IN-SITU DIFFRACTION STUDIES OF RATE DEPENDENCE OF TWINNING, PHASE TRANSFORMATION, AND SLIP IN SHAPE MEMORY ALLOYS

by
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ABSTRACT

Many advanced materials show strong rate-dependence in their responses, even at time scales considered to be quasi-static. This is especially true for shape memory alloys. While theory is well established for rate dependence in cubic metals due to slip, few attempts have been made to develop similar theories for twinning and phase transformation, and their coupling with slip in low symmetry structures. This absence is largely because little is known about rate dependence in lower symmetry alloys. Toward filling this gap, classical phenomenological formulations of strain-rate sensitivity developed for slip of cubic alloys were applied to new shape memory alloy data to understand if analogous mathematical models could be extended to the more complex inelastic deformations. It was found that the models do not describe relaxation phenomena of shape memory alloys. Thus high-energy X-ray diffraction was employed to elucidate microstructural roles of twinning, phase transformation, and slip during cross-head arrest stress relaxation tests. This thesis documents these empirical results toward first understanding low symmetry twinning in isolation, then competition between twinning and phase transformation, and then the coupling of plasticity with twinning and phase transformation exhibited by monoclinic and phase transforming (cubic to monoclinic)
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Chapter 1

Introduction

The classical approach to quantify strain rate sensitivity in alloys is to apply Cottrel-Stokes law. Cottrel-Stokes law was formulated for slip of face centered cubic (FCC) crystal structures. We proceed to review this established theory in Section 1.1 as a starting point for introducing rate sensitivity of alloys. We note, however, that it is not expected to physically apply to nickel-titanium (NiTi) SMAs (shape memory alloys), as they transform between phases of cubic symmetry and phases of lower symmetry, as reviewed in Section 1.2. Thus, inelastic deformation may be dominated by phase transformation and twinning in addition to slip. After reviewing this classical theory and SMAs, there will be a discussion of the inelastic mechanisms (phase transformation and detwinning) that are proposed to contribute to the dynamic rate sensitivities of NiTi SMAs [1] (Section 1.3), followed by a discussion on thermomechanical considerations in characterizing NiTi (Section 1.4). The Introduction concludes with a brief primer on how x-ray diffraction can be used quantify elastic and inelastic deformation mechanisms of a metal in Section 1.5.

1.1 Strain Rate Sensitivity

Stress relaxation tests have been used for decades to quantify strain-rate dependence of FCC crystal structures (stress relaxation tests are the same as load relaxation tests and cross-head arrest tests) [2]. A stress relaxation test is
performed by deforming a material at a constant strain-rate, then fixing the cross heads or grips of the machine at a constant displacement or strain and measuring stress response as a function of time. In metals, the stress will usually decrease in magnitude (assuming the loading resulting in increasing the magnitude of stress) due to the relaxation of the internal stresses as a result of microstructure rearrangements. Since elastic deformation is time-independent below shock regimes by definition [3], during a quasi-static stress relaxation test, these microstructure rearrangements are due to inelastic deformation mechanisms. In Figure 1.1 is a graph of displacement-and absolute stress vs. time of a NiTi SMA sample provided here to depict a stress relaxation measurement.

Figure 1.1: A portion of the displacement and absolute magnitude of stress (Abs Stress) vs. time of a stress relaxation test performed on a NiTi SMA.
The classical theory for a stress relaxation test is based on the Cottrel-Stokes law [4], which was also heavily examined and used by Hart [2,5]. More recently, Kocks and Mecking more deeply examined plasticity of FCC materials (predominantly aluminium (Al) and copper (Cu)), including the different theoretical ‘stages’ of strain hardening and how rate and temperature effect hardening rates [6,7].

Classically, strain rate sensitivity is quantified using Equation 1.1.

\[ m = \frac{d \ln(\sigma)}{d \ln(\dot{\varepsilon})}, \]

(1.1)

While differentiation of discrete numerical data presents challenges, classical numerical differentiation is an accepted methodology to analyze data from a stress relaxation test to calculate \( m \) [5]. For most FCC polycrystalline materials, the value of \( m \) will be on the order of \( 10^{-2} \) to \( 2 \times 10^{-1} \) at room temperature [8], and will increase with increasing temperatures [9]. It should be noted that \( m \) is calculated as a constant per a given relaxation, strain, and strain rate. Cottrel-Stokes law predicts a strain independent value of \( m \), however, many experimentalist have found that even in polycrystalline FCC materials \( m \) does change with strain-rate [5,8,9,10,11]. A material is considered to be superplastic if it has a strain rate sensitivity value that is \( m > 0.3 \). Contrarily, if a material has a negative \( m \) value, this implies instability in the material and the Portvein-LeChatelier (PLC) phenomenon may be found in the stress-strain curve [12]. PLC is associated with materials that have an inhomogeneous plastic
deformation that creates instability in plastic flow, resulting in a serrated stress-strain curve.

The assumptions made for the calculation of $m$ in Equation 1.1, are based upon the analytic equation for flow stress, which can be decomposed into the product of a structure sensitive term and a rate sensitive term [6]:

$$\sigma = \alpha \mu b \sqrt{\rho},$$

(1.2)

where $\sigma$ is the flow stress, $\mu$ is the shear modulus, $b$ is the magnitude of the Burgers vector, $\rho$ is the dislocation density, and $\alpha$ is a constant that depends on the strength of dislocation interaction, which is in turn dependent upon thermal activation; i.e., temperature. If there are other non-negligible terms to the plastic resistance, they can be additive to the flow stress found in Equation 1.2 (e.g., solution hardening, lattice resistance, or grain size effects). The flow stress found from Equation 1.2 is the basis for Equation 1.1. The results of Equation 1.1 are usually presented on a Haasen plot, which plots $m$ vs. stress. If Equation 1.2 holds for the FCC material, then the strain rate sensitivity should be linear with stress, with a $y$-intercept that goes through the origin. If there are other additive terms to the flow stress, then linearity should be maintained, but the intercept should be non-zero. Positive linearity makes sense for the classical case, since it has been proposed that the transient is based on dynamic recovery; at higher strains, more dislocations have been created, which means the potential for larger stress recovery by means of dislocation elimination. It is important to keep
in mind, that even with pure FCC polycrystals, deviations from Cottrel-Stokes law can be readily seen once the material has reached 'stage III hardening [6].

1.2 Phase Transformation in Shape Memory Alloys

The ability to of a SMA to remember a previous shape is due to the reversible, solid-state phase transformation between the austenite and martensite phases of the material [13]. This martensitic transformation is fully reversible. Martensite is a first order, diffusionless transformation. It's considered diffusionless, since the transformation isn't happening on an atom-to-atom basis, much like an ice cube melting. Instead, entire rows of atoms are simultaneously in motion during a transformation. Like all transformations, phase change can occur by either applying a stress or changing the temperature, or any combination of the two. The high temperature/lower stress parent phase is called austenite, and is simple cubic in the case of the examined NiTi samples in this experiment. While the lower temperature/higher stress daughter phase is called martensite. Martensite is monoclinic for the NiTi samples examined herein.

In Figure 1.2 [13] is a cartoon illustrating the changes in the crystal structure and microstructure that occur during a transformation.
Figure 1.2: A simple two-dimensional cartoon to illustrate the symmetry and microstructural changes undergone in the NiTi martensite transformation [13]. The austenite (Figure 1.2a) phase may forward reverse into different variants of martensite (Figure 1.2(b & c)). Due to the symmetry changes that are brought on by forward transformation, the material is able to accommodate large amounts of reversible strain as the material is stressed. In Figure 1.2 there are two variants of the martensite structure that are not frame indifferent; meaning, one variant cannot be rotated in the plane of the page to be of the same orientation of the other. When frame indifference is extended to the three-dimensional case for NiTi SMAs there are 12 different monoclinic variants of the cubic phase [13]. Upon forward loading, the variant chosen for the monoclinic structure is determined as the variant that can best accommodate the induced strain and, consequently, lower the free energy of the material the most. The bottom portion of Figure 1.2(d – f) will be discussed in Section 1.3.
Since a basic description of the principles of a SMA have been presented, it can be understood why they have become an integral part of medical, aerospace, and acquisition systems over the last few decades, a continuation of its knowledge base is pertinent for designing better alloys. It has been shown that pseudoelastic NiTi alloys exhibit a rather dynamic stress-strain response with varying quasi-static strain-rates [1]; this makes shape memory alloys a model material system to study to further understand how inelastic mechanisms influence strain rate dependence. In Figure 1.3 [1], a developing change in strain-rate by only 1.5 orders of magnitude within the quasi-static regime, changes transformation onset, transformation plateau shape, and hardening rates.

