SAMPLE SIZE EFFECTS RELATED TO NICKEL, TITANIUM AND NICKEL-TITANIUM AT THE MICRON SIZE SCALE

DISSERTATION

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ABSTRACT

Micron-sized compression specimens, fabricated using a focused ion beam (FIB), indicate a dramatic strengthening effect as sample dimensions are reduced from 20µm to sub-micron diameters in nickel and gold microcrystals. To understand this effect, novel microscopy techniques were utilized to study the mechanical properties and dislocation substructures from microcrystals of pure nickel, Ti-6wt.%Al, Ti-6Al-2Sn-4Zr-2Mo-0.1Si (Ti-6242) and Ti-50.8at.%Ni. The dislocation behavior that governs plasticity is quite different between each of these materials and as such produces different size effects at small sizes.

The nickel compression results indicate a dramatic increase in strength as sample dimensions are reduced. Quantitative dislocation density measurements performed on slip-plane TEM foils extracted from nickel microcrystals indicate an increase in stored dislocation density at smaller sizes. However, hardening contributions from forest-hardening and source truncation hardening were insufficient in explaining the high observed flow stresses. This result suggests that other hardening mechanism are operating in the nickel microcrystals.
The titanium alloys exhibit a much less dramatic strengthening effect compared to the nickel microcrystals. The titanium microcrystals, at all sample sizes tested (1-60µm), are stronger than bulk compression specimens. Even at the 60µm sizes bulk behavior is not observed, while at only 20 microns nickel microcrystals exhibit bulk properties. Transmission electron microscopy (TEM) investigations indicate several dislocation pile-ups of both screw and edge character at the microcrystal surfaces. These pile-ups appear to be related to ion damage induced by the fabrication of these samples, resulting in a strengthening effect that follows a Hall-Petch relationship.

Nickel-Titanium alloys deform through a phase transformation, as well as dislocation motion. The microcrystal compression results indicate no observable size effect related to the strength of the 5µm and 20µm crystals. TEM studies indicate an increase in dislocation activity, ⟨100⟩⟨110⟩, with the number of loading cycles. However, determining the relationship between plasticity and the martensitic transformation was inconclusive.

This work indicates a need for further investigations into the effects of dislocation junction formation at small sizes and the effects that gallium ion damage has on the mobility of edge and screw dislocation segments for microcrystals fabricated with the FIB. Each of these may contribute a strengthening effect in the nickel and titanium alloys, respectively. Coupling microcrystal compression experiments with TEM provides a unique methodology for studying a poorly understood relationship between plasticity and the martensitic phase transformation in NiTi alloys.
Dedicated to my loving wife, Melinda.
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NOMENCLATURE

\( \alpha \) forest-hardening coefficient that is related to the ensemble-strength of dislocation junctions
\( \gamma \) stacking fault energy
\( \gamma_p \) plastic shear strain
\( \lambda \) mean free path of a dislocation
\( \rho_f \) forest dislocation density
\( \sigma_f \) flow stress, the stress at which plasticity transitions to perfect plastic behavior
\( \sigma_M \) critical stress to induce B19' martensite
\( \sigma_i \) critical stress at which the dislocation accomplishes continuous glide by infinite motion. This is in turn related to \( \tau_p \) and \( \tau_t \)
\( \sigma_{ys} \) yield stress of a material, typically given at 0.2% plastic strain.
\( \tau_f \) shear stress contribution from forest interactions
\( \tau_p \) Peierl’s stress
\( \tau_{rss} \) resolved shear stress on a particular slip system based on a given loading direction.
\( \tau_r \) total reference stress, the summation of the Peierl’s stress, the initial forest-
hardening stress and the source-truncation hardening stress.

\( \tau_t \) maximum resistance to dislocation motion from the entire obstacle configuration in bowing-mode crystals.

\( A_{ts} \) total area swept out by the dislocation loops

\( b \) Burgers vector

\( D \) grain diameter

\( d \) equilibrium distance between partials

\( G \) shear modulus

\( k \) locking parameter, indicating the relative hardening contributions from the grain boundary.

\( T_t \) transformation temperature
CHAPTER 1

INTRODUCTION

Understanding the mechanical properties of a material has always been of great importance in determining suitable applications. However, recent applications such as microelectronics, functional coatings, and micro-electromechanical systems (MEMS) has confined plasticity to very small volumes of material. The small sizes require knowledge of the mechanical properties on the nano- and micron-size scales. Recent technologies have allowed a means for fabrication and testing volumes of material on the order of a few microns in size on virtually any conductive material. Coupling mechanical results with transmission electron microscopy, correlations between the mechanical size effects and sample dimensions can qualitatively and quantitatively be explored across a host of materials and crystal structures.

A review paper by Nadgornyi [4] has suggested that a material be classified into either of two categories based on the nature of the dislocation motion: bowing-mode or kink-mode. Bowing mode materials exhibit low lattice frictional stresses, such that the strength of the material is strongly dictated by the obstacles that interact
with the dislocation segments. Therefore, these materials are also referred to as "obstacle controlled." The second class of materials, kink-mode, exhibit significant frictional stresses, particularly related to the screw dislocation segments. In most cases, this is a result of the dislocation core structure being dissociated onto multiple slip planes, creating a significant drag on the moving dislocation segments.

Therefore, the purpose of this work is two-fold. First, using the framework that Nadgornyi has purposed, materials from each of the two categories were studied on the micron size scale to determine if an intrinsic size effect exists. Secondly, if a size effect is observed, the dislocation ensembles were studied to determine, qualitatively and quantitatively, why such an effect exists. As such, the materials in this study consisted of single crystals/colonies of pure nickel (bowing-mode), titanium (kink-mode), and nickel-titanium (phase transformation).

Chapter 2 will begin with an introduction on the sample size effects that have been explored over the last decade; specifically, the observations from the early whisker experiments, grain-size effects, and sample surface effects. All of which indicated an increase in strength as the dimensions were reduced.

The next section in this literature review will highlight recent observations on small-scale nickel and gold microcrystal experiments, accompanied by current ideas that the modeling community believes are contributing to the observed size effects. Lastly, the metallurgy and dislocation dynamics associated with each of the materials used in this study will be introduced.
Chapter 3 will serve as an overview of the experimental procedures that were used for all materials in this work, discussing the intricacies of microcrystal fabrication, microcrystal testing and transmission electron microscopy (TEM) sample preparation techniques. The procedures that are specific to a given material are found in their respective chapter, 4, 5 or 6.

Chapter 4 will investigate the dislocation ensembles that were produced during the deformation of nickel (bowing-mode) microcrystals, ranging from 1 to 20 microns in diameter. Utilizing TEM imaging/diffraction techniques, correlations between the dislocation density, forest-hardening and source operation will qualitatively and quantitatively be compared to the observed flow stresses in each of the microcrystals tested. These results will be discussed in the context of current theories and experimental evidence.

In chapter 5, microcrystal compression results from each of the titanium alloys (kink-mode), ranging from 2 to 60 microns, will be discussed and compared to the results presented for nickel and other bowing-mode materials. Differences and similarities between each of the titanium alloys will be addressed and supported with observations from TEM foils extracted from each of the microcrystals after deformation.

In chapters 4 and 5, plastic deformation was driven by the motion/interaction of dislocation segments. Therefore, Chapter 6 will concentrate on deformation processes that are not driven by dislocation motion, specifically a martensitic phase transformation in NiTi. Microcrystal compression results from 5 and 20 micron
diameter samples will be compared to the results from the kink-mode and bowing-mode materials discussed previously. TEM studies performed on the 5-micron diameter samples provided new insights as to the role that dislocations play during the phase transformation process.
CHAPTER 2

LITERATURE REVIEW

2.1 Size Scale Effects

Mechanical size effects associated with the plasticity of crystalline materials can broadly be separated into two specific trains of thought depending on the imposed constraints. First, there are the size effects that are related to deformation of a material in the presence of strong strain gradients. Such is the case for nano-indentation experiments where a Berkovich tip is forced into a bulk substrate inducing heterogeneous deformation and geometrically necessary dislocations (GND’s). These GND’s are an artifact of the Berkovich tip geometry from which dislocations must be created to accommodate the shape of this tip. These dislocations are typically immobile and strong barriers to dislocation motion. The consequence is a well-known size effect, ”indentation size effect,” that is present solely due to the geometry of the tip. The research field has agreed upon the nature of such an effect and will not be discussed any further, see for reference [5, 6].
A second set of size effects occurs under homogeneous loading conditions in the absence on any large strain gradients; however, dramatic increases in strength are still achieved as samples dimensions are reduced. Experiments in the mid 1900’s on perfectly grown whiskers (little or no dislocations) indicated large increases in strength as sample dimension were reduced. In addition, recent studies using a microcompression technique developed by Uchic et al. have illustrated a similar effect even though the crystals are not perfect, containing a large initial dislocation density. The specific details are not fully understood nor agreed upon and as such, a topic of this research. Therefore, the context of this chapter will solely be related to size scale effects in the absence of large strain gradients.

2.1.1 Whiskers

In the early 1900’s, experimentalists discovered a large discrepancy between the calculated theoretical shear stress and that determined from experiment. In 1934, Taylor, Orowan, and Polanyi each postulated that there must be a lattice defect allowing the strain to propagate through the material without shearing the entire plane of atoms simultaneously, namely a dislocation. In 1952 Galt and Herring showed the strength of very small single crystals (whiskers) of Sn could approach the theoretical strength. This resulted in a great deal of research in the area of perfect crystals (1-50µm in diameter) having little or no lattice defects throughout the gauge length of the material. In the literature there are primarily two testing methods that were used to measure these mechanical properties, bending and
tension 13–20. Although the bending technique is much easier to utilize, it has a large disadvantage in that the imposed strain is inhomogeneous both across and along the sample, leading to large strain gradients. It is for this reason that the following discussion will be limited to the results determined only from the tension experiments.

The effect of size on the strength of Fe and Cu whiskers at room temperature (RT) is illustrated in Figure 2.1 13–17. Although there is a lot of scatter in the data, it is apparent that the strength of the crystal increases with decreasing sample size. A similar trend was also observed in NaCl 21 and C-graphite 18. For ductile materials, this size effect was attributed to a reduction in the probability that the crystal contains a dislocation source, internal or external, as the sample dimensions were reduced. This required very large stresses, on the order of the theoretical shear strength, to nucleate a dislocation source.

The scatter in the data was attributed to several different variables, such as, dislocation content, impurity content, and surface imperfections. Each of these can be accredited to the conditions and manner in which the whisker was grown, via chemical reduction, chemical reaction, vapor condensation, precipitation, electrolysis or growth from solid. Each of these techniques is specific to a desired crystal system and the processes involved are not trivial to produce perfect whiskers and therefore will not be discussed further.

Although these whisker experiments provided insight as to the effect that an imperfection has on the properties of a single crystal, there have been few studies
that probe the same size scale while several dislocations are present. These types of experiments are critical in understanding the internal mechanisms that are contributing to the strengthening of the material, such as the mechanisms that control dislocation glide, storage and multiplication.

2.1.2 Grain Size Effects

A common size-scale effect that has been exploited over the last fifty years is that of grain size refinement. E. O. Hall, in the early 1950s, discovered that if a plot of the yield strength, $\sigma_{ys}$, versus the inverse square root of the average grain diameter, $D$, for several polycrystalline samples was constructed, a linear trend resulted \[22\]. This result indicated that the strength of the material is inversely proportional to that of the grain size and follows the empirical expression:

$$\sigma_{ys} \propto \sigma_0 + D^{-\frac{1}{2}}$$

(2.1)

where $\sigma_0$ is the yield strength for a single crystal. Based on the work of Eshelby et al. \[23\], I.R. Koehler \[24\] and N. J. Petch \[25\], a theoretical expression was derived for the yield strength of a crystal as a function of the grain diameter. Petch’s derivation is based on the stress concentration produced at the front of a dislocation pileup against a grain boundary,

$$\sigma_{ys} \propto \sigma_i + kD^{-\frac{1}{2}}$$

(2.2)
where $\sigma_i$ is the critical stress at which the dislocation accomplishes continuous glide by infinite motion and $k$ is the locking parameter, which measures the relative hardening contributions of the grain boundary. Eqn. 2.2 is typically referred to as the Hall-Petch equation.

2.1.3 Surface Strengthening Effects

S.S. Brenner postulated that a surface oxide could contribute a strengthening effect due to the impediment of dislocations from escaping the sample or the inactivation of surface dislocation sources. However, he concluded that this would be unlikely in ductile materials. In 1976, Tabata et al. demonstrated that a surface oxide contributes to the strengthening of the material by studying the in situ dislocation evolution in thin aluminum wires (5-200 $\mu$m). Using a TEM operating at 2MV, Tabata et al. observed dislocations nucleating from the interior of the specimens and piling up against the surface of the sample. Upon yielding, these dislocations rapidly escaped the sample to form slip bands. This is similar to the Hall-Petch model for grain size strengthening and follows an inverse square root dependence on the sample diameter. To determine if the strengthening was indeed due to the surface oxide, samples of Cu-0.15 wt% Ag were tested. The results were similar, showing an increase in strength as sample diameters were decreased. The authors justify the results by suggesting that impurity atoms, such as sulfur and carbon may segregate to the Cu (111) surfaces and that the lattice constant of materials becomes larger at the surface as opposed to the interior.
2.1.4 Microcrystal Compression Experiments

Recent experiments on gold and nickel microcrystals have shown that the yield strength for single crystal microcrystals increase dramatically as dimensions are reduced below 20 µm, these results are summarized in Figure 4.1a [7, 27–29]. This phenomenon is different from that of the previous whisker experiments because the starting dislocation density of the whiskers contained <10^{10} /m^2, whereas the initial densities for the micro-compression tests are on the order of 10^{12} /m^2. These size effects also differ from those observed in nanoindentation experiments in that, the imposed strain is homogeneous throughout the sample minimizing any strain gradients and/or geometrically necessary dislocations.

