) nature are very similar and resembles deformation in regime III of tensile loading. For the tensile curve, the region corresponds to Region III and has been
characterized by presence of (-2 1 0) deformation twins and S3 and S4 could be loading with variants that are less favorable CVs for detwinning in Regime II.

![Texture comparison](image)

**Figure 3.8** Texture comparison between the tensile sample and samples S1, S2, S3 and S4. For each sample, the first and second row represent the initial condition and peak load condition along with the difference IPF between them. For example (a) and (b) are IPF with MRD values from initial condition.

![Loading curves](image)

**Figure 3.9** Loading curves of S1 (red solid), S2 (green solid), S3 (indigo solid) and S4 (aqua solid) along the tensile loading curve (blue solid) of virgin sample. The dotted lines are the shifted curves by 5% for S3 (indigo) and S4 (aqua).
3.3.2 Detwinning of variants during deformation are reversible

In this section, we examine if the detwinning occurred by transformation twins in B19 during loading are reversible when the mechanical load is removed. For the purpose the difference of the IPF between initial condition, highest tensile and compressive load condition has been shown in Figure 3.9. The first column indicates the MRD values and the second column represents difference plot from the previous state. For example, in Sample S1, Figure 3.9 (d) is the difference between the IPF at initial state (Figure 3.9 (a)) and 3% peak load (Figure 3.9(b)) and difference plot Figure 3.9 (e) is the subtraction result between the IPF at 3% peak load (Figure 3.9 (b)) and -0.8% strain (Figure 3.9 (c)). Similar plots are made for samples S2 and S3 in Figure 3.9 (aa-ee) and (f-j) respectively.

During the loading to the peak strain, preferred variants with poles around (1 -5 0) and (0 1 0) parallel to the loading direction start forming and the poles around (-2 0 2), (0 1 0), (112) and (131) for sample S1 and S2. Along with the mentioned poles, there are additional poles (110) and (-3 10) that have increased in the MRDs values for S4 sample that have been discussed earlier. Following the unloading into compression loads, the poles that had increased and decreased MRDs values during loading are reversed at stress level below -350 MPa for all the samples. This indicates that (0 11) type I and [0 -1 1] type II detwinning that occurred during loading have mobile interfaces are reversible that is essential in terms of cyclic stability in this range.

Another observation that can be made under compression, preferred variants having strong MRD values along (1 1 1) are formed due to detwinning under -200 MPa for similar texture NiTi samples [33], [107]. In comparison with sample S1, although some intensity has increased around (1 1 1) poles at stress level of -350 MPa the MRD values are weak in comparison to the reference above. Thus, it indicates detwinning mechanism have reversed in nature and are dominant when unloading from tension into compression rather than activating new detwinning mechanisms. The elastic unloading regime (unloading from highest stress to zero stress) is also examined to check the if any reversed detwinning has occurred as unloading is characterize by elastic strains in detwinned martensite. Since, the experiments were strain controlled and data weren’t collected at exactly zero stress level, thus IPF from stress level close to zero for sample S1 and S4 are examined. The IPF for unloading from 3% strain level to 2% strain along with stress values for the neutron data collect are shown in figure 3.10.
Figure 3. 10 IPF of MRD values and difference plot for sample S1, S2 and S3 in three loading stages.

The decrease in poles across (-1 5 0) and (0 1 0) provides evidence that inverse detwinning is active during elastic unloading and indicates the resistance to interface movement of transformation twins are minimum. This is interesting in terms of numerical modeling of unloading to zero strain level from peaks loads as there can be contribution of strains from various competing mechanisms:

(a) Unloading of elastic strains in martensite
(b) Reversed detwinning that occurred loading of self-accommodated microstructure
(c) Detwinning into preferred orientation as a result compressive stress
Figure 3.11 Evolution of texture during the unloading for samples S1 and S3. The stress and strain values for each IPF values are presented at the bottom of the IPF.

Figure 3.10 (b) shows the lattice strains evolution from (-110) and (-111) poles with respect to macro strains and since neutron data are collected for the poles normal loading direction for sample S1 and S3. The positions of largest stains levels are labelled as 1 and unloading to near zero stress levels are labelled as 2. The trend of lattice strain increasing and decreasing with the applied macro strain indicate lattice strain are almost linear to the applied macro strain. The lattice strains are negligible at zero stress level and thus indicates that elastic unloading and reversed detwinning occur together at the elastic unloading process.

3.3.3 Strain hardening of martensitic NiTi is history dependent

During cyclic loading of B19’, the stress-strain curve alters in first few cycles before the stabilization of cyclic curve. As to earlier discussion, one of the factors for these changes in this
stress-stress response is due to different microstructure (in present case we are focused on texture evolution) that leads to selective detwinning and reorientation mechanism and is manifested stress-strain response. In sample S1, the stress-strain curves are almost identical with some hardening present in second cycle compared to first. In contrast, stress strain response in sample S3 are very different from cycle 1 to cycle 2 - cycle 1 has higher detwinning stress but cycle 2 has higher strain hardening slope. Thus, to investigate the role of initial texture during first two cycles, difference plots are made between the similar loading steps are made as shown in Figure 3.11. Similar to above, first and second column IPFs correspond to first and second cycle respectively and third column IPF is the difference plot from first cycle to second cycle.

The MRD values for the are slightly stronger in first cycle with comparison to second cycle for S1 (refer to Figure 3.11). No prominent alternation in detwinning mechanism between cycles are observed as the difference plots does not indicate any positive values in the difference plots in Figure 3.11. The reduction of MRD valves can be attributed to introduction of dislocation during detwinning that have been observed in TEM samples[60], [98] and possible reason for slight hardening observed in the second cycle as they acts as barrier to the twin interface movement. Two poles (3 1 0) and (-1 2 0) have positive values in the difference plots at 0% strain. The positive values around (3 1 0) pole can be correlate to the favorable variants forming due to detwinning in compressive loading to -0.8%. (-1 2 0) poles is likely to be the remnant of (0 1 1) type I and [0 -1 1] type II twins that has occurred during the first cycle that could also leads to the lowering of the critical stress for detwinning in the second cycle.

In sample S3, it should be noted that (-2 1 0) deformation twins formed during the initial loading of the cycle, can be further deformed by detwinning by (1 0 0) compound twins during compression – (1 1 0) poles lose intensity and (-3 2 1) gain intensity that is also observed in Figure 3.13 (also refer to section 3.1.1 for discussion). When the second cycle in initiated the inverse detwinning of same variants occur as the intensity around (-3 2 1) decrease in the difference plot and the intensity around (1 1 0) pole is similar in Figure 3.11 (ff) and figure (ii).
Figure 3.12 Texture Evolution of B19’ for sample S1 and S3 during two sample. (a)- (m) are the IPF for S1.

More clarification is present with the difference plots made for each strain level with respect to the 0% strain (start of cycle) as shown in Figure 3.12. The initial condition (Figure 3.12 (a) and Figure 3.12 (aa)) are taken as the reference plot for each cycle and difference plot are made for each strain increment. This allows to identify the increasing and decreasing intensity of poles that have actually contributed to strain accommodation during the cycle. Comparing the difference plots between Figure 3.12 (dd) and Figure 3.12 (j), it can be said that higher poles around (-3 2 1) that were present from the first cycle via detwinning of (0 0 1) compound twins has vanished and poles around (1 1 0) have increased (refer to Figure 3.2(j)). This could be due to reversal of detwinning via compound twins that have occurred earlier during or additional contribution of deformation twins forming during loading of second cycle. As stated earlier in Figure 3.2 (ii), the intensity around (1 1 0) are the same for cycle 1 and 2 and thus, no additional deformation twins are formed in comparison to previous cycle. The favorable scenario would be reversal of detwinning of (0 0 1) compound twins that also have lower critical stresses than previous case.
This can explain the reduction in critical stress for detwinning in second cycle. As the loading continues in cycle 2 (loading from 2% strain to 3% strain), the strain hardening is higher and this has been attributed to interaction between the interfaces of Mode A (1 0 0) compound twins and (-2 1 0) deformation twins formed during the first cycle [116]. In general, the residual variants from the previous cyclic loading can assist in reducing of critical stresses required for detwinning and reorientation but deformation twins’ interfaces and dislocation introduced can work harden during the second cycle.