![Stress-strain curve](image)

**Figure 1.3:** Stress strain curve of equiatomic NiTi demonstrating the associated strain rate sensitivity for the material [1].
One objective of this experiment, is to de-convolute the reversible phase transformation from the martensitic de-twinning from the plasticity in the classical regimes that each of the aforementioned inelastic responses tend to dominate. In this way, it can potentially be phenomenologically determined how much each inelastic deformation contributes to strain rate sensitivity. In Figure 1.4 is a stress strain curve that depicts the classical regimes and micromechanic processes that are taking place in a pseudoelastic alloy [14].

![Stress-strain curve](image)

**Figure 1.4:** The classical regimes of a pseudoelastic SMA along a stress-strain curve [14].

It’s convenient and applicable to discretize the stress strain curve like in Figure 1.4, but Stebner et al. [15] has shown through diffraction that there is a great amount crossover between the different regimes. In fact, it was found that
forward transformation begins much lower than the transformation plateau while the material still appears to be in the elastic region macroscopically. On a similar note, full transformation is not seen at the end of the transformation plateau in a NiTi polycrystal. This is because not all grains are oriented in a direction that favors transformation in respect to the loading direction.

Since many processes in SMAs are so dynamic, it makes this material system an interesting choice to explore strain rate dependence on different inelastic deformation mechanisms outside of slip. Because of this, pseudoelastic NiTi has a very dynamic thermomechanical coupling.

1.3 Martensite Reorientation

The stress-strain curve for a NiTi sample, that is martensite at room temperature, is not all that dissimilar to the stress strain curve of pseudoelastic NiTi. However, in the case of the former, the stress plateau is due to the reorientation of the martensite. In Figure 1.5 is a graph of engineering stress vs. engineering strain with micrographs showing the reorientation of the self-accommodated martensite, which will then start to show dislocations at higher strains [16].
When NiTi goes through a temperature driven transformation into the martensite phase, the density stays constant – meaning, the total volume has not changed. Because of this, the martensite will meet the constraints of the austenite geometry by forming fine twin bands within the parent grain. The fine twin bands that are formed are related to each other through a twinning relation. Once the material begins to strain, these fine twin bands may start to “de-twin” as an inelastic deformation mechanism that allows the material to minimize the free energy by reducing the elastic strain in the material. Reorientation describes a variant of martensite rearranging its atomic structure to become a new variant;
this includes, but is not limited to detwinning. The added strain to the material by
reorientation and detwinning is recoverable by heating the sample past the
austenite finish temperature. The amount of reversible strain is dependent upon
the lattice parameters of the austenite and martensite phases as well as the
twinning modes active in the deformation. Along the same line, texture has a
major role in reversible strain. In polycrystals texture determines magnitude since
certain orientations with respect to loading direction have favorable twin modes to
maximize strain, while others are less favorable [16].

Self-accommodated martensite can be seen to have a “zig-zag” or tent like
structure. The material will twin in such a manner to have a more coherent grain
boundary with its neighbors, which in turn can lower the free energy of the
system. Figure 1.6 illustrates what is happening as martensite detwins [17], while
Figure 1.7 is showing the detwinning of variant A into variant B in a NiTi sheet,
after applying a 6% tensile strain [17].

![Figure 1.6: A two-dimensional cartoon representation of a twinned and detwinned microstructure [17].](image-url)
Figure 1.7: Detwinning of variant A into variant B to accommodate a 6\% tensile strain [17].

The number of twinning modes depends loosely on the number of martensite variants that can be made; more specifically, the greater the disparity of symmetry between the austenite and martensite phases, the greater the number of variants that can be formed. Monoclinic NiTi has 12 variants that can be produced. What primarily dictates the length of the twinning plateau are the lattice parameters as well as the texture of the polycrystal. There are three types of twins that can be formed: Type I, Type II, and compound twins [16]. Going into the details of the different forms of twins is out of the scope of this paper, since we are only after the phenomenological macroscopic effects of twinning in a SMA.
One point of consideration is that Liu et al. [18] have shown that reorientation may not be the favorable deformation mechanism for martensitic equiatomic NiTi in compression. However, for the same samples in tension, reorientation is still very prominent. It was shown that for equiatomic binary NiTi strained in tension to 4% that reorientation had actively been occurring, while the generation of dislocations was minimal. However, for the same material strained in compression to 4%, the martensite microstructure was unchanged from the undeformed sample, but a high density of lattice defects was produced. It has also been shown that some twins in equiatomic binary NiTi can only be produced via deformation [18, 19]. This is due to the reorientation that martensitic materials can use to help accommodate strains in the material. It’s also worth noting that in the paper by Liu et al. [18], that minimal strain rate dependence was seen in tension and compression as the strain rates were varied from 0.0003[s\(^{-1}\)] to 0.015[s\(^{-1}\)]. However, direct comparison of the stress-strain curves in Liu et al. [18] may not be wise, since the samples had slightly different chemistry as well as a different post processing procedure, and therefore may have little correlation to the Ni\(_{49.9}\)Ti\(_{51.1}\) compression samples in this experiment.

Two of the samples tested in this experiment are self-accommodated martensite at room temperature, which will be tested in compression. Because of this, it may be seen that slip will be the primary inelastic deformation mechanism for these samples. Looking at the sample processing in Liu et al. shows that the samples were cold drawn wires that were then annealed at 450 and 800°C for 30
minutes followed by a water quenching [18]. Because of this, the compression samples used in [18] experiment may have different texturing then the samples used in this experiment. Texture can play a role in determining how much slip or reorientation can occur since these mechanisms have a crystallographic dependency with the loading direction.

It has been found that some SMAs will have a “rubberlike” behavior when strained to small values (roughly 1%). If the loads are released quickly, all of the strain is recovered and the twins will reappear. Bhattacharya et al. have created models to attempt to capture this effect [20,21], based on experiments conducted by Lieberman et al. [22]. Many mechanisms have been proposed to explain the phenomenon, but none have been proven to be the main mechanism. Without going into the details of all the proposed mechanisms, the general consensus is that the area the moving twin boundary moves over, the free energy temporarily increases. This free energy can be decreased readily by unloading the material. If the load is held on the sample for an extended period of time, then the material will find some other way to minimize this free energy to a new minimum. It’s thought that the mechanism is a thermally activated process. Even though this rubberlike effect may not apply directly to NiTi SMAs, it further validates the thermally and temporally dependent-like behavior that can be found in reversible martensitic materials.
1.4 Thermomechanical Considerations