Besides the large strengths observed in these microcompression experiments, there are two major aspects of a typical stress-strain curve that differ from a bulk compression experiments. The first is the stochastic nature in the strain response evident from the large bursts of strain as the samples is loaded. These bursts are then followed by nearly elastic loadings until a threshold stress is reached and the sample continues to plastically deform until the sample is unloaded. A second noticeable feature of these tests is the lack of any hardening for engineering strains up to ∼40%. This correlates to huge extensions of Stage 1 glide, whereas bulk samples transition into Stage II at only ∼2% engineering strain.
Previous work by J. T. Fourie has shown that the reduction in sample diameter, from 1 mm to 61\(\mu\)m in copper single crystals, has a dramatic effect on the extension of Stage I glide to larger strains [30], but has little or no effect on the CRSS or the work hardening rate (WHR). Stage I glide is the region of the stress strain curve that observes limited hardening due to the easy glide of dislocations through the material. Fourie attributes this extension to the mean free path of a dislocation, \(\lambda\), the average distance that a dislocation travels before intersecting an obstacle. Therefore, if \(\lambda\) is constant as the diameter of the sample is reduced, the probability of a dislocation interacting with a barrier is also reduced and free to exit the sample.

2.1.5 Current Theories Related to Microcrystal Size Effects

Prior to the microcompression experiments [7, 27–29], Gil Sevillano et al. suggested that an intrinsic size effect exists in the absence of a strain gradient by relating the motion of a dislocation to that of a liquid through a porous medium, invasion percolation [31]. In doing so, he determined that a characteristic length is defined by the average separation distance between pinning points. If the sample dimensions approach this characteristic length, then changes in the mechanical behavior are to be expected.

Adding to the idea of size scale effects, atomistic simulations, using the embedded atom method (EAM), were utilized by Horstemeyer et al. to study size scale and strain rate effects under simple shear conditions in single crystal nickel [32]. Similar to the whisker experiments, the virtual samples were initially dislocation free. The
sample dimensions varied from 100 atoms to 100 million atoms with strain rates of $10^7$ to $10^{12}$ s$^{-1}$. The results of this work are very similar to those determined from experiment in the early whisker studies. The stress-strain data shows a linear elastic region followed by an upper yield, or macro-yield, point that decays to a plateau stress. The macro-yield point was highly sensitive to the number of atoms or volume of the virtual samples, such that samples with only 196 atoms showed a three-fold increase in strength compared to a sample with $10^5$ atoms. Furthermore, a power law dependence was reported by the authors based on a volume to surface area ratio: \[ \frac{\tau_{rss}}{G} = 3.2 \times 10^{-5} \left( \frac{V}{A_s} \right)^{-0.38}, \] where $\tau_{rss}$ is the resolved shear stress, $G$ is the shear modulas, $V$ is the volume and $A_s$ is the surface area. In all cases, dislocations initiated from the surface, which was attributed to the lack of an initial dislocation density, suggesting that the macro-yield point is attributed to the activation of the first source. Although the atomistic model predicted a size effect common to micro-compression testing the key difference is the initial density of $\sim 10^{12}$ /m$^2$ found in the microcrystal compression experiments. There may also be a significant influence of the extremely high strain rates used in atomistic simulation ($\sim 10^9$/sec).

The results from the nickel and gold microcrystal compression experiments has spurred a host of ideas as to the cause for an increase in strength as sample dimensions are reduced. The majority of which are related to the idea of a dislocation starved state suggested by Greer and Nix \[33\], whereby at smaller sizes there is a higher probability that mobile dislocations will exit via a free surface than to multiply or interact with other dislocation segments. Therefore, if the density of
escaping dislocations is greater than the density of dislocations being nucleated then a dislocation-starved state would exist such that an increase in stress would be required to nucleate new dislocations. Using two-dimensional discrete dislocation simulations (2D-DDS), Deshpande et al., Benzerga and Shaver, and Balint et al. have shown that if a dislocation starved state were to exist in small samples then a size effect would result.

Deshpande et al. used 2D-DDS to study plasticity size effects in tension and compression under constrained and unconstrained conditions. Virtual samples varying in width from 0.25 \(\mu\)m to 8 \(\mu\)m with an aspect ratio of 1.5:1 (Length:Width) were seeded randomly with discrete point sources on the active slip planes. Plastic deformation was described by the nucleation and glide of discrete edge dislocations along the active slip plane. The results of these simulations indicated that for samples that are constrained, such that the loading axis is not allowed to rotate, there was little size effect associated with the flow stress. The constraints produce GND’s and result in linear hardening and an increase in dislocation density with sample size. The GND’s acted as barriers to dislocations motion, preventing mobile dislocations from escaping the crystal easily and making it difficult to reach a dislocation starved state. The unconstrained simulations, comparable to the micro-compression experiments, indicated a large size dependence with the flow stress and an increasing dislocation density with sample size. The authors report a power-law relationship for the flow stress, \(\sigma_f\), as a function of the dimensions of the sample as \(\sigma_f = 67 \times 10^{-5} (W/W_0)^{-0.49}\). In the small samples, 0.25 \(\mu\)m, a steady state was
reached, whereby the dislocation nucleation rate was approximately equal to the rate of dislocations exiting the sample. However, in the larger samples, 8 µm, this state was never reached and the nucleation rate dominated.

Similar results were determined by Balint et al. [34] using 2D-DDS on unconstrained virtual samples between 0.15 µm and 8 µm in width. These simulations were performed on single crystals and polycrystalline samples with a high source density (HSD) and a low source density (LSD). The results indicated that grain boundaries in the polycrystalline samples acted as barriers to dislocation motion, similar to the GND’s previously, such that a dislocation starved state was never reached for the LSD and HSD samples and no size effect was observed. However, for single crystal samples between 1µm and 8µm a large size effect was reported for both the LSD and HSD conditions. The authors suggested that there are two contributions to this size effect. The first was a result of the source density being constant with samples size, so that the large samples would contain more sources and a higher probability of having a weaker source. The second is related to the dislocation starvation model suggested by Greer and Nix and modeled by Deshpande et al., whereby the density of dislocations exiting the sample is greater than or equal to the nucleation rate of new dislocations.

Building off the work of Deshpande and Balint, Benzerga et al. [35] used mechanism-based discrete dislocation simulations to study the scale dependence of mechanical properties. Benzerga et al. incorporated constitutive rules and the use length and time scales to explicitly model dislocation nucleation and interactions.
This allowed the authors to study dynamic junction formation, dislocation nucleation, and the destruction of junctions. Furthermore, Deshpande et al. and Balint et al. simply specified a source density and an associated strength for the activation of each source. Benzerga et al. allowed for the calculation of source strengths based on the arrangement (separation distance) of immobile dislocation junctions that are formed based on a starting dislocation density. Similarly, Benzerga et al. reported a size effect over the size range tested, 0.4 µm to 2 µm in width, such that the yield and flow stresses increased with decreasing sample size. The authors suggested that this apparent size effect is directly related to the source lengths that were formed from the network of immobile dislocation junctions prior to deformation. Therefore, the larger samples had a greater distribution of source lengths resulting in a greater probability of activating a large source, which is weaker than a small source. The longer source lengths in the larger samples resulted in a lower stress to initiate plastic flow. In the results published by Benzerga et al., a slight increase in the mobile dislocation density was observed as sample dimensions were reduced. This result is contradictory to the results published by Deshpande et al. and Balint et al.

Further study was performed by Parthasarathy et al. on the effects that source lengths and free surfaces play in size scale effects associated with small volume deformation. The model is built on the framework that if an initial/starting dislocation density exists in a sample prior to deformation, then there are internal sources associated with the immobile segments (junctions) of this density. An average source length is then given by the average separation distances between these junctions.
Similar to the ideas presented by G. Selviano, if the sample dimensions are decreased such that they begin to affect this average source length, then a size effect would evolve. If a double-pinned Frank-Read source exists near the surface of the sample, such that one pin lies outside the sample, then the dislocation arm/source length is truncated to a length defined by the internal pin and the sample surface. Given a random distribution of sources in a sample, at small sizes this source truncation effect would be more pronounced and cause a greater strengthening effect. The results of the model indicated that a source-truncation effect was sufficient in explaining the reported size effects in nickel and gold. The authors also suggest that a source activation process is controlling the size effects and not a source nucleation process as is the case for the early whisker experiments.

The modeling efforts provided by the previous authors are all very intriguing and offer interesting insights as to the cause of the reported size effect in the microcrystal compression experiments. However, the models are only based on experimental mechanical test data coupled with classical theory. The purpose of this work is to marry mechanical test results with transmission electron microscopy (TEM) analysis to gain insight and understanding into sample size effects related to the microcompression experiments in nickel, titanium, and nickel-titanium alloys.

2.2 Nickel Dislocation Dynamics

Nickel has a face-centered-cubic crystal structure (FCC), with a close-packed plane and direction, \{111\} and \langle 110 \rangle respectively. As such, dislocation motion
occurs on the \{111\} planes with a Burgers vector of \(a/2\langle 110\rangle\). In many FCC crystal structures the perfect \(a/2\langle 110\rangle\{111\}\) dislocation dissociates into two partial dislocations of type \(a/6\langle 112\rangle\{111\}\) dictated by the following reaction.

\[
\frac{1}{2}[\overline{1} 1 0] = \frac{1}{6}[\overline{1} 2 \overline{1}] + \frac{1}{6}[\overline{2} 1 1] \tag{2.3}
\]

The resulting partial dislocations, Shockley partial dislocations, are then separated by a stacking fault resulting from the change in stacking sequence of the \{111\} planes. For instance, the stacking sequence for the \{111\} plane, \(...ABCABCABC...\), is altered to \(...ABABCABC...\) with the passing of one partial dislocation. The dissociation of a perfect dislocation into partials results in a reduction in the overall line energy of the system; however, there is an increase in the energy needed to create the stacking fault. This creates a balance between these two energies and the separation distance, \(d\), between the two partials. The separation distance follows the following relationship,

\[
d = \frac{Gb^2}{4\Pi\gamma} \tag{2.4}
\]

where \(\gamma\) is the stacking fault energy and \(b\) is the Burgers vector. From this relationship, materials with high stacking fault energies would have a smaller separation distance between the partials than a material with a low stacking fault energy. This is important with regards to the mobility of the screw dislocation components. In order for a screw segment to cross-slip onto another plane the two partials must
constrict to form a perfect dislocation. Nickel has a relatively high stacking fault energy and therefore, cross slip is relatively easy compared to other FCC materials like copper and gold.

Nickel, with an FCC crystal structure, is classified into the bowing-mode class of materials based on the classification suggested by Nadgornyi. The primary strengthening mechanism associated with nickel single crystals are interactions between dislocations that are intersecting/interacting during plasticity. This strengthening effect, forest hardening, is then directly related to the number of dislocation segments that are inhibiting dislocation motion (the forest density, \( \rho_f \)) through the following relationship,

\[
\tau_f = \tau_p + Gb\alpha \rho_f^{\frac{1}{2}}
\]  

(2.5)

where \( \tau_f \) is the shear stress contribution from forest interactions and \( \alpha \) is the forest-hardening coefficient that is related to the ensemble-strength of dislocation junctions [37]

### 2.3 Titanium Metallurgy

Titanium alloys are typically composed of two phases, the low-temperature hexagonal-close-packed (HCP) \( \alpha \) phase and the higher temperature body-centered-cubic (BCC) \( \beta \) phase. Depending on the volume fractions of these two respective phases the alloy is typically classified as \( \alpha \), \( \alpha + \beta \), or \( \beta \). The majority of aerospace
titanium alloys consist of low volume fractions of the beta phase and therefore, the remainder of this document will be limited to α and near α (small volume fractions of β) alloys.

Pure titanium goes through an allotropic transformation \((α \rightarrow β)\) at 882°C. Alloying elements, substitutional and interstitial, are added in order to raise or lower this transformation temperature, and are classified as either alpha or beta stabilizers, respectively.

2.3.1 The Titanium-Aluminum Phase Diagram

The primary alpha-stabilizing element used in the majority of the commercial titanium alloys is aluminum, the titanium-aluminum phase diagram is found in Figure 2.2. Aluminum has been found to increase elasticity, decrease density and to be a strong substitutional strengthener, however, commercial alloys typically contain a maximum of 6 wt% Al to avoid any appreciable formation of the hard ordered Ti₃Al phase which has been found to embrittle the material [38]. In combination with these stabilizing elements, thermo-mechanical heat treatments can be performed to obtain several different microstructures, ranging from simple equiaxed α grains to Widmanstätten colony and basket-weave microstructures, as illustrated in Figure 2.3.
Table 2.1: Observed slip systems in alpha and near-alpha titanium alloys [1].