### 3.3 Conclusion

Neutron diffraction, a nondestructive technique, has be utilized to various understand reorientation (detwinning) mechanism occurring in NiTi with different initial CVs during mechanical loading. The texture at the beginning of each cycle can influence the stress-strain response in each cycle and is not solely dependent on initial microstructure of the material. Thus, history of loading influences the reorientation mechanics and microstructural information have to be incorporated during numerical implementation reorientation mechanism. The microstructure information has to reflect the number of individual CVs that can potential reorient under mechanical loading. Secondly, the contribution to transformation strain from the reorientation is correlated to the $V_r$ of most favorable variant along the loading direction. But, activation of various
modes of detwinning mechanism can produced multiple CVs simultaneously to accommodate the strain due to reorientation. Lastly, reduction of elastic strain and reversal of detwinning occur concurrently during mechanical unloading.
4.1 Introduction

Nickel Titanium (NiTi) alloys, also known as NiTiNOL, have been put into various applications (especially in actuation, biomedical devices, vibrational damping, couplings) for their superelastic and shape memory effects [1-3]. Both, superelastic and shape memory effects, are attributed solid-to-solid transformation which is reversible and diffusionless between the B2 phase (Pm3m cubic structure) and B19′ phase (P21/m monoclinic structure) [4, 5]. Traditionally, the domain of shape memory and superelastic effect is defined based the stable phase at application temperature and the nature of loading required to undergo phase temperature. For the shape memory effect, B19′ phase is stable phase at the application temperature and can be deformed elastically with detwinning and reorientation of the variants. When heated after deformation, B19′ transforms into B2 phase and upon cooling the phase B19′ is recovered to its original twinned structure. For the superelastic application, B2 is the stable phase at the ambient temperature and on application of mechanical loading, B2 phase (parent) transforms into hierarchical twinned variants of B19′ phase (daughter). The twinned is B19′ reversed back to initial parent phase upon removal of load. The reversible strain produced during the phenomena is higher than general structural material - around six percent for most polycrystals and nine percent for single crystals. In the current work, we are interested in superelastic regime and thus following discussion will be more focused on it.

Microscopically, twinned microstructure of B19′ formed form B2 during thermo-mechanical experiments is described using Phenomenological Theory of Martensite Transformation (PTMT) (also referred to as WLR [120] and BM theories [121]) that estimates orientation relationship between the phases, invariant planes (planes between the twinned daughter phase and interface between the phases) and shearing of lattice. These parameters have been verified experimental for NiTi in references [8, 9]. As presented in these models, the overall transformation consists of three operations - Bain strain, invariant shear and rigid body rotations. The Bain strain gives the changes in lattice dimension between the phases, but shear is required to transform parent lattice to the form observed daughter lattice. Following the solutions of PTMT,
12 unique variants of B19’ phase can be formed from B2 based on the symmetry of parent phase (cubic) and daughter phase (monoclinic). But single variant is unable to create habit plane between the phases, as no principal values of deformation matrix is equal to unity indicating undeformed plane between the phases cannot be formed. Thus, pair of twinned B19’ variants with different volume fractions (V_f) are calculated that satisfy the invariant plane solutions and has been supported experimentally. The pair variants satisfy the interface compatibility conditions between B2 and B19’ and thus creates an invariant plane (habit plane). 192 possible combinations of habit plane have been calculated from possible 12 variants[10-12]. Furthermore, there is possibilities of formation of multiple CVs in polycrystals due to the different orientation of grains, granular constraints for compatibility of strains due to transformation and the accommodation of applied strains [13-15].

During multiaxial mechanical loading, these phases are subjected multiple deformation mechanisms (elastic deformation, transformation from parent to daughter phase, reorientation of variants and plastic deformation) to occur concurrently leading to different stress strain responses. During uniaxial tensile and compression test, B2 deforms elastically during the initial loading until a critical stress value is reached for transformation during a strain-controlled experiment. At a critical stress level, transformation initiates from B2 phase into B19’ phase with constant stress level (stress plateau) for tensile test. Whereas material hardening is observed during transformation under compression loading [16, 17]. The transformation is defined to be complete as most of the grains favorable to transform are converted into B19’ phase. The strain observed during the stage is combination of transformation between the phases and reorientation(or detwinning) of twinned B19’ to accommodate the deformation from external loads[14, 18]. Most of the strain obtained during transformation is reversible and the initial B2 phase is obtained when unloaded to zero strain. Microscopically, evidence of incomplete reverse transformation due to variant locking of martensite [125] and plasticity in B2 phases during the unloading [20, 21] has been experimentally observed. Along with stress direction, experimental studies in the past have also shown the mechanical response are influenced by orientation depended (texture in sense of polycrystals) [18, 22], precipitates formed during the heat treatment[23, 24] and cold work during the processing [128]. But putting processing parameters aside, the multiple mechanisms occurring concurrently are nonlinear during uniaxial loading and this has made the development of constitutive relations becomes very challenging. This has been expressed as main motivation of the research work too.
Total strain is at any instant is summation of strains from individual mechanisms [26, 27] and experimental data to support strain partitioning have been every limited that leads to optimizing large set of parameters for the models. The total strain partitioning ($\varepsilon_{\text{total}}$) during phase transformation and plasticity is given by additive summation of individual strain as

$$\varepsilon_{\text{total}} = \varepsilon^e + \varepsilon^{\text{inr}} + \varepsilon^p$$  \hspace{1cm} (4.1) 

$\varepsilon^e$ is elastic deformation at the initial stages in B2 matrix. During the elastic deformation, the stress rises linearly with the application of strain and is fully recoverable in most materials. $\varepsilon^{\text{inr}}$ is the inelastic recoverable strain obtained that consists of multiple mechanisms - phase transformation, reorientation of the B19' variants as discussed in Section 1.2. Following the same discussion, we will try to answer the similar question presented path dependence during phase transformation NiTi. The change in loading path can have two consequences:

- Formation of new B19' variants as the loading path changes untransformed austenite grains becomes favorable for transformation.
- Reorientation (Detwinning) of previously formed B19' plates can form optimized microstructure to align along the loading axis to accommodate the strain.

Until now, most of the analyses have either been in macro-scale examining the stress-strain curves that are incapable of identifying mechanisms or have been in microscopic in nature that can identify the micromechanics but is difficult to quantify the bulk behavior using them. Neutron Diffraction experiments have been used in last two decades to bridge overcome length scale barrier in experimentation to characterize bulk texture [35, 36], volume fraction evolution [14, 37], phases strain evolution in individual crystallography plane (refer as hkl from here on) [21] and anisotropy in Young’s modulus [38, 39].

In this chapter, we use neutron diffraction experiments to characterize the bulk evolution of volume fraction evolution in individual phases under proportional and non-proportional loading paths under biaxial loading. Following the bulk characterization, we also present result from HEDM experiments to validate observations are followed in grains scale level. HEDM are high-energy synchrotron x-ray techniques capable of grains level information for individual phases.

### 4.2 Experimental Details

The background to the NiTi used to prepare cruciform samples for biaxial loading has been presented in Section 2.1. Two different specimens, with same heat treatment, were used for...
Neutron diffraction and HEDM experiments and care was taken that both specimens have the rolled direction oriented similarly with respect to the biaxial testing machine. Displacement control test was performed on custom designed servo hydraulic MTS machine with four actuators with each connected to LVDT for displacement measurement and load cell for force measurement. Each specimen were subjected to three types of loading paths as shown in Figure 4.1 (b) were performed with start \( u_{xx} = 0 \text{ mm}; u_{yy} = 0 \text{ mm} \) and end displacement \( u_{xx} = 0.55 \text{ mm}; u_{yy} = 0.55 \text{ mm} \) been the same. Path 1 (blue color) describes the proportional loading where equal displacement on both axes at same rate is being applied to the specimen. Path 2 (red color) and Path 3(green color) describes the non-proportional loading condition with displacement is applied to one-axis direction while the displacement on other axis is kept on hold and reverse the condition on the next stage.

![Figure 4.1 (a) EDM Biaxial Sample (b) Schematics of three loading paths for proportional and non-proportional loading.](image)

### 4.2.1 Neutron Diffraction Setup

The neutron diffraction experiments were conducted using SMARTS instruments at Manuel Lujan Jr. Neutron Scattering Center (LANSCE) at Los Alamos National Laboratory. SMARTS instruments utilized white beam of neutrons that are diffracted on all directions after striking the specimen placed at the path of the beam [88]. Diffraction data were collected for 60 minutes for all the reading presented in this manuscript. The specimen is placed at 45° to the incoming beam so that the scattering vectors are perpendicular and parallel to the loading plane. Two detectors are placed at ±90 degrees (hereon refer +90 detector as Bank 1 and -90 detector as
Bank 2) to the incoming beam such that Bank 1 and Bank 2 receives data from planes that are perpendicular and parallel to the applied load plane. The setup for biaxial machine in the hutch along with schematic of neutron diffraction experiment is shown in Figure 4.2.

![Biaxial Machine setup in the hutch.](image)

Figure 4.2: (a) Biaxial Machine setup in the hutch. (b) and (c) Schematics Diagram of Neutron Diffraction Setup. (b) Top view along Y lab direction (c) Front view normal to the sample surface.

Figure 4.2 (c) shows the schematic of the diffraction volume of the material (grey) along with the diffraction vectors and the loading axis (blue arrows). The Q1 vectors (green arrow) are diffracted of the planes that satisfy Bragg’s condition and lie normal to the biaxial loading plane. Both tensile and shear loads are present for the planes depending upon the applied displacement. Similarly, the Q2 vector (red arrows) diffracts of the planes satisfying the Braggs conditions and the diffraction beam is directed towards the Bank 2. The reflections of planes observed in the Bank 2 are loaded the compression, as the diffraction vectors are vectors normal to the loading planes in all loading conditions. Throughout the paper, the coordinate system referred as loading axis (X_{load}, Y_{load}) are along the X direction and Y direction (blue arrows in Figure 4.2 (c)) and Z_{load} lies along the out of the loading plane. Similarly, the lab coordinate is described as X_{i} along Q1 vector of diffraction, Z_{i} along the diffracted beam towards the Bank 2 and Y_{i} is the vertical direction in physical space. Thus, Z_{load} coincides with the Z_{lab} direction and the plane that contains X_{load} and Y_{load} is rotated by 45 degrees along Z_{load} (equivalently Z_{lab}) to align them.
4.3.2 HEDM Experimental Setup

The FF-HEDM experiments were performed at 1-ID at Argonne Photon Source with the monochromatic x-ray beam of 71.332 KeV. The GE-41RT square detectors with 2048 X 2048 pixels with pixel size of 200-micron X 200 micron were used to collect the data. The detector was placed 1452 mm in order to four complete hkl reflections for the austenite (B2 cubic) and fifteen martensite (B19 monoclinic) phase. The total diffracting volume for the experiment was 1000 microns X 1000 microns X 300 microns using a beam size of 1000 microns X 500 microns and collecting data for 2 layers (each 500 microns). Detector was placed behind the sample in line to the incoming beam and the diffraction vector observed in detector made Braggs angle as shown in Error! Reference source not found.. The diffraction patterns were collected at every 0.25 degrees with the omega rotation (rotation along vertical direction of the biaxial frame) between the -155 to -25 degrees and 25 to 155 degrees.