Like all phase transformations, the martensitic transformation of NiTi either produces energy (forward transformation) or absorbs energy (reverse transformation). The question is, is the latent heat negligible, or does it contribute to the macroscopic response of the material. Shaw et al. performed a series of tests on “nearly” equiatomic NiTi to discover the thermomechanical contributions to the macroscopic responses [23]. It was shown that the internal heating or cooling did alter the stress strain response. Figure 1.8 shows samples that were kept in either air or water while they were stressed. Water acts as a heat sink, and will much more quickly and efficiently absorb or give energy as the material is transforming. It can be seen that the material in air has a higher forward stress plateau, and a lower reverse stress plateau. This is because the material has a chance to locally retain the latent heat that is produced from transforming from austenite to martensite, which in turn, drives up the stress needed to transform since martensite is the lower temperature phase. Since the conventional way to perform mechanical tests on a material is in the air, considerations must be made with shape memory alloys since false conclusions may be made due to the non-isothermal nature that localized heating can induce.
The mechanical tests that Shaw et al. conducted were continuous and at a fixed strain rate; because of this, the material self-heating and cooling may be greater than for a stress relaxation test that is pausing at every ~1% strain to collect data. Two things should be pointed out, that may fall out as a consequence of the above information. While testing a pseudoelastic specimen, transformation will start to occur at higher stresses. Due to the latent heat of transformation, the material will locally heat up as forward transformation continues. The higher temperatures will make it more difficult to forward
transform into the low temperature martensite phase, which means greater stresses will be needed to continue transformation. However, once the cross heads of the machine are fixed intermittently (to collect stress vs. time data during the stress relaxation test), the built up latent heat has a chance to decrease with time allowing the material to approach an equilibrium temperature with the ambient environment – this will accelerate the transformation process. As forward transformation is occurring during the arrest of the cross heads, the macroscopic stress will decrease faster since the transformed martensite phase can better accommodate the stresses and strains placed on the material. This stress relaxation is a macroscopic measurement, whereas the transformation is happening locally, but a decrease in average stress will slow down forward transformation. This interplay between the changing local temperatures and stresses during a relaxation is brought up to illustrate that a SMA has strong thermomechanical coupling, and is part of the reason why NiTi SMAs can have such a strong dependence on strain rate.

In any crystalline material, defects or irregularities may exist in the crystal structure. As a material is stressed into plastic deformation, these dislocations and defects are generated. Dislocations can move in an atomic lattice along slip planes (slip planes are crystal orientations that favor dislocation movement). The direction and magnitude of a dislocation is described by the Berger’s vector. The easier a dislocation can pass through a material, the lower the plastic flow stress; dislocation networks, grain boundaries, and precipitates are all examples of
structures that can inhibit the movement of a dislocation. There are long range and short-range barriers that can increase the needed stress to continue the movement of a dislocation. The magnitude of the stress to overcome these energy barriers is called the Peierls-Nabarro stress [24]. Long-range barriers increase the resistance to dislocation motion on a greater length scale than a short range barrier can. Added thermal energy cannot help overcome long range barriers, but they can help overcome a short range barrier since short range barrier energy field is on a similar length scale as the thermally dependent atomic vibrations (at any energy above 0 K, atoms will vibrate due to thermal energy). As the temperature increases the vibrations of the atoms becomes greater. The added thermal energy reduces the amount of stress needed to pass a short-range barrier – this phenomenon is called thermal activation [25].

Dynamic recovery is the process of two dislocations annihilating against each other [3]. As dislocations move around in the crystal lattice, if two defects have a Berger’s vector that is equal in magnitude but opposite in direction, they can coincide and eliminate each other. As a material has undergone a considerable amount of plastic strain, the number of defects will increase; this will increase the potential for dynamic recovery to occur. At higher temperatures, thermal activation will increase the movement of dislocations, and therefore increase the potential for dynamic recovery.

In basic elastic-plastic FCC materials, thermal activation and dynamic recovery can be considered as contributions to the stress relaxation. In fact,
according to Kocks et al., dynamic recovery is the principal reason for the transient in the stress relaxation [26]. Since both of these processes are thermally driven and temperature dependent, the thermomechanical coupling will play a role in the way that thermal activation and dynamic recovery will contribute to the macroscopic measurements. Once the material starts to heat up due to the latent heat of transformation, it can be expected that during a relaxation dislocation movement may be increased since the larger, short-range energy barriers may be overcome easier with the added thermal energy as predicted by thermal activation. Concurrently, it could be predicted that as the kinetics of the material start to catch up during a relaxation there could be in increased chance of dislocation annihilation due to dynamic recovery.

1.5. High Energy X-ray Diffraction

Diffraction measurements provide a non-destructive means to empirically elucidate active deformation mechanisms at the microstructure scale, including those responsible for relaxation. All testing conducted for this experiment was done at the Advanced Photon Source (APS) of the Argonne National Lab, as further described in Section 2. At APS they centripetally accelerate electrons around a ring to create synchrotron radiation that is then directed at the sample. When the sample is illuminated with these high-energy photons, the photons may diffract through the material according to Bragg’s law:

\[ n\lambda = 2d\sin(\theta), \]
where \( n \) is an integer, \( \lambda \) is the wavelength of the photon (or incident particle), \( d \) is the atomic lattice spacing, and \( \theta \) is the angle associated with the scattering.

“Powder diffraction” refers to diffraction experiments where many (usually thousands or more) grains are illuminated at once. Traditionally, these measurements were done of samples that were literally powders, but today, this terminology is loosely used for most polycrystalline measurements. Figure 1.9 shows a one-dimensional diffraction pattern of a 2-phase (cubic and monoclinic) NiTi SMA, with the majority of the sample in the monoclinic phase. In a diffraction pattern, each peak represents a statistical distribution of an atomic lattice spacing of the material. By fitting models of crystal structures of the material to the data, one is able to quantify such things as relative peak intensities between and within phases, peak widths, peak centers, etc. that can all be used to quantify different material properties.
Figure 1.9: A powder pattern of intensity vs. D-spacing.

Elastic strain can be readily found by the changing peak positions. If peak positions change as the load macroscopic load on the sample increases, this implies lattice spacings that are increasing or decreasing in size, elastic strain is related to the amount that the peaks have shifted with respect to the no load peak positions. Peak widths can be used to quantify slip and dislocation evolution in a material. In a pure single crystal with no dislocations, the peaks would theoretically converge to the delta function about the D-spacing values of the material. This is because all lattice spacings perfectly satisfy Bragg’s law. If lattice defects are generated, the peak widths of the diffraction pattern would start to spread out since the dislocations, in effect, add a small perturbation to the ideal lattice spacing. This perturbation comes from missing atoms. Due to the missing atoms, the surrounding lattice will have a fluctuation in the atom spacing to equilibrate with the loss.
For a two-phase material, peak fitting can identify which peaks belong to which phase. Measuring the relative intensities of peaks will determine the macroscopic phase fraction of the material in the gage section. Phase fraction quantification is most accurate when the entire two-dimensional diffraction rings are integrated into a single one-dimensional powder pattern. Using the entire pattern provides greater counts, which give better statistics, and it also mitigates the effects of texture, which can skew relative peak intensities.

Quantification of reorientation is seen from the growth of a peak at the expense of another peak. This exchange in intensities is from one variant reorienting itself into another variant that can better accommodate the large strains placed on the material. With the use of in-situ diffraction, it is not possible to determine if the material is detwinning, it is only possible to quantify if there is reorientation within the martensite structure.

Figure 1.10 is the raw diffraction data that was used to create Figure 1.9. The radial limits of integration are defined by the area between the two blue circles, while the azimuthal limits of integration are defined by the red slice. In Figure 1.10 what is being shown are the B2 rings disappearing as the material is forward transforming into its monoclinic parent phase.
Figure 1.10: The Debye-Scherrer rings of the data used to create Figure 1.9. Integration was over a 10° slice of data that is associated with atom planes with a plane normal transverse to the loading direction.

Going radially outward from the center of a diffraction pattern (like Figure 1.10) shows variation in lattice D-spacing. According to the detector setup at 1-ID at APS, we know that the top and bottom of the diffraction pattern deals with the planes of atoms that are roughly oriented in the loading direction, while the sides of the pattern are associated with lattices oriented in the Poisson’s direction. Therefore the azimuth angle describes D-spacing orientation with respect to the sample reference frame. This becomes useful for identifying elastic strains in specific sample directions (i.e.: loading/transverse direction) or creating IPFs for
twinning analysis. To analyze the evolution of phase fraction it is best to integrate over the entire pattern as opposed to a cake of information in a given direction. By integrating over the entire pattern we are using all information and data from the diffraction rings as they are turned into a diffraction pattern that can be used for fitting and extrapolating pertinent information.
Chapter 2. Methods

Section 2.1 will give descriptions of the materials examined in this experiment. Section 2.2 is built for the comparison of the different active inelastic mechanisms and material properties between the samples tested juxtaposed with a typical FCC polycrystal material. In Section 2.3 will be a description of how the diffraction measurements were taken. Finally, Sections 2.4 and 2.5 will discuss the analysis techniques for the macroscopic and diffraction data respectively.