2.3.2 Deformation Modes in Alpha and Near-Alpha Titanium

The HCP $\alpha$ phase deforms via slip or twinning modes at low temperatures and predominantly by slip at higher temperatures, the various slip planes and directions are presented in Table 2.1 and Figure 2.4 [1]. From the symmetry of the hexagonal crystal, 6/mmm, the 3 $a$-type slip directions ($\frac{1}{3}(1\bar{1}20)$) are identical on the basal $(0\ 0\ 0\ 2)$ and prism $(10\bar{1}0)$ planes. The Critical Resolved Shear Stress (CRSS) needed to activate $c+a$ dislocations is much higher ($\sim 800$MPa) than that needed to activate $a$-type ($\sim 200$MPa) and therefore the majority of grains will deform via $a$-type slip [42]. However, if the loading is parallel to the $c$-axis, then dislocations with $a$-type Burgers vectors are immobile and the primary deformation mode is twinning.

In near $\alpha$ alloys, such as Ti-6Al-2Sn-4Zr-2Mo-0.1Si, a Burgers orientation relationship (OR) has been observed by Suri et al. between the $\alpha$ and $\beta$ phases (ie. $(101)_{\beta} || (0002)_{\alpha}$ , $[1\bar{1}1]_{\beta} || [2\bar{1}10]_{\alpha}$) producing three distinct slip directions on the basal plane [43], refer to Figure 2.4. The anisotropy produced by the OR has been implicitly studied by Savage et al. [44]. Their findings indicate a marked
disparity in the critical resolved shear stress between the $a_1$ basal, $a_2$ basal and $a_3$ basal slip systems. This is attributed to the difference between the burgers vectors of the two respective phases. For HCP crystals, the close-packed directions are $\langle 2110 \rangle$ type, whereas, in body-centered cubic (BCC) crystals they are the $\langle 111 \rangle$ directions. From the OR it is apparent that there are only two closely matching directions between the two phases, the $a_1$ and $a_2$. The $a_3$ has no matching burgers vector based only on the closed packed directions and therefore, the propagation of a dislocation through the $\beta$ phase would be very difficult. In contrast, along the $a_1$ direction, there is only a $0.7^\circ$ misorientation between the Burgers vectors of the $\alpha$ and $\beta$ phases, producing minimal strengthening from the beta phase. Experimental results by Savage et al. [44] confirm the CRSS’s ordering for the three systems as $\tau_{a_1} < \tau_{a_2} < \tau_{a_3}$.

As mentioned previously, $\alpha$ and near-$\alpha$ titanium alloys are classified into the kink-mode category for dislocation motion, dictated by the large Peierl’s stress. It has been shown by V. Vitek [45] that this large frictional stress is based on the dissociation of the dislocation core onto multiple slip planes. For example, nickel with an FCC crystal structure exhibits very little lattice friction as the core is distributed along the active glide plane, $\{111\}$. However, in titanium alloys deformation typically occurs along the $\{10\overline{1}0\}$ or the $(00\overline{0}2)$ with a Burgers vector of $\langle 11 \overline{2}0 \rangle$. The core is then distributed onto the $(00\overline{0}2)$ and $\{10\overline{1}0\}$ planes simultaneously, creating a substantial drag force, or lattice friction, on the moving dislocation.
2.4 Nickel-Titanium Metallurgy

Nickel-titanium alloys are very interesting materials due to the two unique properties that they exhibit, specifically, pseudo-elasticity and the shape memory effect. These properties are related to a martensitic phase transformation that occurs when the material is subjected to an externally applied load. In Figure 2.5 several stress-strain curves are presented for a Ti-50.6at.%Ni alloy tested at several different temperatures. The results indicate a transition in the shape to the flow curves at a temperature between 223.7K and 232.5K, corresponding to the solid-solid phase transformation temperature, $T_t \sim 225$ K for this alloy.

The flag shape is indicative to pseudoelastic behavior that results from the martensitic phase transformation. During loading cycle, the phase transformation from austenite to martensite begins at the critical transformation stress, $\sigma_M$. In Figure 2.5 this is indicated by a single arrow on curve ”j”. Further straining induces more transformation to occur until the sample is unloaded. Upon unloading, there is a remarkable recovery in strain, resulting from the transformation back to austenite. At higher temperatures there is an increase in the non-recoverable strain that remains after loading. Similiarly, at temperatures below $T_t$ the majority of the strain induced during deformation is non-recoverable; however, if the sample is subsequently heated to above the transformation temperature, a full recovery in strain is achieved. The later is termed the shape memory effect and has become very popular in the medical fields, particularly with coronary stents.
The transformation stress, $\sigma_M$, and transformation temperature, $T_t$, can be tailored by varying the at.% of titanium present in the alloy. The Ni-Ti phase diagram, presented in Figure 2.6, indicates that there are many different phases that are observed, depending on the composition and cooling conditions. For purposes of this document, we are concerned only with the composition Ti-50.7Ni at%. Thus placing the composition slightly on the nickel rich side of the phase diagram. The Ni-Ti phase is an ordered cubic phase taking on the $B_2$ (CsCl) crystal structure and is stable at temperatures from $\sim 700 \, ^\circ C$ to $1090 \, ^\circ C$. Above $1090 \, ^\circ C$ Ti-Ni goes from the ordered $B_2$ structure to a disordered BCC crystal structure.

2.4.1 Ni-Ti Deformation modes

As mentioned previously, the primary deformation mode in Ni-Ti alloys is the transformation from the $B_2$ crystal structure to a martensitic variant. In solutionized alloys, this transformation occurs from the $B_2$ structure directly to the monoclinic $B_{19}'$ structure. A schematic of this lattice transformation is found in Figure 2.7. In this figure, 4 unit cells of the $B_2$ lattice are represented by the lightly colored lines in (a) and the tetragonal $B_{19}$ lattice is represented by the bold lines. In order to get the $B_{19}$ lattice (the dotted unit cell in (b)) to the $B_{19}'$ lattice, the $\lbrack 0 \quad 0 \quad 1 \rbrack$ vector shrinks to become $a$, the $\lbrack 0 \quad 1 \quad 1 \rbrack$ vector shrinks to become $b$ and the $\lbrack 0 \quad 1 \quad 1 \rbrack$ vector expands to become $c$. This is followed by a shear to change $\beta$ from $90^\circ$ to $96.8^\circ$ to create the monoclinic $B_{19}'$ lattice.
In addition to the transformation, dislocation motion has also been observed by several authors \[48-51\]. A study by Y.I. Chumlyakov et al. \[48\], performed on single crystals of Ti-50.8 at.%Ni-0.3 at.%Mo, determined that dislocations within the B2 phase prefer a $\langle 1\,0\,0 \rangle \{1\,1\,0\}$ even though the Schmidt factor for a $\langle 1\,0\,0 \rangle \{1\,0\,0\}$ was much higher in some cases.

It is well known that there is a loss in pseudoelastic behavior as the material is subjected to repeated loading cycles \[52\]. Transmission electron microscopy (TEM) performed on single crystals by Hurley et al. \[49\] determined that there was an increase in the dislocation density as a function of the number of cycles. However, these were qualitative comparisons and no determination of active burgers vectors or slip planes was performed. It is currently unknown how dislocation motion contributes to the martensitic transformation in nickel-titanium alloys.
Figure 2.1: Copper and iron whisker data collected from [13–17], indicating a substantial increase in strength as the wire diameters were reduced.
Figure 2.2: Titanium-aluminum phase diagram.
Figure 2.3: Common titanium microstructures: (a) Ti-6Al single phase globular $\alpha$ [39]. (b) Widmanstatten colony microstructure, $\beta$ is the dark phase [40]. (c) Basket-weave microstructure in Ti-6Al-4V, $\beta$ is the dark phase [41]. (d) Duplex microstructure consisting of globular $\alpha$ and $\alpha + \beta$ colonies, $\beta$ is the white phase [41].
Figure 2.4: (a) Slip planes and directions in the HCP \( \alpha \) phase \[1\] (b) The orientation relationship between \( \alpha \) and \( \beta \).
Figure 2.5: Stress-strain curves for a Ti-50.6at.%Ni alloy as a function of temperature [2].
Figure 2.6: The Ti-Ni Phase Diagram [2].
Figure 2.7: A schematic illustrating the lattice change from the parent B2 (a) to the tetragonal B19 (b) i, j and k refer to the B2 lattice and i', j' and k' refer to the monoclinic B19' lattice [2].
CHAPTER 3

EXPERIMENTAL PROCEDURES

3.1 Introduction

This section will serve as an overview of the experimental procedures that are common to each of the three material systems studied. The procedures specific to an individual system are found in subsequent chapters.

3.2 Bulk Sample Preparation

Bulk samples were cut to button size, similar in size to that of a dime, using a South Bay slow speed cut-off wheel, Model 660, to minimize dislocations formed during the cutting process. The button samples were then mounted to a parallel polishing puck with Super-Glue to be used on an Allied High Tech MultiPrep System. This system provides the capability to polish sample surfaces parallel with high fidelity, this becomes very important with regards to sample alignment during compression testing. The two large surfaces of the button samples were polished using silicon carbide polishing paper followed by a lapping of 0.05 µm colloidal silica.
to reach the desired surface finish. The button samples were then removed from the polishing puck with acetone and attached to a standard SEM stub with silver paint.

### 3.3 Microcrystal Fabrication

Microsamples were fabricated with the use of a dual beam Focused Ion Beam (FEI DB-235), whereby large gallium ions were accelerated at the surface of the button samples to preferentially remove material. This process involved two steps suggested by Uchic et al. The first step involved ion-milling perpendicular to the samples surface, such that material was preferentially removed from areas around the center point of the circle, refer to Figure 3.1a. As material was continually removed, a post with tapered sidewalls, a "perform", was created with its base continuous with the substrate, evident in Figure 3.1b. As second step was required to make the side-walls parallel. This step was very similar to that of a lathering operation, whereby the ion beam is no longer perpendicular to the sample surface, but rather at a glancing angle. An automation script (written by M. Uchic and M. Seekely at Air Force Research Laboratory in Dayton, Ohio) removed material from the tapered sidewall, rotated the sample 5-10 degrees to expose another increment of the tapered sidewall and removed material again. This process was repeated through the 360 degrees needed to make a full rotation. The result was a microcrystal with parallel sidewalls, a constant gauge length and a base continuous with the substrate material. Utilizing these techniques, microsamples were fabricated with sizes ranging from 1 to 60 microns in diameter.
Figure 3.1: a) A "preform" produced by ion milling perpendicular to the sample surface b) The finished compression specimen produced by lathing away the tapered side-walls.
3.4 Uniaxial Compression Testing

The microcrystals were uniaxially compressed using an MTS Nano Indenter XP outfitted with a flat diamond indenter tip. To ensure proper sample alignment with the indenter tip, a goniometer stage was used to make fine adjustments. Time, load and displacement data were acquired using MTS Testworks© software at an acquisition rate of 50Hz.

3.5 Transmission Electron Microscopy

Due to the size of the compression specimens, conventional TEM foil preparation techniques were not useful. Therefore, TEM foils were extracted from the deformed microcrystals with the use of an insitu plucking device, OmniProbe™. This process is depicted in Figure 3.2. A thick platinum cap was deposited on top of the sample to protect it from ion damage during the extraction process. The FIB was then used to isolate material by milling away the surrounding material. The OmniProbe was then lowered until contact with the selected material was made and attached by depositing platinum onto the OmniProbe and the selected material, essentially ”gluing” the two together. The selected material was then released from the bulk material by milling away the contact point. The result is a piece of deformed material attached to the OmniProbe. At this point there is no way to place the sample into the TEM. Therefore, the sample must be transferred to a special copper TEM grid. This is accomplished by again attaching the TEM foil to the copper grid with platinum and subsequently ion milling away the area where
the Omni-Probe and TEM foil are in contact. The result is a piece of deformed material attached to a copper TEM grid. At this point the TEM foil is not electron transparent because the thickness is larger than \( \sim 250 \text{nm} \). Therefore, subsequent thinning is performed using the FIB until electron transparency is achieved.
Figure 3.2: TEM sample extraction process (a) Microcrystal prior to sample extraction (b) Platinum is deposited on the slip trace of interest to protect the sample surface, then the top portion of the microcrystal is ion milled away with the FIB (c) The OmniProbe is attached (not shown in this image) and the slip trace is undercut, freeing the TEM sample from the base (d) The TEM sample is then transferred to a copper grid by attaching the TEM sample with platinum. The OmniProbe is then cut away from the TEM sample with the FIB (not shown in this image). Subsequent thinning is then performed with the FIB until the TEM foil is electron transparent.
CHAPTER 4

NICKEL

4.1 Introduction

Over the last 50 years, numerous experiments at the micro-scale have examined the effect of sample size on mechanical behavior. Much of the early work in this field during the late 1950’s and 1960’s focused on tension experiments of metallic whiskers (nominally dislocation-free crystals) having micron-scale diameters \(9, 13-18, 54\). These experiments clearly showed for a number of different material classes that dramatic strengthening occurred as the sample diameter decreased. Whisker experiments were, however, limited to specific material that could be easily grown in this form, often via chemical vapor deposition. These crystals were essentially defect free containing little or no dislocation content, and the increase in flow strength was attributed to the difficulty to nucleate dislocations in these small volumes. However, this lack of dislocation substructure is far different from most engineering materials that contain a starting dislocation density of at least \(10^{12} \text{ m}^{-2}\). Therefore, the effect of sample size for small volumes that contain significant initial dislocation
densities remains an open question. Recent advances in micro-sample fabrication methods have helped spur a renewed interest into mechanical size effects associated with sample dimensions at the micro- and nano-scale. For example, micron-size compression samples have been fabricated from bulk crystals with the use of Focused Ion Beam (FIB) microscopes \[7, 27, 28, 55\]. Unlike the whiskers, these microsamples have microstructures that are nominally representative of bulk crystals that have a grown-in dislocation forest. Still, the results of these tests indicate a dramatic increase in strength as the sample dimensions are reduced to sizes smaller than 20 microns in diameter \[7, 27–29, 55, 56\].