![Figure 4.3 HEDM setup for Far-Field Diffraction Experiments.](image)

4.3 Results

4.3.1 Mechanical Loading

Single specimen was used for all three loading paths in order of proportional loading, non-proportional loading with initial load in X<sub>load</sub> direction and non-proportional loading with initial load in Y<sub>load</sub> direction. The outputs from individual arm for force and relative displacement...
recorded from force cell and LVDT respectively and are shown in Figure 4.4. Red and blue color represents the reading from $X_{\text{load}}$ and $Y_{\text{load}}$ direction respectively and solid and broken lines are used to differentiate between reading obtained during HEDM and neutron diffraction experiments. Interruptions were made at various load intervals, to collect the diffraction data for all six experiments (3 loading paths for neutron diffraction and HEDM experiments) at the same displacement values that are presented in table1. The remaining details of the experiments are presented in Table 4.1.

![Figure 4.4](attachment:image.png)

Figure 4.4 Force and Displacement values for (a) Proportional loading (b) Non-Proportional Loading with initial load in X direction followed by Y direction (c) Non proportional loading with initial load in Y direction followed by X direction.

The displacements values for diffraction data collection are presented in the fourth column and the maximum force observed during the entire test are presented in column 3. Since the experiments were displacement controlled, there is a rise of force in the axis that is kept at hold while the other axis is being loaded. The increase in force value was around 5-6 KN for all non-proportional loading paths. Another point to take notice is that the force and displacement curves overlap for neutron and HEDM experiments in the first loading and starts to vary when the load path direction is changed. In PXY path, force and displacement curves are overlapped for $X_{\text{load}}$ and $Y_{\text{load}}$ direction up to 0.62 mm and alter as the unloading proceeds. Similarly, the force and displacement curve for $X_{\text{load}}$ overlap up to 0.55 mm but as the loading is started in $Y_{\text{load}}$ direction the force and displacement curves vary. Similar, observation has been made with NPYX loading path with overlapping force and displacement curves when loading $Y_{\text{load}}$ direction initially.
Table 4.1 Details of in-situ Neutron Diffraction and HEDM experiments.

<table>
<thead>
<tr>
<th>Loading Path</th>
<th>Final Loading displacement (mm)</th>
<th>Maximum Force (KN)</th>
<th>Displacement at diffraction data collected (mm)</th>
<th>Number of Diffraction Reading</th>
</tr>
</thead>
<tbody>
<tr>
<td>PXY</td>
<td>X -0.62, Y -0.62</td>
<td>X-11.82 Y-11.46</td>
<td>X – 0, 0.11, 0.2, 0.27, 0.34, 0.41, 0.48, 0.55, 0.62</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Y- 0, 0.11, 0.2, 0.27, 0.34, 0.41, 0.48</td>
<td></td>
</tr>
<tr>
<td>NPXY</td>
<td>X -0.55, Y -0.55</td>
<td>X-12.5 Y-12.5</td>
<td>X – 0, 0.11, 0.2, 0.27, 0.34, 0.41, 0.48, 0.55, 0.55, 0.55, 0.55, 0.55, 0.55, 0.55, 0.55, 0.55, 0.55</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Y- 0, 0, 0, 0, 0, 0, 0, 0, 0.11, 0.2, 0.27, 0.34, 0.41, 0.48, 0.55</td>
<td></td>
</tr>
<tr>
<td>NPYX</td>
<td>X -0.55, Y -0.55</td>
<td>X-14 Y-13.6</td>
<td>X-0, 0, 0, 0, 0.11, 0.27, 0.41, 0.48, 0.55</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Y-0, 0.11, 0.41, 0.48, 0.55, 0, 0, 0, 0, 0, 0</td>
<td></td>
</tr>
</tbody>
</table>

4.3.2 Neutron Diffraction Analysis

Reviled Analysis was done on the powder patterns obtained from TOF neutron diffraction experiments using the GSAS [130] software and batch processing were performed with add-on SMARTSware developed for neutron data processing [111]. The powder patterns are collected on two detectors (referred as Bank1 and Bank 2) and both were analyzed together with detector orientation input in them. The output from Rietveld analysis gives averaged lattice parameters,
elastic strains, volume fraction and texture over the entire volume of diffraction. The initial lattice parameters used for powder analysis are given below.

B2 cubic (Pm3m)  
$a_a = 3.015$ Å  

B19′ monoclinic (P2$_1$/m)  
$a_m = 2.889$ Å  
$b_m = 4.12$ Å  
$c_m = 4.662$ Å  
$\gamma = 96.8^\circ$

In GSAS, the phase fraction is calculated as a scale factor for the intensities observed for all the peaks in powder histogram based on the structure factor of unit cell as using individual peaks for the calculation might exclude the influence of texture. Detail description of using spherical harmonics to obtain texture in B2 and B19′ phases have been discussed in Section 2.2.2.1 can be found in reference [90]. Inverse Pole Figures (IPF) are plotted for initial condition with the MRD values from 0-4 range in Figure 4.5 and these will be used as benchmark for evolving texture during biaxial loading. The MRD values obtained for out of plane direction ($Z_l$) (also the normal direction (ND) on the rolled plates) shows strong $\{111\}_a$ poles and minimum values are obtained around the $\{100\}_a$ poles. The maximum MRD values obtained around $\{110\}_a$ poles along $X_l$ direction, which is aligned at 45 degrees to the rolling direction but are more diffused than the previous. These textures obtained in ND is in agreement with the texture studies done on rolled plates in previous [131].

To study the evolution of volume fraction and influence of variant reorientation during different loading paths, IPF for volume fraction are calculated using the MRD values. By definition, volume fraction of intended hkl pole (intervals in orientation space) is equal to the normalized MRD value at the same intervals to the total MRD value for the entire orientation space [14, 48]. Following the procedures, IPFs of volume fraction and difference plots obtained by subtracting IPF at current state with reference state (initial loading for B2 phases and first loading when B19′ phase) are generated.
Figure 4. 5MRD values for initial loading conditions. Left and right column represents the texture from the out of plane texture and planes normal to loading respectively.

For the PXY loading path (refer to Figure 4.5), the intensity decreases around the \( \{100\}_a \) poles with the maximum decrease in \( \{511\}_a \) poles in normal direction. It can be observed that \( \{111\}_a \) poles are less favorable for the transformation and have slight increase in \( V_f \) at the end of loading. Similarly, in \( X_l \) direction, the transformation is more uniform around the \( \{100\} \) poles but the texture changes are very small to make any tangible conclusion. The first B19’ peaks are observed when the displacements value reaches 0.34 mm on both \( X_{load} \) and \( Y_{load} \) with maximum around \((-101)_m, (101)_m \) and \((120)_m \) in \( Z_l \) direction. On further loading equally on both the axis, \((-101)_m \) and \((101)_m \) gets stronger but the intensity around \((120)_m \) relatively remains the same and is verified by negative values (represented by broken lines) around that region by the difference IPF.
For the NPXY loading path (refer to Figure 4.7), MRD values obtained along Z_l direction show that grains around the \{112\}_a poles transform when loaded along the X_{load} and starts spreading around the the \{111\}_a poles when loaded along the Y_{load}. The transformation along X_l direction is more distribution and the only highlights the resistance of \{111\}_a poles to transform. B19’ phase is first observed with displacement at 0.41 mm at X_{load} direction while keeping the Y_{load} fixed at zero displacement. Initially, variants with strong poles similar to proportional loading are formed with similar evolution in Z_l direction. The variants with maximum V_f poles at (1 2 0)_m and (-1 1 2)_m are formed in the X_l direction while loading in X_{load} direction but as the loading path is changed, variants with stronger poles (1 -5 0)_m are formed.

For the NPYX loading path (refer to Figure 4.8 Error! Reference source not found.), the first region to transform is around the \{111\}_a poles that also have the most intense MRD values in the Z_l direction. This is totally in contrasts to the previous loading paths (both PXY and NPXY) where \{1 1 1\}_a are had very little decrease in MRD values after loading. The B19’ phases are first observed when the displacement values in Y_{load} direction reaches 0.41 mm. The initial poles are formed around (1 2 0)_m and (-1 0 1)_m direction on Z_l direction. As the loading increases on the other direction the \{101\}_a poles stronger. On X_l direction, the stronger poles are observed around (1 2 0) direction and with the change in direction the stronger poles rotate around (-1 2 0) direction.
Figure 4.7 IPF of Volume fraction and Difference plot for NPXY loading.