2.1 Materials & Samples

Three different NiTi alloys were examined in this experiment. Each of the three samples has a varying degree of complexity that should help to determine what inelastic deformation mechanisms play a stronger role in the relaxation of a material.

2.1.1 Ni\textsubscript{50.8}Ti\textsubscript{49.2}

The Ni\textsubscript{50.8}Ti\textsubscript{49.2} material has previously been examined by Stebner et al. for in-situ neutron diffraction experiments [15]. It is commercial-scale low-oxygen grade that is marketed as having extra low inclusion (ELI) volume fractions. Ni\textsubscript{50.8}Ti\textsubscript{49.2} (in atomic percent) was manufactured at ATI Metals (Albany, Oregon) by multi-cycle vacuum-arc remelt processing. The wrought material was a 25.4 mm diameter bar in accordance with ASTM F2063 standards. In its wrought form the chemical composition and inclusion distribution was characterized. ELI Nitinol
has a significantly lower oxygen (less than 60 mass ppm) and carbon (less than 200 mass ppm) content than the ASTM specification that results in a maximum inclusion length of 17 microns and area fraction of non-metallic inclusions of 0.28%. The fully annealed $A_t$ was -11°C for the bars.

The ELI Nitinol bars were then cold drawn with successive 35% cross-sectional area reductions, which was then stress-relief heat treated at 510°C for 5 minutes prior to machining. The tension-compression samples were machined from 10 mm diameter rods to have a cross-sectional diameter of 1 mm in the gage. The cylindrical dogbone specimen details can be found from Figure 2.1.

![Figure 2.1: Sample geometry for the Ni$_{50.8}$Ti$_{49.2}$ specimen.](image)

After the specimens had been machined, they were then stress relieved at 520°C for 5 minutes to achieve an approximate $A_t$ of 17°C. The DSC
thermograms have revealed peaks that are associated with the forward transformation of austenite into R-Phase, and then later onto martensite upon further cooling. Upon heating of the sample, the martensite to R-Phase and R-Phase to austenite peaks happen nearly concurrently. The $A_f$ temperature is $\sim 30^\circ C$ below the ambient testing temperature, allowing the material to be pseudoelastic.

It should be noted that the Ni$_{50.8}$Ti$_{49.2}$ sample used in this thesis had already been through two mechanical cycles. This is less than ideal, however, since more qualitative observations are to be made in this experiment it should not prove to be a major issue. Figure 2.2 shows the first two mechanical cycles that the sample had undergone.

![Stress and strain graph](image-url)

Figure 2.2: Stress and strain of the first two mechanical cycles of analyzed sample.
During the first cycle, very little plasticity had been introduced in tension (~1%), since it was just coming out of the “transformation plateau”. More plasticity (~2%) was created when the sample was loaded in compression to a little more than 80 MPa. Coincidentally, upon the second mechanical cycle close to all plastic strain was erased by the high compressive load. However, the damage induced by plasticity is still present in the sample, even if macroscopic strain does not show a plastic strain.

2.1.2 Ni\textsubscript{49.9}Ti\textsubscript{50.1}

The Ni\textsubscript{49.9}Ti\textsubscript{50.1} sample used in this experiment has also been examined before by Stebner et al. [27] for different in-situ neutron diffraction experiments. The specimen was hot extruded and then hot-straightened. The phase transformation temperatures are \( m_\text{s} = 71°C, m_\text{f} = 46°C, A_\text{s} = 86°C, \) and \( A_\text{f} = 109°C, \) according to Qiu et al. [28]. Before any stressing of the sample, the self-accommodated crystallites within the grains were seen to have average widths and lengths on the order of 10 nm and 1 micron respectively, according to transmission electron microscopy. Measurements using a HIPPO and 6 unique samples, found the mean (std. dev.) lattice parameters to be \( a = 2.8931(9) \) Å, \( b = 4.630(2) \) Å, \( c = 4.111(1) \) Å, and \( \gamma = 97.30(1)^° \) for the P 1 1 2\_1/m space group. The textures of the self-accommodated martensite were found to be nearly random, with no orientations over 2 MRD. The specimens were cylinders of 2 mm in length and a 1 mm in diameter.
2.1.3 \( \text{Ni}_{50.3}\text{Ti}_{35.7}\text{Hf}_{14} \)

The \( \text{Ni}_{50.3}\text{Ti}_{35.7}\text{Hf}_{14} \) samples have been alloyed with hafnium to increase the strength of the material. This material is martensitic at room temperature, and will not undergo a stress-induced phase transformation. The test specimens were cylinders with a length of 2 mm and a diameter of 1 mm. The samples were aged at 550°C for 3 hours and then air-cooled. Since the samples have been aged, it has been solid-solution strengthened by precipitates. No DSC thermograms have been produced for this specific chemical composition, however NASA has made thermograms for \( \text{Ni}_{50.3}\text{Ti}_{37.2}\text{Hf}_{12.5} \) and \( \text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20} \) for the same aging temperatures and times. With the use of linear interpolation the transformation temperatures were found to be \( m_s = 47.6^\circ C \), \( m_f = 21^\circ C \), \( A_s = 65.6^\circ C \), and \( A_f = 98.4^\circ C \). Even though \( m_f \) is right around a typical room temperature, no austenite peaks could be found in the diffraction images. Therefore, it is no concern that the samples were not directly cooled below the interpolated \( m_f \) temperature.

2.2 Mechanical Loading Matrices

In Figure 2.3 is a graph showing the respective complexities of the three chosen materials juxtaposed to the classically examined material class for strain rate sensitivity (FCC materials).
Figure 2.3: A material complexity line made to illustrate the hypothetical complexities as they vary from FCC elastic-plastic to the examined materials.

The point of the Figure 2.3 is to illustrate the differences in complexity from material to material. We expect simple elastic-plastic FCC materials to be the most simplistic since slip is their main inelastic deformation mechanism that will drive their strain rate sensitivity. Next, the Ni\textsubscript{50.3}Ti\textsubscript{35.7}Hf\textsubscript{14} sample is the most simplistic of the three chosen samples, since twinning in isolation is the proposed inelastic deformation mechanism; slip will be present, but due to the solid-solution strengthening with hafnium it is much stronger, and limits dislocation movement via precipitate pinning sites. Ni\textsubscript{49.9}Ti\textsubscript{50.1} is expected to be a little more complicated due to its low strength, which would inherently imply that relatively
more slip would be occurring than in the Ni$_{50.3}$Ti$_{35.7}$Hf$_{14}$ specimen. Lastly, the Ni$_{50.8}$Ti$_{49.2}$ sample is the most complex. This is due to the transformation at the beginning, which is thermally dependent and allows for a large amount of reversible strain. Next, variant reorientation and de-twinning can be expected in the sample, but to what degree is unknown. Lastly, as this material is of medium strength, relative to the other materials, slip will play a role in the rate sensitivity. These mechanisms will be happening concurrently, however, depending on the strain and stresses that the sample is currently under will dictate what mechanism will be most dominant. The classical regimes where each proposed inelastic deformation mechanism should be most dominant are circled and labeled in Figure 2.3.

2.3 Diffraction Measurements

Because of the sizes of the samples, contact extensometry could not be used. Thus, tests were performed at a constant load rate instead of constant strain rate as the experiments lacked a real-time strain feedback channel. The approximate loading rate was 135 [N/s]. The points at which the constant loading was stopped – to take stress vs. time data during a stress relaxation – were not chosen at a set displacement interval. Instead, it was desired to have multiple relaxations in every interesting classical regime. For instance, the cross heads of the machine were stopped multiple times during the transformation plateau since, hypothetically, the main driving force of a relaxation will be the martensitic
transformation, and in this way one could hopefully come to some conclusions about the influence of transformation on rate sensitivity.