Although much experimental data has been acquired with regards to stress and strain, very little experimental data exists pertaining to the dislocations and arrangements that are possibly driving this behavior in these microcrystals. This in turn has led to several hypotheses and publications based on intuitive insights, classical theory and dislocation plasticity models. Greer and Nix \[28\] suggest that small-scale size effects are associated with the starvation of mobile dislocations, as the proximity of free surfaces allows for the movement of dislocations out of the sample before they have a chance to multiply. Using two-dimensional discrete dislocation plasticity, simulations have verified the starvation ideas purposed by Greer and Nix whereby the rate of dislocations exiting the sample is approximately equal to the dislocation nucleation rate \[34, 36\]. Alternatively, Volkert and Lilleodeen \[55\] suggested that free surface image stresses and dislocation source-limited behavior are contributing a loss of mobile dislocation density resulting in an increase in stress.
to activate a Frank-Read source. Considering the stochastics of dislocation source lengths, Parthasarathy et al. \[57\] has eluded to a strengthening mechanism caused via the truncation of a source arm length as sample dimensions approach the source length of a Frank-Read source.

Given the state of experimental evidence, the objective of this study is to quantitatively characterize changes in the dislocation substructure for previously-published microcrystal deformation experiments of pure Ni \[7, 27\]. Specifically, we have performed quantitative dislocation density measurements on undeformed microcrystal samples, and deformed samples ranging from 1 to 20 microns in diameter. These results are discussed in context to current theories of microcrystal deformation.

4.2 Experimental

4.2.1 Nickel Compression Results

Pure nickel microcrystal compression samples were fabricated using a Focused Ion Beam (FEI model DB235), following the procedures published elsewhere \[7, 27\]. The samples varied from 1 micron to 40 microns in diameter, having their loading axis aligned along the \([2\ 6\ 9]\) single-slip direction. These samples were subsequently uniaxially compressed using an MTS NanoIndenter XP outfitted with a flattened diamond tip. Nominal deformation strain rates of \(10^{-4}/s\) were achieved under a hybrid loading method, where a programmed constant-displacement rate was imposed on the sample. If under the closed-loop control the loading tip velocity was
found to exceed the programmed rate, the control loop forced a constant load hold. That is, the sample was permitted to experience either an increasing load, or a load hold, but never load shedding until the test was complete.

The results of compression testing indicated a dramatic increase in flow strength as the sample size is decreased \[27\]. Figure 4.1a is a composite plot for all sample sizes that were tested. For illustrative purposes, each curve in Fig. 4.1a is a representative test reflecting the average flow stress from the family of tests conducted at each sample size. Evident from the flow curves is a distinct transition in strain-hardening behavior at sample sizes of 10 microns or less. For samples larger than 10 microns a strain-hardening rate (SHR) of \( \sim G/2000 \) is observed, as is typical of Stage 1 glide for macroscopic samples. However, for samples smaller than 10 microns, there is a variable, sometimes broad, yielding transition strain, that includes intermittent burst periods of flow under conditions of no strain hardening. These burst-like events have been linked to the same scale-free behavior observed in selected macroscopic systems, such as plate tectonics of the earth \[58\]. Furthermore, it has been shown by Dimiduk et al. \[27\], that the flow-stress scaling behavior (stress as a function of sample diameter) correlates closely with the predicted scaling behavior suggested by Gil Sevillano et al. \[31\]. Those predictions were based on an areal-glide dislocation percolation model that remains to be physically validated.
Figure 4.1: a) Nickel microcrystal compression results. b) Critical stresses needed to activate each of the three primary slip systems calculated from the Schmidt factors based on the [2 6 9] loading direction.
4.2.2 TEM Sample Preparation

The majority of the foils that have been examined in this study were prepared from active slip bands in the microcrystals. For these samples, after deformation the primary slip traces are clearly visible (Fig. 4.2). The slip traces were used to align the samples for subsequent transmission electron microscopy (TEM) sample extraction along the primary active (111) slip plane. Due to the small size of these samples, conventional TEM sample preparation techniques were not feasible and, therefore FIB fabrication methods were used to make the TEM foils [59].

This particular study used an FEI Strata DB 235 and an in-situ micromanipulator (OmniProbe™) to extract and subsequently thin the samples to electron transparency.

For most FIB-based TEM foil preparation methods, it is normal practice to deposit a thin film of carbon or platinum on top of the area-of-interest, which keeps this material from milling during the foil-thinning process. However, such a protective film is usually thick enough to obscure surface details when imaging, which makes locating the position of the active slip band difficult after the film is in place. To ensure that the TEM foil contained an active slip trace, a two-step film-deposition procedure was used to define the plane of the active slip band. The first step consisted of depositing fiducial markers of platinum that were placed at multiple locations along a particular slip trace. Here, the fiducial markers were in the shape of a cross, where the intersection of the cross and the surface trace of the slip plane coincided, as shown in Figure 4.2. The second step consisted of covering
the entire slip-plane region with a carbon film to protect the sample during FIB thinning. During the thinning process, the Pt crosses initially appear on the cross-sectional surface as two distinct points along the outer edge of the microsample. As this cross-sectional surface is milled closer to the active slip plane, these two points move closer together and ultimately merge into a single point at the position of the slip trace.

After thinning the foil to thicknesses that were marginally electron-transparent with the DB 235, a second milling procedure was employed to both reduce the ion-damage layer produced by the 30 kV Ga$^+$ ions and, to further thin the foil for improved imaging. Although the Ga$^+$ ion damage appears to have a negligible effect on the compression experiment results [33], these energetic ions produce contrast variations that affect the imaging conditions in the TEM. To minimize this damage, a Gatan Duo Mill was used to perform low-energy milling at voltage settings of 1-2 kV, a beam current of 0.5 mA, and a milling angle of 13 degrees. Milling times varied between 30 minutes to a few hours in order to produce optimal samples. Upon examination of the TEM samples, it was determined that the residual stresses and small sizes associated with these foils accentuate the bend contours imaged by conventional TEM (CTEM) methods. Therefore, scanning TEM (STEM) imaging was used to minimize these effects. Several studies have shown that under certain conditions the time-resolved STEM image is related to the spatially resolved CTEM image by the principle of reciprocity [60, 61], whereby the incident angle in CTEM is equal to the exit angle in STEM and vise versa. This principle allows for the
Figure 4.2: A series of secondary electron images taken from the FIB to illustrate the TEM extraction procedure from a $\mu$m diameter sample. a) Typical sample after deformation indicating several slip traces. b) Platinum crosses are placed along regions of the desired slip trace to act as fiducial marks during the final thinning process. c) Excess material is FIBd away to leave only the slip trace of interest. d) The TEM sample is attached to the OmniProbe needle and then transferred to a copper grid. e) The TEM foil is attached to the copper grid using carbon and platinum deposition. f) The TEM foil is thinned to electron transparency from both sides until the platinum fiducial marks are reached.
imaging of defects, such as dislocations, in bright-field-STEM mode (BF-STEM). Maher and Joy have shown that by increasing the convergence angle in STEM mode the signal to noise ratio is increased, thereby minimizing extinction contours such as thickness fringes and bending contours. However, the increase in convergence angle also causes a loss in dynamical information, such as contrast related to dislocations and stacking faults. Therefore, a convergence angle of 9 mRad was used as a compromise between minimizing the contrast of the bending contours while maintaining adequate contrast from the dislocations. Maher and Joy also demonstrated that when using an appropriate convergence angle a two-beam condition can be obtained and g-b analysis can be performed to determine dislocation Burgers vectors. All TEM microscopy for this study was performed on a 200 kV FEI/Phillips Tecnai TF20 outfitted with a field-emission electron source. Energy filtering and image collection was utilized via the use of a Gatan imaging filter (GIF) and BF/DF STEM detector.

4.2.3 Dislocation Density Measurement

Dislocation densities were calculated using two different methods. A line/point-intercept method was used for the TEM foils sectioned parallel to the slip-planes, whereby 5 randomly-placed lines of different angular orientation are drawn over the TEM images. This was facilitated by use of the image-processing and measurement software Fovea Pro 4.0 by Reindeer Graphics. Points are manually placed at the intersection of each dislocation with the random lines. The density, $\rho$, is simply
the number of points, $N$, divided by the total line length of the random lines, $L_r$, multiplied by foil thickness, $t$ [62]:

$$\rho = \frac{N}{L_r t} \quad \quad (4.1)$$

The accuracy of the density measurements, determined using this formula, relies foremost upon precise measurement of foil thickness, which, in the present study, was determined using an energy-filtered convergent beam electron diffraction (EF-CBED) technique [63, 64]. In a CBED pattern there are intensity oscillations, otherwise known as Kossel-Möllenstedt fringes, which occur in the $\{0 \ 0 \ 0\}$ and $\{h \ k \ l\}$ discs under a two-beam condition. Knowing the extinction distance and the spacing of these intensity oscillations, the thickness can be deduced [64, 65]. These concepts are used in a simulation program developed by P. Stadelmann, JEMS [66]. The microscope conditions were input into the simulation package and the intensity oscillations for several thicknesses were compared to the actual CBED image taken on the microscope. From this comparison, the foil thickness was determined. Energy filtering was employed to accentuate the fringe patterns by eliminating inelastically-scattered electrons using an energy window of $\pm 10$ eV centered around the 200 keV elastic-energy peak. After collection of the EF-CBED pattern using a CCD camera, pixel averaging in the direction parallel to the fringes was also used to further improve the signal-to-noise ratio. Figure 4.3 shows a representative pixel averaged EF-CBED pattern compared to a CBED pattern simulated in the JEMS.
software. Kelly, et. al., has shown that thickness measurements having an accuracy of ±2% or better are routinely determined using this type of CBED measurement [64].

A second technique was used to check the reliability of the dislocation-density results obtained from the line/point intercept method. This method calculated the density by measuring the total dislocation line length within the TEM foil, which is a much more difficult task to perform using image-processing software as compared to the line/point intercept method. For selected foils, the dislocation structure was traced manually using Adobe Photoshop software, and the total line length, $L_t$, was calculated using the Fovea Pro software. The total density, $\rho_t$, was calculated using the following relationship [67]:

$$\rho_t = \frac{L_t}{At} \tag{4.2}$$

where $A$ is imaged foil area. Figure 4.4 illustrates the two different techniques used to determine the dislocation densities. The difference in the measured densities between the two techniques is minimal compared to other errors that are present during the measurement. For this reason, the line/point method was determined to be sufficient for dislocation-density measurements. For the measurements taken from foils cut parallel to slip planes described in this study, all imaged dislocation segments were considered which resulted in a measured total dislocation density for the sample (as opposed to the forest-dislocation density).
4.2.4 Errors in Density Measurements

There are two primary, quantifiable, sources of error related to the present dislocation-density measurements for any given TEM sample. The first was mentioned earlier and is associated with measuring the foil thickness, $\pm 2\%$ being typical for CBED measurements. However, this value assumes a constant foil thickness over the viewing area, which is not the case for real samples. During the FIB-thinning of the extracted TEM foils, there is usually a constant taper to the samples from one end to the other, which is evident in thickness measurements taken at different locations within a foil. Figure 4.5 shows a plot of three thickness measurements taken along the long axis of the elliptical-shaped view areas of the foils, for both a 2 $\mu$m- and 20 $\mu$m-diameter microcrystal. This plot demonstrates that for the preparation methods used in this study the taper is constant and, therefore, one must only measure the thickness in the middle of the foil to make a reasonable determination of thickness. From the analysis of these two foils, it was determined that using only a single measurement increases the error of the thickness value to $\pm 5\%$. Thus, for most of the foils, only a single measurement from the center of the foil was used to determine thickness.