Figure 4.8 IPF of Volume Fraction and Difference plot for NPYX loading.

4.3.2 HEDM Analysis

The FF-HEDM experiments were analyzed using MIDAS software that is currently been developed in Advanced Photon Source [133]. The accuracy of results from indexing is close to 1° for the orientation of grains, resolution of $10^{-4}$ micro-strain for six components of strain and 10
microns for radius of grains [74]. The position and tilts of detector were calibrated using standard CeO$_2$ sample with known lattice parameters and distance between detector to sample center was obtained 1451.3217 millimeters. B2 grains were indexed with 0.7 confidence level as cut off during analysis and tolerances in omega and detector position are put to 0.25 degrees and 600 microns respectively. B19’ grains could not be indexed as they lack spottiness in their hkls reflection that is necessary to index a grain. The microstructure formed by multiple CVs in polycrystals are in very small domains (small as nanometers) and the intensities diffracted from these domains aren’t bright enough. Furthermore, combining this many small domains diffracting together, the spots overlap each other that hinders indexing of grains accurately. Another difficulty in indexing B19’ is that lower symmetry crystals like monoclinic have reflection spots from multiple hkls very close to one another.

Figure 4. 9 Detector image of initial and final load stages for frame number 500 that during PXY loading path. (a) Maximum over all for initial state (b) Magnified section of box in figure(a). (c) Maximum over all for final load (d) Magnified section of box in figure (c).
Figure 4.9 (a) and (c) shows the detector image at initial condition and highest load condition for PXY experiments respectively and section within white box is shown are shown in (b) and (d). The \((110)_m\) reflections from B2 grains are separated between them and easier to index whereas most of the \(hkl\)s reflection coming from B19’ phase is spread along the ring indicating there is high disorientation present within the grains. Also, the reflections (for example \((111)_m\) and \((020)_m\) in Figure 4.9 (d)) are very close to each and lie within tolerances given during processing and thus can’t be assigned to individual grains.

The spatial position of indexed B2 grains at initial stage for three loading paths PXY, NPXY and NPYX are shown in Figure 4.10 (a), (b) and (c) respectively with the color code representing CL for the indexed grains. For the initial condition, 1120, 634 and 454 grains were indexed for PXY, NPXY and NPYX respectively.

![Figure 4.10](image)

Figure 4.10 B2 indexed grains at load 0 for all loading paths. (a) and (b) are COM and IPF of PXY respectively.

The number of indexed grains reduces in NPYX caused by incomplete reverse transformation from retained B19’ phase and defects introduced from previous two cycles. Figure 3.10 (a) – (c) show the maximum over all images for initial loading stages for loading paths labelled along the figures. Additional spots are seen in NPXY (figure 3.10 (b)) and NPYX (Figure...
3.10(c)) as marked by red arrows that corresponds to reflections from B19’ and this provides evidence of retained B19’ are present after complete unloading. The consequences from retained B19’ are that all the B2 grains indexed in PXY can be tracked to NPXY and NPYX and thus causes reduction in indexed grain number. This is problematic for comparing the different loading path as the initial conditions are not identical but as mentioned above HEDM analysis in current work will be used to examine if the observation in the bulk from neutron diffraction experiments are also present on grain scale level rather than using it to identify the dominant mechanism.

Figure 4. 11 Maximum over all detector images for initial loading stages (a) PXY (b) NPXY (c) NPYX

IPFs of indexed grains along the $Z_l$ direction (similar to Bank 2 in neutron diffraction setup) that corresponds to ND in the sample are shown in Figure 4.12 (d), (e) and (f). Most of the grains have [111] direction aligned to the ND sample direction that is alike to texture along $Z_l$ obtained from the analyzing the neutron diffraction. The color bar is based on the equivalent strain from 1 to 1.5 calculated from the six strain components as:

$$
\epsilon_{eq} = \frac{2}{3} \sqrt{\frac{3(\epsilon_{11}^2 + \epsilon_{22}^2 + \epsilon_{33}^2)}{2}} + \frac{3(\epsilon_{12}^2 + \epsilon_{23}^2 + \epsilon_{31}^2)}{2} \quad (4.2)
$$

11, 22 and 33 subscripts represent normal strains and 12, 23 and 13 subscripts present the shear strains. The equivalent strain of less than 1% strain are observed at the initial condition for most grains in PXY. Higher strain values are present in some of the grains could be a result of residual strain from EDM during sample preparation. Following the later cycles, B2 grains show increased equivalent strain as large as 4% that is produced from the previous cycles. The presence of elastic...
strain may trigger early transformation in some grains, but it is unlikely that any change in competing mechanism will be altered.

![Histograms](image.png)

Figure 4. 12 Histogram of equivalent strain of indexed grains for (a) PXY (b) NPXY (c) NPYX. The count of grains is for the range is shown on y-axis.

The evidence of phase transformation is observed from the caked data for load step 0 (blue), load step 4 (green) and load stepm8 (red) as shown in Figure 4.13. Caked data of HEDM data refers to summation of intensity observed during the experiment at all omega rotations along Y-axis during at the single load step and plotting intensity as a function of radial distance in detector (refer to [134] for details). The poles for B2 and B19’ are separated by ‘a’ and ‘m’ for austenite and martensite at the end of labels for each pole as done before. The \{110\}_a have the largest intensity compared to the other poles in B2 similar on the structural factor for the CsCl structure and should decrease as the loading is increased due to transformation. But during to experiment, the attenuation was reduced from during load step 3 to capture the lower intensity B19’ phase during transformation. This explains the lower intensity \{110\}_a of loading step 0 (blue) compared
to loading step 4 (green). (001)$_m$, (002)$_m$, (11-1)$_m$, (020)$_m$ and (111)$_m$ for the B19′ phase increased with increasing load from stage 4 to 8.

Figure 4. 13 Powder Pattern after caking HEDM data for load 0, 4 and 8 for PXY loading path.

4.4 Discussions

4.4.1 Volume Fraction Evolution is Path Dependence

After Rietveld analysis of neutron diffraction spectra, volume fraction obtained at different loading stages mentioned in Table 3.1 are shown.

At final loading stage, $V_f$ of B2 are calculated to be 0.788, 0.687 and 0.601 for PXY, NPXY and NPYX respectively. The values calculated for B19′ are based on sum of two phases must be unity during diffraction spectra analysis. The x-axis labelled as vector norm is the scalar value of displacement vector:

$$\text{vector norm} = \sqrt{(x \text{ displacement})^2 + (y \text{ displacement})^2} \quad (4.3)$$
The final displacement in all three loading cases are equivalent but the amount of volume fraction for both the phases are different that can be viewed as the influence of different loading paths on transformation events occurring. From mechanics point of view, amount of B2 grains participating in transformation must vary based on loading path direction to produced different volume fraction.

To examine, difference plots are created from neutron diffraction experiments for final loading state by subtracting the volume fraction IPF from each other for B2 phase between the various loading paths as shown in Figure 4.15. Since, the results from Bank 1 (Error! Reference source not found. – 3.8) are diffused for B2 phase and no concrete conclusion can be drawn and thus the discussion will be focused on results of Bank 2 that represent the ND or Z_l direction will be taken into account. It is observed that the volume fraction of B2 grains around \{111\}_a poles is proportional to the observed B2 volume fraction in general. PXY has highest B2 volume fraction (0.788) at final loading stage and difference plot between PXY and NPXY show decease of intensities around \{111\}_a pole (seen in Error! Reference source not found. (c)) indicating more B2 grains are present at end of PXY loading path. Similarly, NPYX has less B2 volume fraction (0.602) than PXY (0.788) and the difference plot shown in Error! Reference source not found. (f) shows that B2 grains are present in NPYX that is similar to results as in PXY and NPXY. This verifies the observed \( V_f \) in figure 3.14 (a) are path dependence that depends upon the favorability of B2 grains to transform that vary based on loading path.
Figure 4. 15 Volume Fraction IPFs and difference plot of B2 at final loading stage. The first and second columns are observed volume fraction and the third column is the difference plot obtained by subtracting column 2 from column 1.

One variation that must be mentioned here is that increase of volume fraction follows the same order of loading cycle i.e. PXY is the first cycle followed by NPXY and NPYX respectively. The question thus can arise that ruminant B19 from the previous loading and deformation could alter the volume fraction during these experiments.

On individual grain scale level, B2 grains are tracked between the different loads using the MIDAS during the indexing process. The B2 grains that have disappeared in subsequent loading steps is attributed to phase transformation and the IPFs of those set of B2 grains are shown in Figure 4.16 (a), (b) and (c).
Figure 4.16 IPF of transformed grains for different loading paths (a) B2 grains transformed during PXY. (b) and (c) show grains transformed during NPXY and NPYX loading path. (d) Common B2 grains that transformed in all loading paths. € Unique grains that transform for particular loading path. For example, the grains marked in red only transform during PXY.