The DAQ system that collected the load, displacement, and time data only pinged information at a 1 Hz rate. This was less than ideal, but for the sample size, strength, and load gage resolution, a stress data point every second is appropriate. In fact, sampling at a higher rate would only result in more data points at a given force, when duplicity was already found for many relaxations at a 1 Hz frequency. The resolution of the load gage was 0.006 Newtons.

Approximately 1 meter behind the sample is a GE detector that has an array of 2048x2048 square pixels each of 200 microns in dimension. Diffraction patterns were taken upon the onset of the cross heads stopping. Once the cross heads had stopped moving – which is the beginning of a stress-relaxation – diffraction patterns were taken at an exposure length of 0.25 seconds for the first minute of sample relaxation. In this way, 240 images were taken for every sample relaxation that would later be correlated with stress vs. time data. The x-ray beam width was chosen so that the width of gage cross-section would be illuminated, with a beam height of 0.3 mm. Following the capturing of all 240 images, 2 “dark” images were taken so that detectors could be ran without any incident x-ray bombardment to mitigate any sort of “ghosting” of the GE detector. This ghosting is essentially residual effects of keeping the detector on for too long; ghosting makes it appear that the intensities are higher than they actually
are. Strains were found through the use digital image correlation (DIC), which will be discussed in greater detail in section 2.4.

### 2.4 Macroscopic Analysis Techniques

The macroscopic pre-processed data that was collected for this experiment was the force and corresponding time data and the visible light images of the sample surface during deformation. The force and time data was essential for the classical examination of stress relaxations, involving Equation 1. Force was converted into engineering stress by normalization using the original, undeformed cross-sectional diameter of samples. A Matlab script was written to deconvolute the total stress vs. time data into individual relaxation events, and also to calculate \( m \) according to Equation 1.1. To get \( \dot{\sigma} \), the stress was first smoothed, using the “smooth” moving average function in Matlab to filter data to reduce the amount of noise as well as redundant points (due to low resolution in the load cell) in the stress data. Presence of this noise in unfiltered data was problematic when computing discrete derivatives. A forward seeking 5-point, symmetric, numeric derivative [29] was employed to calculate the stress-rate from the filtered data according to Equation 2.1.

\[
\frac{\partial f(x_0)}{\partial x} = \frac{-3f(x_4) + 16f(x_3) - 36f(x_2) + 48f(x_1) - 25f(x_0)}{12h} + O(h^4) \quad \text{(eq 2.1)}
\]

In Equation 2.1, the \( f(x) \) terms to the right of the equation represent the y-values at position \( x \). In the case of calculating \( \dot{\sigma} \) at point \( x_0 \), \( f(x_0) \) is the value of stress at time \( t = t_0 \), \( f(x_1) \) is the value of stress at time \( t = t_1 \), etc. The \( h \) term
describes the distant between grid points in the x-direction and can be described as \( h = x_{i+1} - x_i \) for all values of \( i \). A symmetric first derivative was applicable since time ("\( h \)") and stress data was collected at equal intervals of every second. A forward seeking derivative was used instead of a central first derivative, since the beginning data of a stress relaxation test is what is most important. By using a forward seeking derivative, no initial data would have to be abandoned after the derivative is used; however, if we used a five-point central derivative, the first two seconds of data would not have been able to be used in further analysis. Once stress-rate was formulated, the moving average was again used to smooth out \( \dot{\sigma} \).

Finally, to calculate \( m \) from Equation 1.1, the derivative of \( \ln(\sigma) \) vs. \( \ln(\dot{\sigma}) \) was needed. Since the data is now highly asymmetric (with regards to the x-axis), the equations in Equation 2.1 could no longer be used. Instead, a 3-point, asymmetric, numerical derivative was first used, but this tended to be extremely noisy. Instead the basic, “rise over run” formulation was used by finding the difference between the \( \ln(\sigma) \) and dividing by the difference in \( \ln(\dot{\sigma}) \).

To calculate strains, a series of .tif images was imported into GOM software that was used for DIC analysis [30]. To use digital image correlation, a speckle pattern had to be placed on the sample prior to taking images. Fine printer ink toner was first applied lightly to give a dark base, followed by fine, white alumina powder. Both were mixed with a solvent and sprayed onto the surface of the sample with an airbrush. The speckles are needed so that the DIC
software can track how all speckles move in reference to each other. One example image that was used for DIC analysis can be found in Figure 2.4.

![Figure 2.4: Surface speckle pattern on one of the test samples.](image)

Since strain is length indifferent, no sort of calibration was needed to quantify speckle movement for strain analysis. Simply, major strains can be exported from the software for every pattern. Two DIC images were taken at every point a stress relaxation had occurred. Even though the samples were cylindrical about the loading direction axis, two-dimensional DIC was sufficient, since planar strain along the long axis was sufficient to create the stress-strain curves of the samples. Out of plane strain was not needed for this experiment. The one-sigma error in the strain is smaller than the markers in all figures that have strain. Figure 2.5 is a DIC image that shows the size of the facets as well as the overlay of the facets onto the image. A region of interest is defined to keep the software from
analyzing the sides of the sample that have poor focus. The facets are rather large compared to the size of the region of interest. The facets needed to be this large so that the software could track the speckles. Larger facets do not detract from macroscopic sample data. Larger facets will not resolve high-resolution local strain data, but this was not a concern for the scope of this experiment.

Figure 2.5: DIC image showing the overlayed facets onto the sample, as well as the defined region of interest in the specimen surface.
2.5 Diffraction Analysis Techniques

Before diffraction patterns could be analyzed, the ceria calibrant images first had to be used to calibrate the detector configuration. The ceria calibrants are essentially a packet of fine powder of pure ceria oxide. These can be used for calibration since we know that no residual stresses will be found in the powder packet, and therefore the diffraction rings can be used as a constant to help find beam center, tilt in the detector, and distance to the detector. The x-ray wavelength used in the testing was a constant of 0.177 angstroms. After calibration using the software Fit2d, the NiTi powder patterns can then be analyzed by using GSAS software.

Looking at Figure 2.6, we see full rings. Different parts of the detector correspond to different grains within the material. The top and bottom portions of the detector correspond to planes of atoms that are relatively aligned in the loading direction. While the left and right of the diffraction pattern are associated with planes of atoms relatively aligned in the Poisson’s direction or transverse to the load. This can be used during diffraction analysis. For the analysis of phase fraction evolution, the entire diffraction pattern is to be used, since we aren’t only interested in grains oriented in a certain way, but we want to look at and examine as many grains as possible. This way, we will have a higher degree of certainty in our values. The first step of diffraction analysis is integration. Depending on what is being analyzed will determine the limits for the integration. If information in the loading direction is desired, then the integration limits will be such that only
a 10-degree slice on the top or bottom will be used to sum the intensities. However, for phase fraction data, the entire diffraction pattern will be integrated, and all the intensities per a given radial distance will be summed together. This reduces the dimensionality of the problem by 1, and what is left is a graph of intensity vs. lattice spacing. A graph of intensity vs. lattice spacing of Figure 2.6 can be found in Figure 2.7.

Figure 2.6: Diffraction pattern from the beginning of the largest stress, stress relaxation. Note the faint lines going from the center of the pattern towards the bottom left are wire leads for a gage that picks up x-rays that were not diffracted by the sample.
Figure 2.7: A plot of intensity vs. D-spacing for the diffraction pattern found in Figure 2.6.

Figure 2.7 is the one-dimensional powder pattern from the beginning of the largest stress, stress relaxation (load # 17 from Figure 3.1). It is to be noted that Figure 2.7 has many peaks of intensity. That is primarily because the martensite phase of NiTi is monoclinic, which has very low symmetry, and therefore more potential peaks can be seen. It is also because we are still currently 2-phase with the cubic austenite phase; the intensities of the austenite and martensite are superimposed on top of one other.