The second quantifiable source for error is related to the difficulty in imaging dislocations that are grouped closely together, whereby their intensity profiles overlap under bright-field-imaging conditions. The error associated with this overlap was determined by measuring $N$, the number of line/point intersections, for a given viewing area both under bright-field- and "dirty"-dark-field-imaging conditions and
comparing the two measurements. The difference between the two measurements made by these two imaging methods, having notably different resolutions and susceptibility to image-peak overlap, is an indicator of what is not detected by the readily-performed STEM imaging. From this measurement, it was determined that there is approximately a 30% underestimate in $N$ when using bright-field STEM imaging. These two errors are combined in quadrature and the results are displayed using error bars for the density measurements that are shown in the rest of this study.

There are other errors that are very difficult to quantify. These errors include magnification errors that are related to the imaging of smaller TEM foils at a higher magnification as opposed to a larger TEM foil. Another error is simply related to the geometry of the TEM foil and the dislocations that lie parallel to the foil normal. These dislocation segments are then truncated to roughly the thickness of the TEM foil. As a result, including tilting limitations inside the microscope, imaging such dislocation segments is difficult and are probably not counted in the total density measurements. As such, all dislocation measurements should serve as a lower bound measurement.

4.3 Results

4.3.1 Dislocations in Undeformed Regions

In order to establish a reference for interpreting the microcrystal deformation behavior, assessments were made of the pre-existing dislocation structure, $\rho_0$, within
the macroscopic crystal. For this TEM samples were extracted from fully-machined but untested microcrystals using sectioning planes oriented parallel to the same primary \((\overline{1} 1 1)\) plane as examined for the deformed samples. A low-magnification view of the undeformed region can be seen in Figure 4.6. From the images, values of \(\rho_0\) were determined to be \(\sim 1.4 \times 10^{13} / \text{m}^2\). The observed high magnitudes determined for \(\rho_0\) clearly distinguish the initial state of the pure Ni microcrystals studied in [7, 27] from that of the dislocation-free state reported for metallic whiskers.

In addition to the \((\overline{1} 1 1)\) foils, TEM samples were also extracted from undeformed material having an orientation off-parallel to the \((\overline{1} 1 1)\). As a result of selecting such foil orientations, the measured dislocation densities are believed to directly correspond to the forest-dislocation density, \(\rho_f\), that will be experienced by the glide system(s) of deformation. Such is not the case for foils sectioned parallel to the primary glide plane and for those measurements some correction factor must be used to determine \(\rho_f\), as discussed later. Density measurements from these foils ranged from \(\rho_0 = \rho_t = \rho_f = 5.5 \times 10^{12} / \text{m}^2\) to \(1.6 \times 10^{13} / \text{m}^2\).

4.3.2 Dislocation Structure from Deformed Bulk Samples

In addition to examining the starting dislocation density in microcrystals, TEM foils were prepared from deformed bulk single-crystal compression samples using conventional sectioning and electropolishing methods. The foils were oriented parallel to the primary \((\overline{1} 1 1)\) slip-plane traces for those crystals. A BF-TEM image of a deformed bulk \((4 \times 4 \times 10 \text{ mm})\) compression sample is shown in Figure 4.7.
along with a BF-STEM image from a deformed 2 μm diameter microcrystal, where both samples experienced the same nominal engineering strain of approximately 2%. This substructure is consistent with the associated mechanical test data, as for this value of strain the bulk crystal is exhibiting late Stage I flow, while the microcrystals can sustain Stage I hardening out to engineering strains in excess of 20%. Qualitatively the dislocation ensembles and heterogeneity are quite similar between the two samples. The bulk samples exhibit larger regions that contain little or no dislocation content; however, this may be a sampling artifact related to the location that the microcrystal was fabricated. In order to draw any conclusions from these defect free zones in the bulk, more TEM samples are needed from small (∼2μm) microcrystals containing similar strain values.

4.3.3 Dislocation Structure Versus Sample Size

BF-STEM images taken from the slip-plane foils of the 1μm, 2μm, 5μm, 10μm and 20μm microcrystals indicate that a dislocation substructure has formed in these nickel microcrystals, as shown in Figure 4.8. In each case, the dislocation structure resembles that of Stage I glide, containing predominately edge-character dislocation tangles [68]. These dislocation tangles consist of multi-polar dislocation braids that are believed to be formed from dislocation annihilation of screw-character segments during cross-slip [69]. Figure 4.8 also illustrates that the scale of the inter-braid spacing remains nominally constant as the sample dimensions are decreased. The inter-braid spacing was measured to be ∼2.2μm for the 20μm diameter microsam-
Table 4.1: The three highest resolved slip system in nickel given the loading direction of $[269]$. 

<table>
<thead>
<tr>
<th>Slip system</th>
<th>Burgers vector</th>
<th>Slip plane</th>
<th>Schmidt factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\frac{a}{2}[101]$</td>
<td>$(\bar{1}11)$</td>
<td>0.48</td>
</tr>
<tr>
<td>2</td>
<td>$\frac{a}{2}[10\bar{1}]$</td>
<td>$(111)$</td>
<td>0.40</td>
</tr>
<tr>
<td>3</td>
<td>$\frac{a}{2}[110]$</td>
<td>$(\bar{1}11)$</td>
<td>0.35</td>
</tr>
</tbody>
</table>

Due to the large stresses experienced by the microsamples, it is expected that multiple slip systems may be operative. Schmidt factor calculations indicate that with a loading direction of $[269]$ the three slip systems having the highest resolved shear stress are found in Table 4.1. The critical stresses required to activate each of these slip systems, $\sigma_c^1$, $\sigma_c^2$, $\sigma_c^3$, are illustrated on the stress-strain curves presented in Figure 4.1. These results
suggest that for samples smaller that 20\(\mu\)m in diameter all three of these slip systems should be active. In fact, slip-trace analysis of the microsamples after loading indicates that (\(\overline{1}11\)) is the primary active slip plane for all samples tested; however, for samples smaller than 10 \(\mu\)m in diameter a secondary system on the (111) plane is operative as well [27]. From the size of the slip steps, the majority of the strain is accrued along the primary (\(\overline{1}11\)) system at all sizes tested, but the secondary system becomes more pronounced at smaller sizes. TEM observations indicate the presence of all three active slip systems in several of the slip plane foils, whereby g-b analysis was performed and the results are shown in Figure 4.9. The numbers in these images correlate to the slip system, as determined from this analysis, for each dislocation segment, 1,2, or 3 designated from Table 4.1. These TEM results indicate that the majority of the dislocations are 1/2[101](111) type with roughly equal contributions from the other two systems. Although each of these slip systems experience a different resolved shear stress, as illustrated in Figure 4.1a, the stresses reached in these microsamples are large enough to activate all three slip systems, at least on the local scale.

4.3.5 Measured Dislocation Density Versus Sample Size

The dislocation densities for several deformed microsamples were measured using the line/point method described previously. These data are plotted on a log-log plot and shown in Figure 4.10. The most important result from these measurements is the increase in the stored dislocation content as the sample size is decreased. As
with any ex-situ or post mortem TEM experiment, the dislocation structure observed is representative of that from the very end of the loading cycle. Careful attention was paid such that the samples were not unloaded until they had recovered from a strain-burst event; that is, until the natural strain-hardening processes led to a cessation of deformation. Therefore, one is assured that the observed dislocation substructure was able to sustain the final stress prior to unloading. It is this final shear stress and ending dislocation structure that was used in all experimental measurements and calculations, unless otherwise stated.

The increasing dislocation density with decreasing sample size observed after deformation (Figure 4.10)–in conjunction with the measurements of significant initial dislocation content–contradicts the hypothesis that the increase in strength in microcrystals can be solely attributed to dislocations leaving the microcrystal (one type of starvation mechanism) [33]. Should that be true, one might expect to observe dislocation densities in deformed samples that are equal to or less than the initial dislocation density. A caveat to these measurements is that it is not possible to stop all tests at the same magnitude of strain, especially for the smaller samples, because of the rapid stochastically-occurring strain bursts during testing. As a result, there are variations in the amount of plastic strain imposed from sample-to-sample. Also, nominal-strain values are reported that are obtained by averaging across the entire gauge section of the sample, whereas the local strains that a given slip trace experiences are much larger.
The systematic increase in dislocation density may be attributed to several possibilities. The first of which is related to the density measurement method used for this study. The density measurements performed in this study are both difficult and time consuming. Throughout this study careful attention was paid in all aspects of the measurement process; however, while imaging in BF-STEM conditions there was variability in the magnification used to determine N. The variability in the magnification was not large and as such is not likely related to the significant increase in density. A more likely scenario is related to the activation of the secondary slip systems. As indicated by the SEM studies by Dimiduk et al., the secondary slip system becomes more pronounced at smaller sizes. This would increase the forest density and increase the effective storage of the system, creating an increase in total density as sample sizes are reduced. Another possibility may be related to the slip localization at smaller sizes. For the larger samples slip may occur on many possibly planes along the gauge length of the sample. However, as the sample dimensions are reduced, the number of possible planes decrease. This creates a higher probability of localized slip on a give slip trace, resulting in a larger density at the smaller sizes.

In addition to the increase in stored density with decreasing sample size, there appears to be no evidence that the observed dislocation density is a significant function of the imposed strain level, as revealed by the data shown in Figure 4.11 for 2 µm diameter samples. In fact, large measured densities exist on active slip bands after only 11% shear strain. These structures are not substantially changed at higher strains (consistent with the Stage I glide model [69]). The results suggest
that dislocation substructure is forming and sustaining the large observed stresses very early in the loading cycle. Perhaps the structures are formed during the early strain hardening, or exhaustion-hardening interval [27], but this point requires further investigation. The density decreases with increasing strain, although the total densities are still in excess of the initial dislocation density. This result is supported by the shape of the flow curves for 2 micron diameter samples in Figure 4.1a, which exhibit little or no work hardening after reaching a critical stress, and is also consistent with the patterning of the dislocation substructure that is indicative of Stage I glide and therefore dramatic increases in density are not to be expected with large changes in strain.

4.4 Discussion

For discussion purposes we propose some useful nomenclature that will be used throughout the rest of this document. Given a single-crystal volume of material, there is an inherent or reference stress associated with the combined effects of the initial dislocation-forest density, Frank-Read source operation and the Peierls-Nabarro or lattice-friction stress. In an isotropic FCC material, at room temperature, the Peierls stress is an essentially negligible constant (for most stress estimates given here, a value of 2 MPa was assumed). Therefore, the reference stress is strongly influenced by the initial forest density and source-operation stresses. All subsequent evolution of the dislocation structure must occur under kinetics governed by attaining an effective stress that exceeds the sum of the reference-stress components.
Therefore, the discussion proceeds first from an evaluation of the components that constitute the reference stress and then to a discussion of the effective stress related to nickel microcrystals.

4.4.1 Forest Hardening

Dislocation interactions were first purported theoretically in 1934 by Taylor \[75, 76\], Orowan \[77\], and Polanyi \[78\] and then empirically supported by Bailey and Hirsch (1960) \[79\]. Those studies purported a constitutive relationship to relate the shear stress to the dislocation forest density, $\rho_f$, or

$$\tau = \tau_p + Gb\alpha\rho_f^\frac{1}{2}$$  \hspace{1cm} (4.3)

where $\tau_p$ is the Peierl’s stress, $b$ is the Burgers vector, $G$ is the shear modulus and $\alpha$ is the forest-hardening coefficient that is related to the ensemble-strength of dislocation junctions \[37\]. From the time that this proposed relationship was carefully evaluated, it was clear that the proposed stress scaling as $\rho_f^\frac{1}{2}$ was not exactly consistent with experiments and, that a logarithmic correction was needed to account for the self interactions of the dislocations bowing at the forest obstacles. Recently, Madec et al \[80\] and Bulatov et al \[81\] examined these relationships with the use of large-scale dislocation dynamics (DD) simulations to study junction formation and strain hardening in FCC and BCC crystal lattices. To accurately describe their simulation results, Madec, et. al., reintroduced the logarithmic term into Eq. 4.3 and yielding the following forest-hardening law,
\[ \tau_f = \tau - \tau_p = k_f G b \ln \left( \frac{1}{\sqrt{\rho_f/b}} \right) \sqrt{\rho_f} \]  

(4.4)

where \( \tau \) is the shear stress, \( \tau_{forest} \) is the forest-hardening component of the shear stress and \( k_f \) represents the average strength of the dislocation forest having a value of 0.1 [80]. However, results from Z.S. Basinski [82] suggest that other values for the scaling coefficient may be more appropriate. Dislocation density measurements from copper published by Basinski [82] indicated that the flow stress scales with forest density through the relation:

\[ \sigma_{flow} = k \rho_f^{0.425} \]  

(4.5)

where \( k \) is a constant. For the present study, estimates of the scaling of stress to the forest dislocation density were made by using the experimental data for Cu given by Basinski. Assuming that the scaling exponent determined for Cu applies to Ni, by adjusting for the values for \( G \) and \( b \) for Ni the values for \( \alpha \) and \( k_f \) were determined. It was found that an \( \alpha = 0.40 \) and \( k_f = 0.061 \) are the appropriate empirically-derived coefficients for nickel to use in Eqns. 4.3 and 4.4, respectively.