Figure 4.16 (d) shows that common B2 grains that have transformed in any two of the loading steps as lesser grains were being indexed latter (NPXY and NPYX) as discussed above. But to ascertain different grains can transform independently depending in loading paths, transformed grains that are unique to certain loading steps are tracked and shown in Figure 4.16 Error! Reference source not found. (e). For example, the grains marked in red have transformed during PXY paths but do not transform in other loading cases. Although there is a possibility that these grains deformed plastically and may give a false impression that they have uniquely transformed. To avert such cases, the grains presented in Figure 4.16 (e) are tracked back their unloaded state and made sure they have reversed transformed to its initial state - For example the uniquely transformed grains in PXY (red grains) are tracked back and checked if they were present in initial loading condition NPXY that is the following loading. Form the HEDM results on transforming grains, it is difficult to make any generalization on role of orientation on transformation, but the results provide us with robust evidence that certain B2 grains do transform unique depending upon the loading paths.

Difference plots for B19’ for final loading stage, similar to B2, are shown in Figure 4.17 to compare the CVs forming during different loading paths. The initial observation made from
final loading stages of B19’ Figure 4.6 to Figure 4.8 is that similar sets of CVs are present for three loading with minor differences. The possible explanation could be certain CVs in polycrystalline NiTi are more favorable in accommodation of external displacements and thus these CVs would be dominant in all cases. But the goal of discussion herein is to identify the relative quantify of each CVs forming that would reflect on trend of volume fraction observed that is dependent on the loading paths. For the purpose difference plot between the final loading stage for all loading conditions and plotted in Figure 4.17. Difference plots between final loading stage of PXY and NPXY loading paths (Figure 4.17 (aa)) show hkls around (102)$_m$ and (10-2)$_m$ poles have higher intensity for the latter whereas (120)$_m$ poles have higher intensity for PXY in Bank 2. Comparing Bank 1 for same loading paths, (1-50)$_m$ pole has higher intensity around NPXY loading. Similar observation can be made between from others comparison as shown in Figure 4.17.

One important observation to be mentioned is the comparison between NPXY and NPYX loading paths are made along Bank 2 – in volume fraction IPFs (102)$_m$ and (10-2)$_m$ are the most intense poles, but the difference plots show poles (1-50)$_m$ have higher intensity in NPXY where poles around (120) are higher in NPYX. This indicates that during both loading cases, same CVs are formed but vary in quantify of individual variants forming dependent on loading path. Chen at el [50] reported similar finding applying tensile-torsion loading on tubes and examining intensities of various hkls peaks during in-situ diffraction and concluded that biaxial loading consists of superposition of variants dependent on the loading path applied. This also in-line with earlier observation that different B2 grains transformed depending on the loading path to form different variants in CVs with relative different volume fraction.

### 4.4.2 Contribution of transformation is larger in comparison to strain from reorientation

The change of loading paths can possibly result in multiple mechanisms to accommodate the external loading:

(a) Growth of the existing HPV
(b) Transformation of new B2 grains
(c) Reorientation (detwinning) of the existing CVs

The growth of existing HPV continues if the movement of interface between B2 and B19’ is not restricted from granular constraints form neighboring grains which are poorly oriented to transform. This describes the first scenario and would be observed as increasing intensity along particular hkls that is proportional to increase in loading from the difference plots. During the
second scenario, change in loading direction increase the driving force for transformation but
directionality associated with it is altered. This causes the new B2 grains to align favorably for
transformation – the resolved shear stress in invariant habit planes is higher than the critical stress
to transform that was absent before the change of direction. Transformation of B2 grains can be
correlated to decrease of intensity in difference plots and vanishing of index grains in HEDM
results. Finally, unfavorable CVs during the previous loading case become favorable and thus
transformation continues.

Figure 4. 17 Volume Fraction and difference plot of B19’ at final loading stage. The first and
second columns are observed volume fraction and the third column is the difference plot obtained
by subtracting column 2 from column 1.
Third case explains the reorientation of variants that leads to either growth of single favorable variant within the existing CV as defined by detwinning or the CVs entirely switch one pair to another pair of variants to form a new CV that is referred to as reorientation. This can be correlated to increases of intensity around hkl’s in difference plots of B19’ that were absent in previous loading path.

Similar to previous analysis, difference plots are made by subtracting the volume fraction IPFs before and after the change of loading paths for the NPXY and NPYX in the Figure 4.18 and Figure 4.19 respectively to examine the changes in B2 and B19’ texture. Bank 2 (Figure 4.18 (aa)) showed that \( V_f \) around \{112\}_a poles for B2 is reduced during the initial loading was made to \( X_{load} = 0.55 \) mm and holding \( Y_{load} = 0 \) mm for NPXY loading path. As the loading path is switched at this stage by holding \( X_{load} = 0.55 \) mm and loading \( Y_{load} = 0.55 \) mm, volume fraction of grains the \{111\}_a poles decreased (Figure 4.18 (cc)). Similarly the results form Bank 2 for NPYX loading path, volume fraction around the \{111\}_a poles reduces when initial loading to \( X_{load}=0 \) mm and \( Y_{load}= 0.55 \) mm is made (Figure 4.19 (aa)). The transformation spreads towards the \{110\} poles as the loading path is reversed to \( X_{load}=0.55 \) mm and \( Y_{load} = 0.55 \) mm (Figure 4.19 (cc)). These results suggest that new B2 grains start to transform as the loading direction is changed along with continuation of transformation. While loading on \( X_{load} \), the grains oriented around \{112\}_a are readily transformed while loading \{111\}_a are more favorable in the \( Y_{load} \) loading direction. Comparing with PXY loading path (Figure 4.8), the poles \{112\}_a that initially transformed continuously decreases up to the final loading stage and no significant new poles decrease in volume fraction IPFs which further strengthen the argument of new B2 grains been transformed.

Similar difference plot for B19’ are made below the of B2 phase for the similar loading state expect for the initial state where B19’ is absent. When the loading direction is changed during NPXY, Bank 2 shows that variants around poles \( (150)_m \) and \( (112)_m \) start to form instead of variants with pole \( (120)_m \) that was dominant before the change of direction (Figure 4.18 (ee)-(ff)). Similarly, for NPYX loading difference plots show Bank 2 has more intensities for similar poles but Bank1 has poles in \( (150)_m \) when the loading axis is reversed (Figure 4.19 (ee)-(ff)). No evidence of reorientation or detwinning is observed as they would appear as negative values in the difference plot in Figure 4.18 (ee)-(ff) and Figure 4.19 (ee)-(ff) as studied in Chapter 3. Although strong reorientation might not be present but there is a possibility that the same reorientation of CVs might be occurring alongside transformation that is difficult detect at the level. Thus, it may
be ideal to say that strain from reorientation is similar and the observed path depended is not a result of it.

![Figure 4. 18 IPF for volume fraction and difference from reference before and after the change of loading paths for NPXY.](image)

To collaborate the observation made in $V_f$ evolution of B2 during neutron diffraction with HEDM results, the transformed grains are grouped into two sets - B2 grains that transformed before (shown in red) and after (shown in blue) the change of direction as shown in Figure 4.20. As in the previous case, it is difficult to relate certain orientation of B2 grains to be transformation favorable before and after change in loading path, but evidence of B2 grains transforming after the change in loading path indicate that transformation kinetics dominates even after the change in direction.
Overall, it can be explained that the competitions between the various active mechanisms are dependent on their complementary driving force and the one with lowest would be activated initially. The driving force for transformation is reduction in the free energy that is the sum chemical energy necessary to stabilize both B2 and B19’ phases and the external mechanical loading expressed in terms of free energy. The resistance to the transformation interface between austenite and martensite from the frictional force provided by the B2 matrix and the dissipation due to any relaxation in the interface energy during habit plane movement. For the reorientation (detwinning), the driving force is the excess of elastic energy due to formation of CVs that are required to accommodate the strains during transformation but do not maximize strains along the loading axis. External loading encourages the growth of favorable B19’ variants with respect to the loading axis but also increase in elastic energy due to accommodation required to interface compatibility [51, 52]. As the elastic energy increase, the interfaces present in B19’ reorganize to maximize strain and thus variants switching is possible. Form the neutron diffraction results, it can
be seen that B2 grains continue to transform as seen in B2 difference plots in Figure 4.6 to 4.8 and further confirmed from HEDM experiments indicating transformation are present. Role of reorientation is minimum that is contradictory to previously reported experiments with reorientation (detwinning) and their contribution to total strain [14, 37, 50, 51] in uniaxial test but those experiments reported were done at significantly higher strain level. Stebner at el [14] observed first signs of reorientation after 3.50 % uniaxial strains in tension that is above our loading conditions and increased rapidly after 6.50% strains. This is also motivation for future work as a critical $V_f$ of B19′ may be required based to the amount of favorably orientation B2 grains before the reorientation mechanism is activated.

Figure 4.20 IPF calculated form individual orientation of B2 indexed grains before and after the change in loading direction.

4.4.3 Neighboring grains influences the transformation

During transformation in polycrystalline material, constraints are presented by the neighboring grains and alter the favorability of the grain to transform and is not solely dependent on the orientation of the grains. The favorability of grains depends upon the capacity of neighboring grains to accommodate the strains produced by transforming grains. To examine this on individual grain level, indexed B2 grains (untransformed grains) are tracked along different
loading and the IPFs of the grains are presented. Figure 4.21 (a), (b) and (c) shows the IPFs at loading level shown alongside it for PXY loading path and the colorbar represent equivalent strain level for individual grains. Similar figures are made for Figure 4.21 (d)-(f) and (g)–(i) for NPXY and NPYX respectively.