GSAS is software that has been built and designed to analyze diffraction data – both x-ray and neutron TOF data. One must first have material data before analysis can begin. This material data is housed and contained in an .exp (experiment) file that GSAS can read, use, and update once least squares refinement has begun on a diffraction pattern. The basic strategy to using GSAS
is to initially only have a few parameters free for refinement. If one turns on and sets all parameters to be refined at once, GSAS will more than likely crash since there are far too many degrees of freedom and the pattern fitting is initially very far from where it should be. The strategy for how to fit a pattern depends on a number of different factors, but typically the first step is allowing the lattice parameters to be refined as well as background parameters. From there, microstrains, phase fraction, profile function parameters, and texture will all need to be allowed to be refined for a good fit. In Figure 2.8 are the results of Rietveld refinement of the histogram from Figure 2.7, but with tighter limits of D-spacing. In Figure 2.8, the red data points are the original data that the green line is being fit to. The purple line is the difference between the fit and data. The black tick marks correspond to the martensite peak positions, while the red ticks are the austenite peaks. Figure 2.9 is a close up of Figure 2.8; as can be seen the fit is rather good even though it is quite complex.

Figure 2.8: Results of Rietveld refinement on the histogram in Figure 2.7.
Figure 2.9: A close up of Figure 2.8 showing how well the pattern has been fit via use of GSAS.
Chapter 3

Results

Sections 3.1.1, 3.2, and 3.3 display the results of the tests for Ni$_{50.8}$Ti$_{49.2}$, Ni$_{50.9}$Ti$_{49.9}$, and Ni$_{50.3}$Ti$_{35.7}$Hf$_{14}$, respectively. In Section 3.4 is a brief analysis on the validity of the code written to analyze and process the strain rate sensitivity values.

3.1 Results for Ni$_{50.8}$Ti$_{49.2}$

The macroscopic data for Ni$_{50.8}$Ti$_{49.2}$ can be seen below in Section 3.1.1, this includes the stress-strain curve of the test and the corresponding $m$ values for the relaxations of the material. In Section 3.1.2, the evolution of phase fraction is examined against stress, and the change in phase fraction during a relaxation is examined in comparison to the change of stress during a relaxation.

3.1.1 Macroscopic data for Ni$_{50.8}$Ti$_{49.2}$ in tension/compression

Even though, this is the 3$^{rd}$ cycle that this sample has been through (recall Section 2.11), the sample is starting approximately at zero macroscopic strain relative to the as-heat treated condition of the machined specimen. The stress vs. strain curve for this sample can be seen in Figure 3.1. The stresses reported for each data point correspond to an averaged out stress once the material has started to approach a steady state value. It is not the initial stress value as the sample begins relaxing. Again, error bars are not added to the plot since the error in x and y is smaller than the marker size.
Figure 3.1: Stress vs. strain for the 3rd cycle, with relaxation data points labeled.

Every data point in Figure 3.1 corresponds to a stress relaxation/riser, therefore at each point a strain rate sensitivity value may be extrapolated. In the following plots, the strain rate sensitivity was plotted against stress; this is classically how strain rate sensitivity has been shown. In Figure 3.2 are the $m$ values for an entire relaxation that spans 153 seconds. Upon examination, one can see that at the beginning of the relaxation, $m$ is quite linear with stress – this occurs for the first ~10 seconds. After that, the relaxation starts to approach an asymptote and the use of numeric derivatives becomes unstable with having stress rate in the denominator. Not only that, but the theory for strain rate sensitivity is only built for the initial ephemeral portion. Because of this, for
subsequent $m$ vs. stress plots, only the first 10 data points will be plotted.

![Plot of strain rate sensitivity ($m$) vs. stress](image)

Figure 10: A plot of strain rate sensitivity ($m$) vs. stress for the 32 data point, found in Figure 3.1.

Figure 3.3, shows the first 9 seconds of the majority of data points found in Figure 3.1. In Figure 3.3, loads 1 and 2 were not shown since the sample is currently in the elastic regime, and therefore no relaxation should be occurring. Therefore, it’s surprising that load 3 had much of a relaxation while load 4 had close to no relaxation. With NiTi SMAs, it has been shown that transformation into martensite may be occurring even though the sample looks macroscopically elastic. With this in mind, it’s conceivable that a stress relaxation is already presenting itself in the 3rd load, by means of forward transformation as it’s inelastic deformation mechanism, but it’s peculiar that the 4th load doesn’t also show a relaxation, under the same logic. Excluding loads 4 and 10, all of the forward loading plots (numbers 3-17) all behave rather linearly. Non-linearity
begins upon unloading, and the sample begins to have a stress riser, instead of a relaxation.
Figure 11: Strain rate sensitivity vs. stress of selected data points.
3.1.2 Phase Transformation During a Stress Relaxation

By analyzing the x-ray diffraction data, it was found that phase fraction did evolve during the relaxation. Figure 3.4 is a plot of phase fraction vs. time for load 6. Note, load 6 was chosen as it is in the middle of the transformation plateau, and therefore we would expect phase transformation evolution to be rather significant for this load step and stress relaxation.

As can be seen, there is a significant trend in the phase fraction during a stress relaxation. It should be noted that the one standard deviation for each of these data points is approximately 0.7 [%]; this is significant, but non-deterring from trend analysis.

In Figure 3.5 is a plot of phase fraction of martensite vs. strain for the Ni_{50.2}Ti_{49.8} sample. For each relaxation, the strain is a constant, but in making this graph, the red markers were displaced by a positive .2% strain so that it’s value
and error bars could be seen better. The error bars represent a plus or minus one sigma of error for the measurement. It's interesting to note, that upon the first unloading step the material increased the martensitic phase fraction.

![Graph](image.png)

**Figure 13:** Phase fraction martensite vs. strain. In blue is the phase fraction at onset of relaxation while red is the phase fraction after 10 seconds of relaxation.

A major part of this experiment is to phenomenologically elucidate what inelastic deformation mechanisms contribute to the stress relaxation of the examined materials. Figure 3.6 was created to see if there are any trends between the amounts of stress that was relaxed in the first ten seconds compared to the amount the sample had stress transformed in the same time frame.
Figure 14: The change in phase fraction and the change in stress for the first ten seconds of relaxation, binned by loading number.

In Figure 3.6, the difference in phase fraction for loads 4 and 5 are quite large, and rather nonsensical considering point 5 is presenting that the phase decreased by 2% back towards austenite after macroscopic stress was increased. The error in the phase fractions for these first two points was rather large with a sigma of roughly 1-2%, coupled with the fact that the diffraction analysis predicted the sample was around 3.5% martensite reduces the data for points 4 and 5 to something that should be neglected in the final analysis and conclusions. The large uncertainty in the phase fraction analysis can be attributed to the very small martensite peaks within the powder diffraction pattern. 

Once the sample has reached higher stress values, phase fraction analysis is much more reliable since the diffraction peaks for each phase is large enough to have a greater certainty in the fitting.
3.2 Macroscopic data for Ni$_{49.9}$Ti$_{50.1}$ in compression

Unfortunately, the DIC images that were taken for this sample were unresolvable within the GOM software. This is less than ideal, but shouldn’t change any findings or results. The absolute stress vs. time data will be shown as well as the stress vs. change in cross head displacement data; however the resolution on the cross head displacement is relatively bad for the length of the compression sample. The displacement resolution is limited to plus or minus 50 microns, which would lead to a strain resolution of $\approx 2.5\%$ for our 2 mm long samples.

In Figure 3.7 is a graph of absolute stress vs. time with the loading steps numerically labeled. In Figure 3.8 is a graph of absolute stress vs. machine displacement.

![Graph of stress vs. time for the Ni$_{49.9}$Ti$_{50.1}$ sample.](image)

*Figure 15: Stress vs. time for the Ni$_{49.9}$Ti$_{50.1}$ sample.*
Figure 16: Stress vs. machine cross head displacement for the Ni$_{49.9}$Ti$_{50.1}$ sample.

In Figure 3.9 are the plots of $m$ vs. stress for every load step. The load step numbers correspond to the numbers found from Figure 3.7.
Figure 17: Strain rate sensitivity vs. stress for all load steps for the Ni$_{49.9}$Ti$_{50.1}$ sample.