When practically applying Eqns. 4.3,4.4 such as is done in this study, it is important to recognize that there is some ambiguity associated with selecting the ratio, \( R \), of the forest density to the total density \( (\rho_f = R \rho_t) \) for a given test geometry and strain value. As mentioned previously, for most of the present dislocation density measurements \( \rho_t \) was determined. Therefore, relating the values of \( \rho_t \) to the
shear stresses associated with forest hardening, using Eqn. 4.4, leads to uncertainty. Attempts were made to quantify the density contributions from each of the three active slip systems; however, as a result of imaging difficulties caused by ion damage, accurate measurements were not possible. Such measurements would have guided selections of the value of $R$. Instead, two values, $1/2$ and $3/4$, were selected to provide lower and upper bounds to the likely range. The lower bound of $1/2$ was taken from Basinski and Basinski [72]. The upper bound value was selected under the assumption that three slip systems of the 12 possible were likely to operate and, those not operating present a dislocation forest to the operation ones.

Using the measurements for $\rho_0 = \rho_f (5.5 \times 10^{12}/m^2$ to $1.6 \times 10^{13}/m^2)$ taken from foils cut parallel to the stress axis, together with Eqn. 4.4, the background internal forest-hardening stress was assigned a range of values from 14 – 26 MPa. These results are presented in Figure 4.12.

### 4.4.2 Source Operation and Source-Truncation Hardening

Recently, Parthasarathy, et. al., purposed a model to describe the increase in strength in microcrystals considering the combined effects of stochastic variations of dislocation source lengths, a limited sample volume, and truncation of sources at the nearby free surfaces [57]. The model is based on the idea that as sample dimensions are reduced to the same order-of-magnitude as the source lengths, a double-pinned Frank-Read source becomes a single-pinned source having a free arm interacting with a surface. Source activation is dictated by the operation of the easiest source or the
source having the largest source length. Thus, if the average maximum source length decreases, the average stress needed to activate a source increases. Therefore, given a random distribution of sources, generated from the initial dislocation density, an average effective source length, $\bar{\lambda}$, is related to an effective truncation stress, $\tau_s$, through the following relationship,

$$\tau_s = k_s G \frac{\ln(\bar{\lambda}/b)}{(\bar{\lambda}/b)}$$  \hspace{1cm} (4.6)

where $k_s$ is a source-hardening constant, having the magnitude $k_s = 0.12$, derived through current-ongoing study.

Using the $\rho_0$ values taken from the undeformed foils sectioned parallel to (111), the strengthening effect associated with source-truncation hardening was derived and, is plotted in Figure 4.12 as a band representing the variation in $\rho_0$ measurements.

### 4.4.3 The Reference Stress

Combining the strengthening terms from the Pierel’s stress, $\tau_p$, initial forest-hardening stress given by Eqn. 4.4, $\tau_f$ and, the source-truncation hardening stress given by Eqn. 4.6, $\tau_s$, an equation representing the total reference stress of the microcrystals is established as:

$$\tau_r = \tau_0 + k_s G \frac{\ln(\bar{\lambda}/b)}{(\bar{\lambda}/b)} + k_f G b \ln \left( \frac{1}{\sqrt{\rho t/2}} \right) \left( \sqrt{\rho t/2} \right)$$  \hspace{1cm} (4.7)
This reference stress is plotted as a function of microcrystal diameter in Figure 4.13. Note that first and last terms are size-independent thus the size dependency arises solely from the source-hardening term. It is apparent, from this plot that at microcrystals larger than \( \sim 5 \mu m \), the observed proportional limits (PL’s) can be accounted for as representing the reference stress of Eqn. 4.7. However, for smaller microcrystals there is a deviation from Eqn. 4.7 suggesting that other hardening mechanisms may be operative in the micro-plastic regime.

The PL’s were determined by isolating the largest linear-elastic slope during the loading of the sample and fitting a line through this array of linear-elastic points. The stress at which a observable deviation from this linear fit occurs is the PL, refer to Figure 4.14. For the smaller samples, this value was typically associated with the first burst event.

### 4.4.4 Shear Stress Prior to Unloading

From the stress-strain curves presented in Figure 4.15, it is clear that there is a transition strain hardening regime between the proportional limit and the maximum sustainable flow stress, especially for the smallest samples. What is less clear is how these samples are able to sustain the very large stresses observed just prior to unloading. Therefore, using the dislocation-density measurements obtained from the sectioned slip planes of deformed microsamples, together with Eqn. 4.4, the values of \( \tau_f \) associated with these densities was determined and compared with the observed flow stress. These results are represented in Figure 4.15.
Note that as discussed previously, three of the slip systems are active in samples smaller than 10 $\mu$m in diameter. Thus it is a possibility that the ratio between the total density and forest density is changing with sample size such that for larger samples the $R$ value is closer to $1/2$, but may be closer to $3/4$ in the smaller samples. This possibility is represented by two sets of calculated values found in Figure 4.15. Nonetheless, accounting for such a possibility is still insufficient to explain the observed shear stresses prior to unloading as occurring from ordinary forest hardening.

Consequently, the combined strengthening effects from all components of the reference stress, with the forest-hardening contribution being corrected for the increase in dislocation density at smaller sample sizes, was computed and compared to the observed flow stresses. A composite plot including the upper and lower bounds of these stresses and the measured stresses was generated and is shown in Figure 4.16. However, even summation of the evolved components of the reference stress was still insufficient to explain the observed flow stresses. This result—in combination with the result of the initial reference stress being inadequate to account for the observed proportional limits—indicates that whatever are additional strengthening mechanisms that raise the effective stress at small microcrystal sizes, they remain active from the proportional limit throughout the duration of the loading.
4.4.5 Exhaustion Hardening

The results presented for nickel and gold microcrystals \[27, 53, 56\] indicate a regime that is characterized by burst activity associated with an effective strain-hardening rate exceeding that of Stage II hardening. The present work was unable to determine the mechanism associated with this regime due to the stochastic nature of the burst events and the inability to stop an experiment just prior to an event. However, the fact that the nickel microcrystals evolve a dislocation density during the deformation that is larger than the initial density and that this density is stored at the early stages of plasticity, suggests that changes may be occurring within the dislocation forest that are contributing to the strength increases. These changes may be related to a change in the forest density as multiple slip systems become operative at smaller sizes. The changes may also be more complex, related to the creation of stronger junctions/obstacles. However, each of these remains to be proven. Coupling the observations from this study, with the fact that the combination of the reference stress and a forest-hardening contribution (being corrected for the increase in dislocation density at smaller sample sizes) were insufficient in explaining the observed flow stresses, indicates that further study in this area is needed to explain this behavior. A suitable study would incorporate the observations determined from this work coupled with computational 3-D dislocation dynamic simulations.
4.5 Summary and Conclusions

TEM studies were performed on thin-foil specimens extracted from slip-traces of the primary (111) slip plane from deformed nickel microcrystals ranging in diameter between 1 and 22 microns. The specimens were examined to identify the attributes of the dislocations present and to quantify their density. The measured dislocation densities were used within various theoretical constructs to evaluate components and micromechanisms contributing to the high observed flow stress for these microcrystals. From those measurements and analyses the following conclusions are drawn:

- The dislocation substructures formed in these microsamples are similar to those formed within macroscopic samples, with the exception of a reduced degree of cellular structure formation at a given strain in the microcrystals. This is consistent with the large extensions of Stage I glide at these small sample sizes.

- The TEM results indicate an increase in the stored dislocation content as sample dimensions are reduced. This result suggests that, at the sizes studied, a starvation-based model cannot solely account for the large observed flow stresses.

- The combination of stresses associated with lattice friction, source truncation hardening and forest hardening are insufficient in explaining the strengthening effects associated with nickel microcrystals at this size scale.
Based on the previous conclusions, the regime previously identified as exhaustion hardening may be related to changes in the dislocation forest at smaller sizes.

4.6 Acknowledgments

Scott Apt, Bob Wheeler, Sang Lan Kim, T.A. Parthasarathy
Figure 4.3: a) Energy filtered convergent beam electron diffraction pattern from a slip plane foil, acquired on a CCD camera, using 200keV electrons. b) A simulated CBED pattern, using JEMS, for a 117 nm thick TEM sample.
Figure 4.4: BF-STEM images illustrating the procedures used for density measurements. a) A BF-STEM image taken from a 10 \( \mu \text{m} \) diameter microsample. b) Random lines are generated with the use of Fovea Pro software. c) Marks are placed at each point where a dislocation intersects a line. d) All dislocation line segments were traced.
Figure 4.5: Thickness variation across a 2 µm and 20 µm slip plane foil.
Figure 4.6: BF-STEM image taken from an undeformed microcrystal along the same \( \{11\overline{1}\} \) plane that is active in the deformed samples. This image illustrates the large initial dislocation density that is present prior to deformation.
Figure 4.7: BF-STEM image taken from a bulk compression sample and a 2 micron diameter microsample. The engineering strain levels are within 1% of each other.
Figure 4.8: Brightfield STEM images taken from 1µm, 2µm, 5µm, and 20µm diameter micro-compression samples.
Figure 4.9: Invisibility conditions from a $2 \mu m$ microcrystal for the three highest resolved shear stressed sip systems, 1, 2 and 3, respectively. a) $g=\langle \overline{1}31 \rangle$, the invisibility condition for (1) b) $g=\langle 20 \overline{2} \rangle$, the invisibility condition for (2) c) $g=\langle \overline{1}1 \overline{3} \rangle$, the invisibility condition for (3).
Figure 4.10: Dislocation density measurements performed using the line/point method indicate an increase in the dislocation density as sample dimensions are reduced.
Figure 4.11: Density measurement from 2µm diameter samples as a function of strain.
Figure 4.12: Using the initial density measurements, the background internal forest-hardening stress and source truncation hardening stresses, $\tau_s$, are plotted as a function of sample diameter.
Figure 4.13: The proportion limit data from experiment is plotted with the total reference stress, $\tau_r$. The total reference stress is the summation of the Pierel’s stress, $\tau_p$, initial forest-hardening stress ($\tau_f$) given by Eqn. 4.4, and the source-truncation hardening stress ($\tau_s$) given by Eqn. 4.6.
Figure 4.14: Plots indicating the selection of the proportional limits (PL’s) from the stress-strain curves of a 2µm and 10µm sample. The deflection point, indicated by the arrow, is the stress at which plasticity begins and is referred to as the proportional limit.
Figure 4.15: The flow stresses prior to unloading are plotted with the stresses associated with forest hardening, from Eqn. 4.4, based on the dislocation density measurements found in Figure 4.10. The upper and lower bounds result from the variability in $R$, the correlation factor between the forest and total density. It is clear from this plot that forest hardening alone cannot account for the observed flow stresses.
Figure 4.16: The combined strengthening effects from all components of the reference stress, with the forest-hardening contribution being corrected for the increase in dislocation density at smaller sample sizes, was computed and is compared to the observed flow stresses. Consequently, the combination of all the hardening effects explored in this study are insufficient to explain the observed flow stresses.
CHAPTER 5

TITANIUM ALLOYS

5.1 Introduction

Recently, several authors have shown a dramatic increase in strength for sample sizes smaller than 10 microns in diameter [7, 27, 29, 55, 56]. In all cases, the materials of study were face-centered-cubic (FCC) derived crystal structures that are typically associated with bowing or obstacle controlled dislocation motion. In these metals, the lattice friction, or Peierl’s stress, is small and therefore the majority of the strengthening is then attributed to the interaction of dislocations with obstacles, in single crystals these are typically immobile dislocation segments (forest dislocations). Transmission electron microscopy (TEM) results from nickel microcrystals, in Chapter 4, indicate that forest hardening in these microcrystals cannot solely account for the large flow stresses observed; therefore, other hardening mechanisms, such as source truncation and exhaustion hardening, must be governing the strength.
Following the ideas of E. Nadgornyi [4], materials are broadly classified into two categories, materials controlled by obstacle-controlled (OC) dislocation motion, mentioned previously, and materials that are controlled by lattice resistance, such that the Peierl’s stress is relatively large. The latter is typically referred to as kink-mode (KM), resulting from the manner in which the dislocation segments propagate through the crystal. These materials are typically body-centered-cubic (BCC) or hexagonal-close-packed (HCP) crystal structures with a very high lattice friction, resulting from a dissociated core structure along certain line directions [45].

It has been shown by V. Vitek [45] that these core effects are based on the dissociation of the core onto multiple slip planes. For example, nickel with an FCC crystal structure exhibits very little lattice friction as the core is distributed along the active glide plane, $\{111\}$. However, in alpha titanium alloys, deformation typically occurs along the $\{10\overline{1}0\}$ or the $(0002)$ with a Burgers vector of $\langle11\overline{2}0\rangle$. The core of the screw dislocation is then distributed onto the $(0002)$ and $\{10\overline{1}0\}$ planes, simultaneously, creating a substantial drag force, or lattice friction, on the moving dislocation.

In addition, in Ti-Al based solid solutions, short range ordering (SRO) is a major strengthening mechanism [83] and also leads to very planar slip. In these alloys, source operation involves sequential generation of dislocation loops, forming extended dislocation arrays in which individual dislocations are strongly interacting elastically with many neighbors [83, 84]. This geometry is quite different from that in FCC crystals and size effects may also be significantly altered.
It is the purpose of this chapter to determine if kink-mode materials exhibit a similar strengthening effect, as obstacle controlled materials at the same size scale, ranging from 1 micron to 60 microns in diameter. Subsequent TEM microscopy was then performed on the deformed microcrystals to study the source operation kinetics and dislocation ensembles produced during deformation.