![Figure 4.21 IPF for the initial loading condition with 273, 213 and 174 B2 grains for PXY, NPXY and NPYX respectively.](image)

Elastic deformation is not homogeneous throughout the specimen and individual grains experience different level of stresses. Uniaxial experiments have shown B2 grains transform around 1.5% strain level in polycrystal [18, 52, 53], but certain grains experience higher strains during higher loading stages. Grains 1 to 5 labelled in Figure 4.21 have strain levels around 4% in the intermediate loading and transform to B19’ in the higher loading stage as hkl reflections from the grains are absent and can’t be indexed in higher loads. Higher strain observed in these grains is not orientation-based property based on Schmid factor as grains with similar orientation around it are capable of transforming. Thus, the grains must be constrained from its neighboring grains that are not favorable to transform. When these grains are loaded further, transformation
can proceed (as in grains 1 - 5) with high elastic strains from either change of direction that altered the stress state in the grain or at higher stress level unfavorable CVs starts to form that are accommodated by the neighboring grains. But one must keep in mind, all grains do not necessarily transform with the change in loading path and the constraints from the neighborhood is significant as seen in tracked grain 7 and 8 in Figure 4.21. Grain 7 was unable to transform during the initial loading path and with the change in direction the elastic strain increases to almost 4% equivalent strain.

4.5 Conclusion

In the current paper, we performed neutron diffraction and HEDM experiments to quantify the volume fraction evolution through different loading paths and present the qualitative analysis on the influence of altering loading paths on transformation. This quantitative analysis of the volume fraction evolution with three loading paths (PXY, NPXY and NPYX) would aid in optimization of internal state variables during calibration of material models. Furthermore, the illustration that transformation precedes reorientation (detwinning) during change of loading paths provides important experimental evidence of path dependence nature of volume fraction that have to be consider during numerical modeling in future.
The current work demonstrates the influence of loading paths on reorientation of martensitic B19’ variants and phase transformation and reorientation between B2 and B19’ during mechanical loading of NiTi alloy. High energy diffraction experiments proved to be very vital experimental technique to understand and validate dominant mechanism occurring during various loading paths.

In chapter 2, texture evolutions during uniaxial loading for as-received sample and sample with “preferred variants” microstructure was compared. As received sample had self-accommodated microstructure and the deformation mechanism during uniaxial test up to 3% and 5% were showed detwinning in (0 1 0) compounds twins and (1 1 2) Type II and the mechanism were fully reversible during ferroelastic loading. Sample with preferred variants microstructure showed strain hardening during tensile loading and the behavior were correlated with (-2 1 0) deformation twins during the first loading cycle and reversible detwinning of (1 0 0) compound twin system was observed during unloading of the sample. The second cycle didn’t provide any evidence of deformation twins initially but reversible (1 0 0) compound twins and [ 1 1 2] Type II twins are formed. Strain hardening was observed for “preferred variants” sample and was correlated with the presence of deformation twins that have been observed at stage III deformation mechanism and was absent in “self-accommodated variants” sample. To further verify, the strain hardening observed was due to deformation twins, the IPF and stress-strain response was compared with results from “reference sample” with self-accommodated variants. The loading modulus and hardening slope for self-accommodated samples were identical to initial loading curves of reference sample. In contrasts, the preferred variants samples showed similar behavior to reference sample after shifting from 4.5 % strain that is the domain defined by deformation twins. This indicates that reorientation mechanics is totally influenced by the history of loading and the deformation mechanism during mechanical loading is dictated by the initial microstructure. The “self-accommodated” microstructure are less affected by internal stresses due to low defeats and the CVs present are not subjected to any additional constraints during detwinning besides the external loading. But the formation of “preferred variants” in NiTi is due to the internally bias stress and thus certain CVs are favored to minimized relax the internal stresses.
Chapter 3 presents results from in-situ diffraction experiments during in-plane biaxial loading of superelastic NiTi. Three experiments with one proportional (PXY) and two non-proportional (NPXY and NPYX) loading paths loaded to the same final displacement values (x=0.55 mm; y=0.55 mm) showed different volume fraction for B2 was 0.788, 0.687 and 0.601 respectively. This indicated that volume fraction is path dependent parameter and transformation kinetics are influenced by it. HEDM results supported that argument showing that different sets of B2 grains transformed during different loading paths along with the constraints presented from the neighboring grains. Change of loading direction during the non-proportional loading also altered the favorability of B2 grains to transform – some B2 grains, that hadn’t transformed and had high elastic strains during certain loading direction, were able to transform after the direction was changed. The reorientation kinetics was not observed in significant quantity in difference plots of B19’ but continuation of transformation was observed through the loading state. Evidence of “preferred variants” formation based on loading direction were observed. Difference plots between the final loading stage for different loading path showed that CVs with (-150)_m poles aligned along ND are more favorable during NPYX loading paths. In contrasts, CVs with (120)_m poles aligned towards ND were formed during NPXY loading. The absent of reorientation mechanics can be understood in correlation with results obtained from reorientation mechanics in Chapter 2. The favorable CVs for certain reorientation (detwinning) mode in preferred variants microstructure formed during the non-proportional experiments may not be favorable to accommodate external loading and may require higher stresses to deform by formation of deformation twins. But in contrast, the transformation of B2 after the change of direction increases favorability of transformation in B2 after the change in loading path and thus transformation kinetics continues in absence of reorientation mechanics. This work answer one of the most fundamental question that neglecting transformation kinetics during the change of loading path is physically not valid and should be avoided during numerical calibration of constitutive relations in SMAs. Although reorientation kinetics were not observed during biaxial loading in the current work, it is worthwhile to note that mechanism have been observed during tensile loading [21], [74]. Along with reorientation, the natural extension of the current work would be to study the influence of plasticity with increased load setting. The evidence of plasticity during phase transformation has been discussed by various author in terms of presence of hysteresis during reverse transformation and cyclic stability during functional fatigue [18], [40], [138]–[140]. Dislocations are observed in the
B2 matrix generated form the interfaces between the B2 and B19’ under TEM experiments [39], [41], [141]. During the formation of multivariant martensite structure results accommodation of strains to maintain compatibility and minimization of interface energy must occur. This accommodation of strain leads to high local stresses in the interface and relaxation of stresses can occur through plastic deformation by dislocation motion. The effect of dislocations can be seen in two roles during cyclic loading in SMAs as promoting the martensitic nucleation [39] and trapping of the martensitic interfaces that hinders the growth of the variants [63]. When extending these concepts to the dependency in loading paths, the dislocations in B2 matrix from the previous loading paths can be nucleation sites for activation variants when the loading paths are changes but also can hinder the growth of the variants reducing the volume fraction of B19’. This leads to an open question about the role of these dislocation during the change in loading paths at higher loading displacement and a comparative study can be done based on the analysis. Previously, bulk tension/compression experiments are performed on superelastic NiTi samples under in-situ neutron diffraction conditions [9], [21]. In the research work, the plastic strains are not calculated directly as the convolution of transformation and reorientation mechanism are occurring simultaneously but the effect of plastic of plastic deformation is observed as altering volume fraction evolution at higher stains and hindering the reversible transformation upon unloading creating asymmetry plastic behavior in tension and compression. Thus, we aim to follow similar approach presented in the previous research – study the effect of plastic strain that alters the transformation and reorientation kinetics and not quantify plastic strain. For the purpose, in-situ neutron diffraction experiments were performed with two different HLR biaxial specimen up to 1.5 mm on each loading direction. The mechanical loading was done using the custom-made biaxial frame for two non-proportional loading paths NPXY and NPYX as discussed earlier. Diffraction data were collected using two banks during the loading at displacement values shown in the Table 5.1. The data collected during the experiments can be batch processed using GSAS and SMARTSware software as discussed in chapter 2 and difference plots can to interpret the transformation and reorientation phenomena along with bulk plasticity.
Table 5.1 Experimental details for neutron diffraction loading under large strain

<table>
<thead>
<tr>
<th>Loading Path</th>
<th>Final Loading displacement (mm)</th>
<th>Displacement at diffraction data collected (mm)</th>
<th>Number of Diffraction Reading</th>
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<td>NPXY</td>
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<td>X: 0, 0.1, 0.2, 0.4, 0.55, 0.7, 1, 1.2, 1.5, 1.5, 0.55, 0.55, 0.55, 0.55, 0.55, 0.55, 0.55</td>
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<tr>
<td></td>
<td></td>
<td>Y: 0, 0, 0, 0, 0, 0, 0, 0.1, 0.2, 0.4, 0.55, 0.7, 1, 1.2, 1.5</td>
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</tr>
<tr>
<td>NPYX</td>
<td>X -0.55 Y -0.55</td>
<td>X: 0, 0, 0, 0, 0, 0, 0, 0.1, 0.2, 0.4, 0.55, 0.7, 1, 1.2, 1.5</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>X: 0, 0.1, 0.2, 0.4, 0.55, 0.7, 1, 1.2, 1.5, 1.5, 0.55, 0.55, 0.55, 0.55, 0.55, 0.55, 0.55</td>
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</table>