As can be seen, almost every plot from Figure 3.9 appears to be linear. This is especially true in all of the forward loading plots (numbers 1-9). There are two major exceptions. In the load 10, there is a junction in the linearity – this can be attributed to the crossover between the sample having a stress relaxation and having a stress rise during the fixed cross head displacement. In load 11 the points seem to double over on one other, this can be attributed to a jump in the load as can be seen in Figure 3.10. This can more than likely be attributed to the machine overshooting its requested load step, but it’s hard to substantiate this claim, since the displacement resolution of the load frame is extremely low. Regardless, this plot should be neglected in final assessment of trends within the sample. Slight non-linearity is also observed in loads 12, 13, and 14 from Figure
3.9. This can be attributed to the sample having a stress riser for these loading steps.

![Figure 18: Close up of stress vs. time curve for 11th load step.](image)

3.3 Macroscopic data for Ni$_{50.3}$Ti$_{35.7}$Hf$_{14}$ in compression

Again for this sample, the DIC images that were taken for this sample were unresolvable within the GOM software. The absolute stress vs. time data will be shown as well as the stress vs. change in cross head displacement data; however the resolution on the cross head displacement is relatively bad for the length of the compression sample. The displacement resolution is limited to plus or minus 50 microns, which would lead to a strain resolution of $\approx 2.5\%$ for our 2 mm long samples.

Figure 3.11 is a graph of absolute stress vs. time with the loading steps numerically labeled. Figure 3.12 is a graph of absolute stress vs. machine displacement. The 20th load step was a mistake made by the experiment.
conductor. Even though the 20\textsuperscript{th} load step was a mistake, this should not be a problem, primarily since the emphasis of the data analysis in this thesis has been placed on the stress relaxations.

Figure 19: Absolute Stress vs. time with loading steps numbered and marked for the Ni\textsubscript{50.3}Ti\textsubscript{35.7}Hf\textsubscript{14} sample.

Figure 20: Absolute stress vs. machine cross head displacement for the Ni\textsubscript{50.3}Ti\textsubscript{35.7}Hf\textsubscript{14} sample.
In Figure 3.13 will be the plots of $m$ vs. stress for every load step. The load step numbers correspond to the numbers found from Figure 3.11.

![Graphs of $m$ vs. Stress for every load step.](image)

Figure 21: Strain rate sensitivity vs. stress for the Ni$_{50.3}$Ti$_{35.7}$Hf$_{14}$ sample.

All of the forward loading steps in Figure 3.13 (loads 1-21) show a rather linear trend with $m$ vs. stress. Load 18 is missing from the Figure 3.13, this is due
to the very small change in force from the previous loading step, and the software written to analyze the relaxations had skipped over it. Again, non-linearity can be seen once reverse loading has begun and the sample slowly goes toward having a stress rise instead of a stress relaxation.

3.4 Error Analysis of calculating strain rate sensitivity

Due to the inherent instability and unreliability of taking numeric first derivatives, a supporting code was written to analyze the variability in the calculated $m$ values. The supporting code went through the original stress data and added a perturbation to every data point. The perturbation was approximately equal to the noise in the stress data ($\sim 4*10^5 \text{ [Pa]}$). With the use of a random mean for the $m$ values.

Figures 3.14 and 3.15 are the average $m$ vs. stress plots for load number 16 and 17 for the Ni$_{50.8}$Ti$_{49.2}$ sample. Load 16 and 17 are the second highest and highest load levels for that test. These two loads were not chosen for any specific reason.
Figure 22: The average value of strain rate sensitivity vs. stress after a 1000 runs for load 16. Error bars show one standard deviation.

Figure 23: The average value of strain rate sensitivity vs. stress after a 1000 runs for load 17. Error bars show one standard deviation.

Looking first at Figure 3.14, it would appear that the random perturbation had little effect on the final results with small error bars that don’t overlap between consecutive data points. Also, the slope of the line is 0.0022, which has a percent difference of 10% from the originally calculated value of 0.002 for this
load step found from the $m$ vs. stress plots in Figure 3.3. Figure 3.15 has error bars that are much greater respectively to Figure 3.14; the error bar widths decrease as the relaxation proceeds (the highest stress is at the beginning at the relaxation for this load step). This could be due to the larger stress rates at the beginning of the relaxation are more affected by the random perturbation.

Likewise, the slope from Figure 3.15 is 0.0028, which is 16.7% off from the originally calculated value of 0.0024.

In conclusion, there is some instability with the calculation of strain rate sensitivity; this can’t be neglected, but the instabilities are minor enough to move forward with the discussion of the results.
In Section 1.1 the classical approach to quantify a stress relaxation had been introduced. In Section 4.1 a discussion will take place to identify if Cottrel-Stokes law can be applied to material systems outside of FCC crystal structures, as well as any trends in the strain rate sensitivity values with strain. One outcome of the Cottrel-Stokes law is that the strain rate sensitivity is constant for a stress relaxation – this comes out of theory, and is seen in practice. In Sections 3.11, 3.2, and 3.3 the calculated $m$ value was found to vary linearly with stress during a relaxation. Potential meaning behind the changing slopes of $m$ vs. stress will be examined in Section 4.2. Phase transformation is an inelastic deformation mechanism that can accommodate applied stress and strain on a material. In Section 4.3 a discussion on how phase fraction evolves during a stress relaxation will be discussed. The Discussion section will conclude with a look at the stress risers found in a SMA during a stress relaxation test in Section 4.4.

4.1 Applicability of Cottrell-Stokes Law

In examining Figures 3.3, 3.9, 3.13, it is apparent that the Cottrel-Stokes law does not directly apply to the studied materials, as the $m$ values are not constant in time. As discussed in the introduction, this finding is not surprising since Cottrel-Stokes law was developed specifically for elastic-plastic, FCC
materials, but the examined materials exhibit inelastic deformation mechanisms other than slip and are comprised of lower symmetry phase(s).

Although Cottrell-Stokes law is not directly applicable to our materials, calculations of strain rate sensitivity still have value in interpreting our data. Since strain rate sensitivity is a quantitative measure of how stress changes with stress rate, it can be used as an analog to ductility, since $m$ can still be thought of as a relative measure of strain rate sensitivity.

The classical theory for strain rate sensitivity says that $m$ should be independent of strain [5]. Stuwe et al. [8] hypothesize that the theoretical constancy of $m$ is limited to small strains in single crystals. Even in polycrystalline FCC materials, experimentally $m$ is not independent of strain. In most cases, it can be shown that $m$ tends to increase monotonically as strain increases for simple elastic-plastic cubic materials [5, 9, 10, 11]. Mecking and Kocks have created phenomenological models to describe the linear trend of $m$ vs. strain, and then the non-linear (but positive) deviation as the sample is strained into stage III hardening. Stage III hardening of FCC materials can be characterized as a decrease in hardening rate, as well as having strong temperature and strain rate dependence [7].

Figure 4.1 shows histograms of the average value of $m$ for the first ten seconds binned as a function of load number for the forward loading direction, for the examined materials. In Figure 4.1, higher loading numbers are analogous to larger strains placed on the material. In Figure 4.1, there appears to be a weak
trend of $m$ decreasing as the load number increases. This is contrary to what is seen in pure FCC samples, where $m$ increases monotonically with strain. Depending on texture, phase transformation and martensite reorientation will start to occur at lower strains relative to slip and dislocation evolution. Since the examined materials in this experiment contain inelastic deformations that can potentially accommodate a large amount of stress and strain, this may be the cause for the decreasing trend of $m$ with higher loads (i.e., higher strains); if phase transformation and martensitic reorientation are favored for the load, they will start to occur after the elastic regime, but their ability to accommodate the strains is limited, and the potential for strain accommodation decreases.
Figure 4.1: The average $m$ value binned by the loading number in the forward loading direction for (a) Ni$_{50.8}$Ti$_{49.2}$, (b) Ni$_{49.9}$Ti$_{50.1}$, and (c) Ni$_{50.3}$Ti$_{35.7}$Hf$_{14}$.
4.2 Slope of $m$ vs. Stress.