5.2 Experimental

5.2.1 Materials

Two titanium-aluminum alloys were used in this study. The first, Ti-6Al, is a single-phase (α) hexagonal close packed (HCP) crystal structure. The second, Ti-6Al-2Sn-4Zr-2Mo-0.1Si (Ti-6242), is a two-phase material consisting of α and a BCC phase (β) in a colony microstructure. Large single crystals of Ti-6Al and single α/β colonies of Ti-6242 and were grown using a Crystalox vertical float zone technique at Wright Patterson Air Force Base by J.M. Scott and M.D. Uchic. Figure 5.1 is an SEM image showing the lathe structure for the large colony crystals.

Bulk samples were then cut and oriented for maximum shear stress along one of the three basal directions, \( \langle 1120 \rangle (0002) \), to produce single a-type slip in Ti-6Al. The presence of the β phase in Ti-6242 produces an orientation relationship between the α and β phases, resulting in three distinctly different basal slip directions \([44]\). To minimize strengthening associated with the β phase, the a1 direction, \( [2\overline{1}0] (0002) \), was chosen since it has only a slight misorientation of 0.56° between the two Burgers vectors for the α and β phases. Therefore, the results for the
a1-basal orientation for Ti-6242 should be more directly comparable with that for single phase Ti-6Al. Samples were oriented using Electron Backscatter Diffraction (EBSD) on a FEI XL-30 ESEM. These samples were subsequently mechanically parallel polished using an Allied High Tech MultiPrep System to 0.05 µm using colloidal silica.

5.2.2 Microcrystal Fabrication

Micron-sized compression samples were machined into the surface of the bulk samples using an FEI dual beam focused ion beam (FEI DB 235), refer to Uchic et al. [53]. Two different types of specimens were fabricated, cylindrical and orthorhombic. The cylindrical samples range between 1 to 60 microns in diameter. The orthorhombic samples consisted of 2 tetragonal samples (10µm × 10µm × 23µm) and four samples with cross-section dimensions of ~15 µm × ~7.5 µm and a height of 23 µm. The aspect ratios for all samples vary between 2:1 and 3:1. The length of time required to fabricate each sample increases with sample size. Therefore, a SARIX Micro-EDM was used for rough fabrication of the 50 and 60 micron samples. Subsequent FIB lathing was performed to remove the recast layer caused by the EDMing process.

5.2.3 Uniaxial Compression Testing

The microcrystals were uniaxially compressed using an MTS Nano Indenter XP outfitted with at flat diamond indenter tip. To ensure proper sample alignment
with the indenter tip, a goniometer stage was used to make fine adjustments. The compression tests were performed under constant displacement rate loading conditions, with a nominal strain rate of $10^{-4}$ 1/s. Two loading methods were used in this study. The first, "OLD", did not allow for the load to drop once plasticity began, leading to increases in the displacement rate once plastic flow was initiated. The second loading method utilized a feedback loop using a proportional-integral-derivative (PID) controller to relax the load allowing for a constant displacement rate throughout the loading cycle. These data points are referred to as "PID" in the subsequent figures.

Representative stress-strain curves from two 10µm diameter microcrystals are presented in Figure 5.2 along with displacement rate data. The two curves are offset on the strain axis for clarity, indicating the differences between OLD and PID control. Under PID control, the load is able to decrease and flow softening is observed following yield point. However, under OLD control displacement bursts are observed with the inability for flow softening to occur. From strain rate data, it is apparent that under PID control the system is able to maintain a constant displacement rate, while the OLD method is not, as indicated by the dramatic increase in displacement rate. Accurate control of strain rate is important since Ti alloys are relatively rate sensitive at room temperature [85].
5.2.4 Transmission Electron Microscopy

Due to the size of the microcrystals, conventional TEM sample preparation techniques were not of use; therefore, TEM samples were prepared with the DB235 FIB, and then extracted with the use of an insitu plucking device, the OmniProbe™. Once extracted, additional thinning was performed with the FIB until the samples were electron transparent (<250nm). All TEM microscopy was performed on a 200 kV FEI/Phillips Tecnai TF20 outfitted with a field-emission electron source utilizing a bright-field-scanning-TEM, the details of which are presented in Chapter 4.2.2.

5.3 Results

5.3.1 Cylindrical Compression Results

5.3.1.1 Ti-6Al Compression Results

Scanning electron microscopy (SEM) images, collected using secondary electrons, are presented in Figure 5.9 for several microcrystals following deformation. For all sizes, the slip traces are consistent with the primary slip system, \([2\overline{1}0\overline{0}]\langle0001\rangle\), that was oriented for the maximum resolved shear stress. For the majority of the microcrystals tested, slip traces originate at the top and/or bottom contact points as these are areas of incompatibilities and stress concentrations.

The flow curves for the Ti-6Al microcrystals, ranging from 1 to 20µm, are plotted as stress versus plastic strain in Figure 5.3. Comparing the yield stresses at 1% plastic strain, it is apparent that all samples achieve strengths larger than that of bulk crystals. In addition, there appears to be a strengthening effect as sample
size is decreased. In the larger samples, an upper yield point is observed, followed by a gradual decay in stress that plateaus to values similar to those obtained in bulk compression testing at similar strains. This result suggests that the offset from bulk behavior is related to mechanisms operating at the early stages of plasticity.

Similar to the nickel results published by Dimiduk et al., refer to Figure 4.1a, the 1 micron Ti-6Al microcrystals exhibit stochastic burst events followed by linear elastic loading. However, the burst events in Ti-6Al are much more controlled compared to the nickel bursts. For instance, the 1 micron Ti-6Al flow curves are plotted with a 1 micron nickel flow curve in Figure 5.5 and it can be seen that the speed at which these events occur is much slower in Ti-6Al. This is evident from the data points plotted on the flow curves for the same displacement and data acquisition rates. There are fewer data points acquired in the nickel sample during a burst event compared to Ti-6Al. This behavior is likely related to the sluggish/viscous dislocation motion present in titanium-aluminum alloys—due to the high Peierl’s stress along screw orientation as well as other frictional forces due to solute and SRO interactions—along with different hardening mechanisms that are governing plasticity.

These bursts events are not observed in larger titanium samples tested using the PID control method. The 1 micron samples were tested using the OLD loading method, such that the load was never allowed to relax. Therefore, a negative work hardening rate or upper yield point would not be observed in the 1 micron tests. If the PID control method was imposed on these tests, serrated-flow would
be expected with multiple yield points. In larger Ti-6Al samples tested using the OLD method (not shown here) only one major burst event occurs such that the sample is not able to recover until the sample is unloaded. This is different from the larger nickel samples which recover from the burst events and are followed by linear elastic loadings. This suggests that the burst events observed in the nickel and titanium may be related to different mechanisms. The single burst event in titanium suggests that there is one primary barrier to deformation and once this barrier is surmounted, subsequent deformation is easier and supported experimentally by the yield point flow softening observed in several of the flow curves.

5.3.1.2 Ti-6242 Compression Results

The flow curves from the Ti-6242 microcrystals are presented in Figure 5.6. Two samples were oriented for a1 Basal slip, such that Sample #2 contains polishing induced dislocation content near the surface to produce a potentially unlimited supply of dislocation sources, refer to Figure 5.7. Similar to the results from Ti-6Al, for all sizes tested (5-60µm), the measured yield stresses are larger than those observed in bulk crystals. This offset from bulk behavior observed in Sample #2, specifically, suggests that source operation is not a contributing factor to the strengthening effect. However, there is not a clear correlation between the yield point and sample size as observed in Ti-6Al and nickel microcrystals.
Furthermore, in nickel, Dimiduk et al. observed bulk properties at sizes greater than \( \sim 20 \, \mu m \) in diameter, however, in Ti-6242 bulk properties are still not observed at \( 60 \, \mu m \) in size. The stress-strain curve from a 60\( \mu m \) sample is found in Figure 5.8. The sample follows linear-elastic loading up to a stress similar to the proportional limit (PL) for bulk behavior, as indicated by the arrow. Following this regime, there is a change in the loading slope that continues up to the yield point of the sample. This deflection point in the loading slope is not observed during the unloading of the sample, indicating that this is real material behavior and not an artifact from the testing system. Therefore, the proportional limits for the 50 and 60 \( \mu m \) samples are very similar to bulk values, but the subsequent hardening behavior is vastly different, suggesting that source operation is not responsible for the deviation from bulk properties.

SEM images indicate the same primary slip system, \([2110](0001)\), is operative with the same slip trace characteristics as in the Ti-6Al microcrystals. There appears to be a larger number of observable slip traces compared to the Ti-6Al microcrystals, suggesting that the beta phase may be inhibiting dislocation motion, resulting in the activation of more sources. The beta phase may also provide additional internal source locations, which would also contribute to multiple slip traces.
5.3.2 Ti-6242 Orthorhombic Compression Results

Due to the symmetry of dislocation mobility in titanium alloys, edge segments move much faster than screw segments resulting in hairpin shaped dislocation loops. Therefore, to ascertain the significance of sample geometry on the mechanical properties, different sample geometries were fabricated and tested (refer to Figure 5.10). The compression results are found in Figure 5.11, indicating that samples with shorter screw length (SS) are weaker than those with longer screw (LS) line lengths. If a fixed source width is assumed (a fair statement since this dimension is an order of magnitude smaller than the smallest microcrystals tested), then this result is surprising based on the following reasons. First of all, the mobile edge segments contribute less strain in the SS case due to the proximity of the free surface. Therefore, at a similar strain value, the strain in the SS sample consists of a larger contribution from the difficult to move screw dislocation segments. Secondly, the harder to move screw dislocations are required to move a longer distance in the SS sample to reach the free surface. Furthermore, the most difficult screw dislocation to move (the lead screw, based on SRO) remains in the sample for a longer period of time in the SS samples. Despite these arguments, the SS samples exhibit a weaker flow stress.

In all orthorhombic samples, SEM imaging indicated that there was only one observable slip trace that originated from the upper corner and likely related to a stress concentration at the corner of the sample.
5.3.3 TEM on Ti-6242 Samples

5.3.3.1 Cylindrical Samples

TEM foils were extracted along the primary active slip trace that was observed in the SEM. Imaging was performed using bright-field-scanning-TEM (BF-STEM) to study the dislocation substructure. Figure 5.12 contains BF-STEM images taken from a 10µm diameter microcrystal that was plastically deformed to 3.4% plastic strain. The dark bands running from top-right to bottom-left are the second phase, \( \beta \), ribs that constitute this two phase alloy. At higher magnifications the large arrays of screw segments are apparent. However, due to the large dislocation densities, subsequent analysis was difficult. Therefore, a second TEM foil was extracted from a microcrystal plastically deformed just past the proportional limit to only \( \sim 0.1\% \) plastic strain, thus allowing the study of the very early stages of plasticity. SEM imaging indicated that this was the only active slip trace. At only 0.1\% plastic strain (0.24\% plastic shear strain), the sample sustained a load of 845 MPa, well above bulk values. This flow curve is presented in Figure 5.13.

BF-STEM images taken from this TEM foil indicate that two near surface or surface sources were operative on this slip plane, refer to Figure 5.13. The sources lie within the continuous alpha phase, located between each of the beta lathes. As in the previous foil, there are long arrays of screw/mixed character dislocation segments resulting from the low mobility of the screw segments.
In order to determine the amount of plastic shear strain, $\gamma_p$, associated with the propagation of dislocation content from these two sources, the following relationship was used,

$$\gamma_p = \frac{A_{ts}b}{V}$$  \hspace{1cm} (5.1)

where $A_{ts}$ is the total area swept out by all dislocations and $V$ is the total volume of the compression sample. To determine $A_{ts}$, the dislocation loops presented in Figure 5.13 were manually traced using Adobe Photoshop software and the area for each respective loop was determined and summed using Reindeer Graphics Fovea Pro analytical software. The traced imaged used for this process is found in Figure 5.14. During this process, 12 screw dislocation segments were missing (refer to 5.14), such that the loop area could not be determined. For these segments an average area was estimated based on an extrapolation of the observed loops. It is was determined that the total area swept, $A_{ts}$, is $\sim5.8\times10^8$ nm$^2$, resulting in a plastic shear strain of $\sim0.09\%$. Therefore, all of the dislocation loops found in this TEM foil, 46, constitute only 1/3 of the total dislocations needed to produce the measured plastic shear strain of 0.24\%. This result suggests that many sources must be operating in the micro-plastic regime to produce the measured plastic strain. From this result it seems unlikely that source operation is a contributing factor to the observed offset from bulk strengths.
A TEM foil was extracted from a 5 µm microcrystal parallel to the loading axis such that the Burgers vector is out of the foil plane. BF-STEM images are found in Figures 5.15 & 5.16. The short, straight dislocation segments are foreshortened screw segments, truncated due to the geometry of the TEM foil. Several pile-ups are observed at the sample/surface interface, indicating that these screw segments are having difficulty exiting the sample.