To our knowledge, this is the first set of experimental data to quantify volume fraction during biaxial loading conditions with proportional and non-proportional loading paths. The importance of these experiments lies in using volume fraction quantity as input parameters in the material models that can solely define transformation kinetics all together. Usually SMAs material models have a large number of ISVs as multiple deformation mechanisms have to be tracked simultaneously. Being able to define transformation kinetics based on experimentally data reduces the number of variables to be calibrated and will be increased to increase the accuracy to great benefit. The work also displays the use of high energy diffraction experiments to identify various mechanism during biaxial loading. The change in texture obtain from difference plots from neutron diffraction experiments helps to characterize and identify dominant mechanism during various loading steps and grain level information produced by HEDM can be useful to study.
micromechanics in SMAs. Although orientation of individual grains was used in current work extensively, these experiments open opportunity to study stress-strain evolution and various statistical analysis into variant selection and transformation kinetics. It is worthwhile to mention some recommendation for the implementation of ff-HEDM experiments in future works. Careful measures must be taken to capture initial B19' formation as most of martensite in most SMAs have lower intensities during diffraction due to lower symmetry and smaller plates formation in comparison to austenite crystal. This can be achieved by blocking the highest intensity peaks in austenite so that smaller attenuation can be used during the diffraction experiments to fully capture the martensitic diffraction spots. Another topic in SMAs alloys research is the criterion for variant selection during transformation. Neutron diffraction provides some differentiation between the variants but the resolution of ff HEDM may not be suitable for the studies. Bucsek at el [142], has discussed that nf-HEDM and dark field diffraction techniques have higher resolution that might be suitable for research in those areas.
APPENDIX A
THERMOMECHANICAL SIMULATIONS FOR WELD DROP

The work was published under title “Microstructure Development of 308L Stainless Steel During Additive Manufacturing” in “Metallurgical and Material Transactions A” [143]. The major objective of the study was to obtained phase fraction, internal stresses and temperature profiles during the solidification of weld 308L SS during in-situ high energy X-ray diffraction experiments. The study emulates building blocks of the wire-arc additive manufacturing (WAAM) where weld drops of feedstock are deposited in precise order to create large metal components. The research was unique as very little research is present in literature for quantification of parameters during the solidification of weld drops that can be correlated to microstructure of the built. The objective to use the finite element analysis was to map the temperature profile during solidification of weld drop at different locations and verify the calculated temperature from lattice parameters obtained from diffraction experiments.

The dimension for the weld drop was obtained from a SEM micrography as shown in the Figure A.1. In built thermomechanical module from ABAQUS was used to perform FEA simulations on quarter of drop. Initial temperature of weld drop was maintained at 1600°C and was allowed to cool for 5 sec with heat loss to the base though conduction and form weld surface through convection.

Figure A. 1 (a) SEM scan for weld drop of 301LN SS. (b) Weld drop setup for FEA
The temperature profile was obtained simulations showed temperature gradient during cooling after 0.1 as shown in the Figure A.2 as heat loss from conduction was higher that the natural convection across the weld surface. The temperature gradient explained the radial growth of grains observed under SEM.

Figure A. 2 Temperature profile from FEA for solidification of the weld spot.
APPENDIX B
FINITE ELEMENT ANALYSIS FOR HIGH DEFORMATION DURING COINING

The work was published under the title “Microcoining ripples in metal foils” in International Journal of Mechanical Sciences [144]. The major objective of the paper was to correlate mechanical loads required to imprints ripples in thin metal foils and to understand influence of friction and boundary conditions on the elastic plastic behavior of the material. Experiments were performed for three different material – 304 Stainless Steel (SS), Titanium (Ti) and Tantalum (Ta). To understand the behavior, finite element simulations were done using ABAQUS for various conditions as shown in the Table B. 1 below:

Table B. 1 Parameters for Finite Element Simulation

<table>
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<th>Material</th>
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<th>Pressure</th>
<th>Die Setup</th>
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<td>(micron)</td>
<td>(MPa)</td>
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<td>1000</td>
<td>800; 500</td>
<td>Open</td>
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<td>1200; 800</td>
<td>Open</td>
</tr>
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<td>1050; 500</td>
<td>Open</td>
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<td></td>
<td>Close</td>
</tr>
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<td>1000</td>
<td>300; 500; 700</td>
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The peak valley values indicate the profile of circular die i.e 7 and 10 microns are the value between distance between the peak and valley of a sinusoidal profile. Sample with thickness 50 microns and 1000 microns (1mm) were selected for simulation to match the experimental samples. Quarter model of die and sample as shown in Figure (a) was simulated using ABAQUS explicit as for larger plastic deformation and strains were difficult to control with the implicit
method. The closed and open die conditions are the boundary conditions placed on the sample where material was allowed to displace through A and D surface (refer to Figure B.2) for open die conditions and was restricted for closed die conditions. Load controlled simulations were performed with pressure being applied to the top surface in the die with the values mentioned as pressure in Table B.1. Model validation included mesh studies and balancing the total energy to reduce any dynamic effect in the model by controlling the time step for the model. The parameters normalized pressure with material yield stress \( p/Y \) and \( r \) (measure of pattern transfer) were used to compare with the experimental observations.

Figure B. 1 (a) Initial die and sample setup for finite element analysis. (b) Comparison between \( p/Y \) and \( \alpha \) for close die and open die obtained from experiments with finite element simulation. (c) Von mises stress obtained for closed and open die boundary condition. (d) Vertical displacement profile for open and close die condition.

The results from the simulations showed that the pressure required to the imprint a perfect pattern \( (\alpha = 1) \) in samples with thickness 50 microns required higher stresses compared to the thicker samples of 1 mm. The results were overlaid with experimental observation for open (solid line in Figure B.1 (b)) and closed die conditions (broken line in Figure (b)) and 50 microns samples behaved as open die conditions whereas the thicker samples of 1 mm behaved as closed die
conditions. The ability to imprints pattern under closed and open die conditions is controlled by the ability of the material to flow by plastic deformation. Under open die conditions or thin samples, the sample can easily deform laterally instead of filling the spaces in the die to form perfect patterns. The simulations results shown in Figure B.1 (d) shows $U_2$ displacements (vertical displacements) under similar loading conditions are lower for the open die samples indicating the lateral displacement are higher. In contrast, the material flow in closed die is higher along the vertical directions that will allow higher transfer of pattern. Thus, the simulations results support that closed die conditions have more ability to transfer the die pattern compared to open die conditions.
The phase transformation in austenitic steel provides high strength and increased ductility during deformation as is commonly referred to as transformation induced plasticity (TRIP) phenomena. The strength is attributed to role of martensite ($\alpha'$) phase as a reinforcement phase present after transformation from austenite phase ($\gamma$) as similar to composite materials [145]–[148]. As the $\alpha'$ are nucleated due to plastic deformation, and large plasticity in $\gamma$ phase is observed to accommodate the volume change and these nucleated martensite act as barrier of dislocations motion in leads to higher strain hardening in the material. On further loading, volume of $\alpha'$ increases along with plastic deformation in the phase further providing larger work hardening at large strain and provide ductility to the material. This has been observed in in situ neutron diffraction experiments by studying the evolution volume fraction and lattice strain in individual phases. The hardening value has been correlated to the measured volume fraction of $\gamma$ at different temperature and increased in hardening value has been observed for certain temperature range that are favorable for $\gamma$ transformation [149].

During transformation, $\alpha'$ (BCC phase) are nucleated along intersection of the shear bands formed of intermediate HCP phase and stacking faults or mechanical twins in $\gamma$ (FCC phase). All the forms of deformation can be macroscopically corelated to nonlinear (or plastic) strain of $\gamma$ phase and have been used as basis for modeling volume fraction evolution [148], [150]–[152]. Experimentally, the measure of shear bands has been analyzed by measuring the dislocation density in $\gamma$ phase to explain the role of transformation in observed work hardening and ductility [148], [153]. This implies that characterization of plastic strain becomes important to quantify and understand phase transformation locally in strain induced transformation. Among various parameters, texture of $\gamma$ phase is one of the parameters that influences the plastic deformation. Evolution of initial gross and cube texture in $\gamma$ phase been shown to be transformed into different texture for the $\alpha'$ phase as the transformation from FCC to BCC is crystallographic process and texture influences the variant selection process [154]. Form all of these references,
common conclusion can be derived that variant selection is primarily dependent initial texture of the austenite.

Similar, texture-based transformation results were observed for 301LN stainless steel in tension and compression that is focus of ongoing study. In-situ neutron diffraction experiments were performed at LANL under tension and compression loading for specimens cut at different orientation as respect to the rolling direction. The volume fraction $\gamma$ phase was less volume fraction in tension than in compression for all the samples as shown in Figure C.1 indicating higher transformation activity was present.

![Figure C.1 Volume fraction evolution of austenite phase obtained from neutron diffraction conditions. The plot includes results from three samples with different orientation loaded in tension and compression](image)

The results from bulk behavior clearly shows the dependence on initial texture and loading nature but to provide concrete reasons local stresses and constraints to individual grains must be taken in account. It has been previously shown that generation of multiple slip bands in comparison to planar favored more martensitic transformation during tensile testing [155]–[157]. Higher generation of slip bands increases the number of potential sites for nucleation and favorable variants to give higher volume fraction martensite. Most of the experiments discussed here relating to influence of plastic deformation on transformation kinetics in TRIP steels are based on macroscopic responses to mechanical loading varying temperature or microscopic TEM and SEM
studies to dislocation interactions. There is a huge gap in presenting mesoscale data that can validate bulk behavior from the prospect micromechanics modelling and high energy diffraction techniques could be useful. For this purpose, HEDM experiments were selected to study transformation in 301LN SS alongside transformation that can provide us with 3D information relating to individual grain. Two major objectives were placed in mind while doing HEDM experiments with the material:

(a) Present statistically relevant analysis on deformation of 301LN SS to examine the difference of rolling direction (RD) and transverse direction (TD) as observed in from neutron diffraction analysis.