In the classical case of FCC materials, $m$ is a constant per a given relaxation [9]. This falls out of theory, and experimentally authors will use linear fits to solve for $m$, which in turn leads to a single strain rate sensitivity value for a relaxation [8, 9, 10]. For this experiment, it was not assumed that $m$ should be a constant during the relaxation; since there were many more inelastic deformation mechanisms at work in the material as well as the lower symmetry of the martensite crystal structure. If slip in FCC and monoclinic crystal structures manifest themselves similarly during a stress relaxation, then hypothetically $m$ would converge to a single value at higher strains, where slip is becoming the dominating inelastic deformation mechanism. However, considering the theory that Cottrel-Stokes law is based upon was written for FCC materials, it would not be a surprise if at large strains $m$ doesn’t trend to a constant value, per a given relaxation.

In Figure 4.2 are the histograms of the value of the slopes from the $m$ vs. stress graphs found above binned as a function of load number. With few exceptions, all $m$ vs. stress graphs above have been given a linear fit. Most of these graphs are very linear, especially for the stress relaxations from the forward loading steps. A large $m$ slope implies a highly variable strain rate sensitivity for that given relaxation, while a small slope would entail a $m$ value that is approaching a constant for a given relaxation. The histograms in Figure
4.2 (a-c) have the same y axis scaling – direct comparisons of histogram size can be made.

Figure 4.2: Slope of $m$ vs. stress for the loading number in the forward loading direction for (a) Ni$_{50.8}$Ti$_{49.2}$, (b) Ni$_{49.9}$Ti$_{50.1}$, and (c) Ni$_{50.3}$Ti$_{35.7}$Hf$_{14}$. 
Starting with Figure 4.2(a), it would appear that there is no strong trend in the data as sample varies across strains. From Figure 3.6, it is known that the role of transformation decreases during a relaxation as the sample goes to higher strains. However, Figure 4.2(a) shows minimal change in magnitude of slopes at higher strains. It was shown from Pelton et al. [31], that in superelastic NiTi the production of latent heat was greater during plastic flow compared to the latent heat released from forward transformation. Even though it was expected that transformation was the greater relaxation mechanism, it may be seen at higher stresses that the increased production of latent heat is cause for a more pronounced thermal activation effect, which then keeps the slope values large at the higher strains.

The histograms of 4.2(b & c) are rather similar. In both cases, the slopes decrease near monotonically to smaller values as the strains/stresses are increased in the material. Since the variance is rather high initially it may indicate that twinning alone (before plasticity) is a more mobile relaxation mechanism. This large slope value is extremely pronounced in the first load of the 4.2c sample. It was discussed in Section 2.1.3 that the Ni_{50.3}Ti_{35.7}Hf_{14} sample had been strengthened by precipitates. These precipitates increase the relative resistance of slip, and therefore it should be expected that Ni_{50.3}Ti_{35.7}Hf_{14} has a greater magnitude of twinning in isolation, at the beginning relative to the Ni_{49.9}Ti_{50.1} sample that has a significant amount of plasticity initially, before any loading has occurred [27].
4.3 Phase Transformation and Stress Relaxations

The histograms showing the relative change in stress and the change in phase fraction by load number (Figure 3.6), was created to see if there was any strong dependence upon transformation for material relaxation. Phase transformation is a potential mechanism to relieve elastic strain in a material, by means of transforming to a crystal structure that can better accommodate the strains. If forward transformation is occurring during a relaxation, then it would contribute to the stress relaxation. However, looking at Figure 3.6, it does not appear that there is any linear correlation between the change in stress and the change in phase fraction during a relaxation. This does not mean that the above statements are incorrect, but rather it implies that there are other deformation mechanisms concurrently at work in the material even in the transformation regime such as variant reorientation.

Looking at Figure 3.5, which shows how phase fraction of martensite is changing with strain, it is interesting to note that the phase fraction actually increases upon the first unloading step. While no speculation can be substantiated, it is possible that as the sample was forward loaded to ~20% strain in tension, that the vast majority of grains that were favored for transformation had already had a forward transformation. Pelton et al. [31] have shown that with superelastic NiTi, even after a couple percent pre-strain, that upon unloading the material maintains a significant amount of residual tensile stress. The high residual tensile stress is attributed to the generation large
dislocation networks that lock in the elastic tensile stress. At unloading, the residual tensile stress could induce compression in the grains that could not originally transform in tension (since they favor forward transformation in compression), which would cause the phase fraction of martensite to increase initially. This induced compressive force could also be coupled with back stresses associated with dislocation pile-ups. Even though this is all speculation, in general, it is a safe statement that there is a competition of many mechanisms working concurrently to create forward transformation upon the first reverse load step.

4.4 Stress Risers

To this point, little analysis has been placed on the stress risers of the material. A stress riser may occur in response to cross head arrest during an unloading event. A stress relaxation may even still occur during the first unloading step, but stress risers can often be found for later unloading steps. In Figure 4.3 is a stress vs. time graph, but the data is taken during the stepped unloading of the sample from a large tensile stress moving back towards zero force.
Figure 4.3: A portion of the stress vs. time data of a cross-head arrest test. Shown is several stress risers captured during a constant displacement.

From Figure 4.3, these stress risers can tend to become larger the closer the sample approaches the no-load state.

One of the more interesting stress risers to look at is from the 25th load step of the Ni$_{50.2}$Ti$_{49.8}$ sample. In this load step, the machine takes the sample just across the threshold of tension and into compression, and the stress riser brings the sample back through zero and once again into tension. This can be seen in Figure 4.4.
In Figure 4.4 the sample overshoots the zero stress point and climbs further into a macroscopic tensile stress since the kinetics of the material is still trying to drive the sample into a tensile stress riser. Because the material is initially in compression, the macroscopic compressive stress assists in the tensile stress riser. Looking at the $m$ vs. stress plot for this load step shows that the sample has high non-linearity; this can be attributed to the assisting compressive load that was placed on the sample before the cross heads of the machine were stopped.
Chapter 5
Conclusions and Future Work

It has been found that Cottrel-Stokes law does not hold for the alloys examined in this thesis. This result was expected, since many of the assumptions made to develop Cottrel-Stokes law for pure FCC materials do not apply to twinning of low symmetry phases and phase transformations of SMAs. One major missing piece of empirical evidence was the quantification of reorientation in the specimens via in-situ x-ray diffraction. Since the de-twinning mechanism has been proposed to be a significant inelastic deformation mechanism, the analysis of de-twinning would be invaluable for this project.

Another point of concern is that the basis for calculating strain rate sensitivity values comes from the force vs. time data, and in this project, sampling occurred at a 1 Hz frequency on a load cell with poor resolution for the small sample cross-sections. Sampling at 1 Hz hardly sufficient since the transient region of a stress relaxation is on the order of seconds. Replicating experiments with a higher resolution load cell as well as sampling at a higher frequency would be essential for future work.

At some point, with the help of the produced phenomenological data presented, it may be beneficial to come up with a strain rate sensitivity model analogous to what Cottrell-Stokes law is for FCC crystals. This model would have to be very comprehensive and robust, since it would have to account for many
more factors (ie: phase transformation, twinning, slip in lower symmetry crystals, stronger thermo-mechanical coupling) than what Cottrel-Stokes law had to model. Before any models could be developed, further diffraction analysis should be completed.

With further experimentation, varying strain rates for a stress relaxation test could prove to be of interest for any final analysis of strain rate sensitivity and identifying trends. With further experimentation, taking the samples to higher strains could also be beneficial in isolating slip as the inelastic deformation mechanism to see the effects. With the use of single crystals, one could isolate the different inelastic mechanisms by aligning the crystal axis in ways that favors transformation, slip, or detwinning. By studying the mechanisms individually, it would be invaluable to determining the respective weights of how the different mechanisms influence rate dependence.
References Cited