(b) Advance HEDM techniques to study plastic deformation in individual grains through spot analysis.

Using high energy x-ray techniques to analyze activated slip system and correlating to plastic strain in individual grains has been an active area of research. Two sets of experiments were performed at Cornell High Energy Synchrotron Source (CHESS) with a single GE detector and a pair of Dexela detector. Monochromatic x-ray beam with energy around 61 keV was used for both the experiments.

For the first experiment with single GE detector, a tensile specimen was loaded up to 11 % strain along the transverse direction. Diffraction images were collected at 0.1 degree rotation interval for 5 layers with 100microns layer thickness. Individual grains were tracked up to 5 % (load number 6) strain with MIDAS as the indexing become difficult with high background noise during the experiments. 871 grains were tracked with confidence level 0.7 at zero load or no-load conditions.
Second set of experiments were performed using two Dexela detectors at a 100 cm distance apart. Three tensile samples were prepared with one sample having RD along the loading axis and two having TD along the loading axis. nf-HEDM experiments were performed for all three samples for 5 layers at 0.1 degrees interval with a beam size of 1mm X 2.5mm. ff-HEDM experiments were performed on two samples with one of each having RD and TD direction along the loading axis. Diffraction pattern were collected from single layer at 0.1 degrees interval with beam size of 1mm X 4.5 mm. Each sample were loaded close to 10% strain with 20 intervals in between to collect the data. At each interval diffraction data and DIC images were collected for strain measurement purpose.

Although the experiment technique has shown potential in characterizing slip system in single crystal, the application for a polycrystals need further research. The foundation for combining diffraction results and grain-level plasticity is based understanding the crystal rotation (based on continuum equations) that compensates for distortion due to slip in individual grains (a micromechanical parameter that characterized the slip). Total distortion tensor ($\beta_{tot}$) in any crystal during deformation can be decomposed into elastic ($\beta_e$) and plastic ($\beta_p$) part and each component can be further decomposed into extension (symmetric part) and its rotation (anti-symmetry): $\beta = \beta_e + \beta_p$
\[ \mathbf{e} + \mathbf{\omega} = \mathbf{e}^e + \mathbf{\omega}^p + \mathbf{e}^p + \mathbf{\omega}^p \]

It is necessary here to mention that the two rotations (\(\mathbf{\omega}_e\) and \(\mathbf{\omega}_p\)) physically is combinations of two phenomena – the rigid body rotation and the crystal lattice rotation. As our description with the HEDM setup the rigid body rotation can be described as the rotation of the sample coordinates after the application of loads with respect to the initial coordinates at the sample position and is negligible for most for mechanical loads we perform. The lattice rotation describes the rotation of crystal orientation with respect to the sample coordinate system. Thus, in most cases the decomposed equations are represented with a single rotation term as

\[ \mathbf{e} + \mathbf{\omega} = \mathbf{e}^e + \mathbf{e}^p + \mathbf{\omega} \]

The compatibility equations for deformation for connectivity of material domain leads to

\[ \nabla \times \mathbf{\beta} = 0 \]
\[ \nabla \times \mathbf{\beta}^e = - \nabla \times \mathbf{\beta}^p = - \mathbf{\alpha}^d \]

The term \(\mathbf{\alpha}^d\) is the referred to dislocation tensor and physically can be understood as geometrical consequence due to plastic deformation and represent quantity relating to the dislocations content in the deforming volume. Each dislocation has contribution to the total plastic strain but only dislocations with certain characteristics (defined by plane and Burgers vector) can exists in crystal.

\[ \alpha_{ij}^d = \sum_{n=1}^{ss} \rho_{ij}^d b n \]

Nye al el. [158] was first to describe the geometrically consequences from all dislocation activity in a deformed crystal to the curvature \((K)\)formed in the crystal as

\[ \alpha_{ij}^d = K_{ji} - \delta_{ij}K_{kk} \]

The curvature tensor \(K\) is the rotation of the material that gives the geometrical shape change provided by the dislocation tensor in a given volume of material. It is necessary to mentioned here that \(K\) calculated in above equation is formed by the dislocation array that responsible for the change of shape of the crystal structure to maintain crystal compatibility during deformation and are called geometrically necessary dislocation (GNDs). Another set of dislocations are present that annihilate each other over the given volume of material and do not contribute to the formation of curvature called statistically-stored dislocations (SSDs) [159], [160]. Thus, been able to quantify \(K\) characterizes \(\alpha^d\) the dislocation tensor that reflects the plastic deformation in individual grains.
The curvature $K$ formed is the change in orientation of material point with respect to its reference orientation i.e. the unloaded state. Mathematically, it can be represented as the rotation along axis aligned towards the crystal axis as:

$$dx_j K_{ij} = d\omega_j$$

$\omega$ is the rotation of imparted by individual slip system activated that is characterized by the plane normal ($n$), dislocation line ($t$) and direction of slip given by Burgers vector ($b$). Based on the nature of dislocation, they are classified into edge and screw dislocation based on direction of Burgers vector and dislocation line- $t$ is normal to the $b$ in edge dislocation whereas they are parallel in case of screw dislocation.

![Figure C. 1 Schematics of cubic lattice deformation during slip due to dislocation (a) edge dislocation (b) screw dislocation.](image)

When slip systems with edge dislocations is activated, the plane normal to the slip system is displaced and can be represented by a rotation $R^p$ around dislocation line $t$. In contrast, the activation of screw can be modeled as a rotation $R^p$ around the direction plane normal $n$ itself. Recently efforts have been made to quantify the $R^p$ from HEDM experiments to characterize the slip system activate to observe the form individual reflections for individual poles [161]. Forward modelling with an additional rotation matrix $R^p$ to allow distortion due to plastic strains in the spots can be utilized. Basic outline for the algorithm along with the caveats is presented below:
a) Individual grains are indexed are initial (zero load) state and the initial orientation ($R^c_h$) and elastic strain tensor is received. During the indexing process, all hkls reflection for individual grains can be obtained. For example, if first 3 hkls in FCC crystals, the total number of possible reflections is equal to 26 but this number depends upon the collection of data

b) Each hkl reflection (hkl) for each grain can be discretized in detector position ($P_{xd}$, $P_{yd}$) and stage rotation omega ($\omega$). Each pixel can be converted into diffraction vector $G_{obs}$ as

$$G_{obs} = \frac{2\pi}{\lambda} \begin{bmatrix} \cos 2\theta - 1 \\ \sin(2\theta) \sin(\eta) \\ \sin(2\theta) \cos(\eta) \end{bmatrix}$$

c) Each detector pixel can be forward modeled and calibrated to matched with the ($P_{xd}$, $P_{yd}$) but the orientation $R^c_h$ for all the detector pixel must be kept the same.

$$G_1 = R^t_s R^c_e B^* G_{hkl}$$

The reason to keep $R^c_e$ same is that zero stress condition is considered to be the reference stage for the deformation. Thus, any prior deformation from processing cannot be calibrated using the following method.

d) The next step is to collect the information of the spots in the deformed stage (higher loading stages) from identical position in the detector and omega and discretized them.

e) Forward modelling of discretized hkls in the deformed stage is done with an additional rotational matrix $R^p$ to spread the spots in the based on the slip system. The distortion in by edge dislocation and screw dislocation are represented by individual $R^p$ given by:

$$R^p_{edge} = \phi \begin{bmatrix} 1 & -t_3 & t_2 \\ t_3 & 1 & -t_1 \\ -t_2 & t_1 & 1 \end{bmatrix} \quad R^p_{screw} = \phi \begin{bmatrix} 1 & -n_3 & n_2 \\ n_3 & 1 & -n_1 \\ -n_2 & n_1 & 1 \end{bmatrix}$$

The values of $t$ and $n$ are defined by the slip system for the crystal system. For example, there are 12 and 6 slip systems defining edge and screw dislocations in FCC crystals. ‘$\phi$’ is the magnitude to the of the slip that is proportional to plastic strain caused by activation of slip system.
\[ G'_1 = R_x^1 R_z^2 R_p B^* G_{hkl} \]

Following the work of Pagan [161], [162], the minimization can be done by overlapping the angles between the forward model vector \( G'_1 \) and \( G_{obs} \).

f) The rotation matrix \( R_p \) can be converted into three Euler angles that defined \( \omega \) around each crystal coordinate system. The omega can be converted into the curvature tensor \( K \) by integrating the equation.

But the integration requires the dimensionality of the grains which is the major task for the future. One way to obtain the dimension is running nearfield experiments (NF) that has been performed for the initial condition or use DCT methods to get the morphologies of the grains during transformation. Following the characterization of the grain volume, the characterization of the slip system can be obtained in terms of \( \alpha_{ij}^d \).
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