It should also be noted that in a few TEM observations minimal dislocation activity was observed below the base of the sample, refer to Figure 5.17. This result is not a surprise since the microcrystals are continuous with the bulk below the base. These dislocations are likely being generated from stress concentrations formed at the intersection of the microcrystal and the base. Since the density is small, it is unlikely that these dislocations are contributing to the strength of the microcrystals.

5.3.3.2 Orthorhombic Samples

TEM foils were extracted from the SS and LS geometries along the active slip traces. BF-STEM images, shown in Figures 5.18 and 5.19 indicate long, planar arrays of dislocation segments similar to the slip plane foils extracted from the cylindrical samples. However, several edge character dislocation pile-ups are found along the exit surface of the sample, indicating that the edge segments are having difficulty escaping to the free surface. Using these pile-ups it is possible to determine the number of sources that are operating in these slip plane cuts. There are roughly 3 times the number of sources operating in the SS case compared to the LS. Coupling
this observation with the stress-strain data, indicating that the SS samples are weaker than the LS samples, the evidence suggests that source operation is not a contributing factor to the offset in strength from bulk behavior.

Similar to the TEM results from the cylindrical Ti-6242 samples, the sources operate in the continuous alpha phase with multiple sources between each beta lathe. The fact that at least one source is observed between each of the beta lathes suggests that it is easier to activate a new source than to propagate dislocation content through the beta lathes.

5.4 Discussion

5.4.1 Titanium vs. Nickel and Gold Microcrystals

As alluded to in the introduction, the purpose of this chapter was to determine if titanium microcrystals exhibit similar strength characteristics and size effects compared to other metallic microcrystals fabricated with the FIB. Figure 5.20 consists of a composite plot comparing the flow stresses for several of the FIB microcrystal studies. For titanium, the flow stresses were selected from Figures 5.4 and 5.6 at 0.3% plastic strain, as this is the first strain level in the 20 µm samples to reach a nearly perfect plastic transition. It is apparent from Figure 5.20 that there is a clear distinction between the kink-mode controlled titanium materials and the obstacle controlled FCC materials. In the FCC materials, there is over an order of magnitude increase in strength as sample dimensions are reduced. This is clearly not the case for titanium.
It has been reported by Dimiduk et al., that for nickel the scaling relationship follows a $1/D^n$, where $n$ is reported as 0.6 to 0.7. Similar values are also found for the gold data. Using this same scaling relationship, $n$ values of $\sim 0.08$ were determined for Ti-6Al and Ti-6242 microcrystals, further, indicating that there are dramatic differences in the response of different material structures at small size scales. This also suggests that the strengthening mechanisms associated with nickel and gold, at these sizes, may be very different to the hardening mechanisms that are responsible for the offset from bulk behavior in the titanium microcrystals.

5.4.2 Dislocation Pile-Ups

The flow curves presented in Figures 5.4 and 5.6 indicate a clear separation in the strength between titanium microcrystals and bulk crystals. The shape of the flow curves, specifically the transition from elastic to plastic, is very similar for Ti-6Al and Ti-6242 microcrystals. Coupling these observations and the fact that both materials experience an upper yield point, it is feasible to consider that the offset from bulk behavior is related to the same micro-mechanisms operating at the early stages of plasticity. Furthermore, the large microcrystals, 50/60 $\mu$m, exhibit similar bulk proportional limit values; however, the upper yield points are similar to the smaller microcrystals. This suggests that the micro-mechanism(s) related to the offset from bulk behavior are not related to source operation.

Additionally, from Figure 5.6, the amount of plastic engineering strain that has occurred prior to reaching the upper yield point is $\sim 0.6\%$, or 1.3% plastic shear
strain. This correlates to the activation and propagation of a minimum of 3,700 dislocations based on the following expression:

\[ \gamma_p = 0.013 = \frac{\Delta x}{X^\prime} \]  

(5.2)

where, \( \Delta x \) is the displacement parallel to the slip plane and \( X^\prime \) is the initial slip plane length, given as \( 60/\cos 45^\circ \). The number of dislocations is simply \( \Delta x/b \), where \( b=2.95 \, \text{Å} \) for titanium, yielding 3,700 dislocations. However, due to the low mobility of the screw segments, many more sources may operate making this value much larger and further suggesting that source operation is not the cause for the size effect in these titanium alloys.

Observations of several dislocation pile-ups at the surfaces of the Ti-6242 microcrystals, both of edge and screw characters, indicate that dislocations have difficulty exiting the microcrystals. A high magnification view of one of these pile-ups is presented in Figure 5.21. Only one-half of the pile-up is visible because during the foil thinning process the other half was ion milled away. However, from this image, the dislocations appear to pile-up along the dark band indicated by the arrow. During the thinning process, ion implantation occurs and is observed as small black dots peppered throughout the foil. These dark spots, resulting from the strain fields produced from the large implanted gallium ions, appear to have a much higher concentration near the exit surface of the sample, as depicted by the arrow in Figure 5.21. Therefore, the possibility exists that during the fabrication of these titanium
microcrystals a surface layer of gallium damage is encasing the samples and having a large effect on the dislocations exiting the sample, resulting in a strengthening effect and an offset from bulk properties. Interestingly, if the Ti-6Al yield stresses are plotted with Ti-6Al polycrystalline results, similar scaling coefficients are observed. These results are presented in Figure 5.22. This result suggests that the behavior in the titanium microcrystal experiments may be comparable to that observed in polycrystalline experiments.

Built on the framework of a pile-up model, a Hall-Petch (H-P) relationship is given by,

$$\sigma = \sigma_0 + kD^{-\frac{1}{2}}$$

(5.3)

where \(\sigma_0\) is the Peierls stress, \(k\) is the H-P slope and \(D\) is the average grain size. The ideas of H-P suggest that for larger grain sizes, a larger pile-up of \(N\) dislocations can occur, resulting in a larger force on the lead dislocation and a lower yield stress is needed to burst through the boundary. These ideas parallel the possible scenario observed in the titanium microcrystals, from which the microcrystals are of varying diameter with a constant surface barrier. The Ti-6Al results presented in Figure 5.20 are recast into a H-P plot, by taking a scaling coefficient of -0.5, along with the results from several grain size studies performed on Ti-6Al polycrystals. These results are found in Figure 5.23. Surprisingly, the Ti-6Al data, specifically \(k\), agrees very well with data published for Ti-6Al polycrystals [86]. In fact, the coefficient of determination, \(R^2\), is larger for the linear fit used in the H-P plot, indicating
that the H-P relationship is a better fit to the Ti data. Furthermore, using short-range-ordering (SRO) arguments presented by T. Neeraj and M. Mills \[83\], the pile-up characteristics, specifically the planarity of slip, are greatly influenced by the amount of SRO present in the material. The SRO is influenced by the heat-treatment applied to the material, such that water-quenched (WQ) samples exhibit little to no SRO because the diffusion time is minimal. Consequently, as aging time is increased so does the SRO. The Ti-6Al results presented in Figures 5.22 & 5.23 contain variations in the SRO state of the material prior to testing: WQ, WQ + Anneal, and Air Cooled (Ti-6Al Microcrystals). These differences are reflected in the H-P slope accordingly, with the WQ samples having the smallest $k$-coefficient of 0.232, the WQ + Anneal having the largest $k$-coefficient of 0.453 and the Air Cooled microcrystals somewhere in the middle with a $k$-coefficient of 0.311.

Similar hardening effects have been observed in aluminum microwires by Tabata et al. \[26\], in which the wires contained an oxide surface layer and in situ TEM indicated that dislocations were piling up at the surface, causing an increase in strength.

Furthermore, observations related to strain rate data support a gallium ion damage layer strengthening effect. Figure, 5.24 is a plot showing the difference in strain rate behavior between a 1 $\mu$m and 20$\mu$m microcrystal. For these tests, the OLD method was used, such that the load was never allowed to drop. In the 1$\mu$m sample a constant nominal strain rate is achieved throughout the loading of the sample. Although there are minor increases in the rate, the sample was able to "recover" and plastically deform at a constant rate. This is not the case for the larger
samples, as illustrated by the 20 µm sample in Figure 5.24. Once plasticity begins, at ~275 seconds, there is a gradual increase in strain rate until the sample begins to plastically deform in a catastrophic manner. At this point the strain rate reaches a maximum and will continue to deform at this rate until the sample is unloaded. The difference in this behavior can be attributed to the size of the dislocation pile-up related to each respective sample size. In the 1µm microcrystal, the number of dislocations contributing to the pile-up is likely to be relatively small compared to the 20µm microcrystal based on the proximity of the operating source(s) and the dislocation pile-up (sample surface). As dislocations pile-up at the sample surface there is an increase in the back-stress on the operating source. The source will shutoff once the back-stress reaches a critical value. Therefore, the number of dislocations, \( n \), that can occupy a distance, \( L \), along the active slip plane between the source and the sample surface is given as:

\[
n = \frac{k\pi \tau_{rss} L}{Gb}
\]  

(5.4)

where \( k \) is \( \sim 1 \) for screw dislocation segments and \( k = 1 - \nu \) for edge segments. This equation (Eqn. 5.4) assumes that the source is operating at the sample surface. If the source is operating in the center of the sample, then \( n \) would decrease by a factor of 4. Therefore, the close proximity of the source to the pile-up in the 1µm sample results in fewer dislocations contributing to the pile-up and yielding a smaller strain rate increase once the ion-damage layer is surmounted.
5.4.3 Atypical Hardening in the 50 and 60 µm Microcrystals

The atypical hardening behavior observed in Figure 5.8 suggests that the large slip lengths of the 50 and 60 µm samples allow for large pile-ups to occur at the surface, resulting in an observable strain accumulation. The cause of the pile-ups in these large samples is inconclusive at the present time. Figure 5.25 contains images from each of the large samples tested in this study. Reflected in these images are regions of a recast layer formed during the EDMing process of these large microcrystals. As mentioned previously, due to the large sample sizes a micro-EDM was utilized to make rough cuts for the 50 and 60 micron samples. Unfortunately, the subsequent FIBing did not remove all of this recast layer and as such, the pile-ups may be related to the recast, the ion damage, or a combination of both.

The locations where the recast layer remains, with respect to the slip direction, is different in each of the samples. However, all samples observe very similar upper yield points compared to each other and to the other Ti-6242 microcrystal data. This result suggests that the hardening contribution from the recast layer may be acting in a very similar fashion to that of gallium ion damage. However, this cannot be proven at this time.

5.4.4 Characteristic Length

A few fine details distinguish the Ti-6Al data from the Ti-6242 data. The first is related to the Ti-6242 samples that were tested with different geometries, SS vs. LS. From the previous discussion presented for a Hall-Petch strengthening effect, the
SS sample should exhibit a higher yield point compared to the LS samples due to the asymmetry of the dislocations loops. The mobility of the edge segments are much greater than that of the screw segments and therefore, pile-ups of edge character would occur faster at the sample surface than screw character pileups, resulting in an increase in strength for the SS case. However, the flow curves presented in Figure 5.11 indicate that the SS samples are softer than the LS samples.

A possible explanation for these observations is related to the second phase, \( \beta \), that is present in Ti-6242 material. Due to the orientation relationship between the \( \alpha \) and \( \beta \) phases, the lathe/beta ribs lie at an angle of \( \sim 10^\circ \) to the given \( a_1 \) slip direction. Even though the Burgers vectors between the two phases are very similar, there is inherent strengthening due to the mismatch in moduli between the two phases. This is apparent by the observation of pile-ups along the beta lathes in several TEM foils. Evident in several TEM foils, dislocation sources activate between the beta lathes in the continuous alpha phase. Given that the average spacing between beta lathes is \( \sim 3.5 \mu m \) and that the sources seem to operate at or near the top surface, then there should be a characteristic length such that if a source is placed anywhere on the surface, the edge components will intersect a beta lathe before escaping the crystal. This distance is given as \( 3.5\mu m/\tan(10^\circ) = \sim 20 \mu m \). This characteristic length is evident when comparing the TEM images from the SS and LS samples found in Figures 5.18 and 5.19. There is a much higher probability that edge dislocations emanating from a near surface source will intersect with a beta lathe in the LS sample, resulting in a strengthening effect for the LS case.
This also suggests that cylindrical Ti-6242 microcrystals smaller than 20 µm will experience a softening related to this lathe effect. However, due to the large scatter in the Ti-6242 data, presented in Figure 5.20b, no correlations can be drawn. The large amount of scatter present at the 10µm size is likely related to the sampling of beta lathes. Given that the average spacing between beta lathes is ∼ 3.5 µm, the possibility exists that 1 to 3 beta lathes may be contained in a given 10 µm sample, thereby creating a large variation in the observed strength levels.

5.5 Conclusions

Microcrystals ranging from 1 to 60 microns in diameter were fabricated from Ti-6Al and Ti-6242 alloys. Subsequent TEM was performed on several samples after deformation. The results indicate that:

- The titanium alloys used in this study do not exhibit the dramatic strength increase observed in other metallic systems, such as gold and nickel, at similar size scales.

- There is an offset from bulk properties in both the Ti-6Al and Ti-6242. TEM indicates pile-ups of edge and screw character at the sample surfaces, which are most likely caused from interactions with the strain fields produced by gallium ions implanted during the sample fabrication process.

- The Ti-6Al data at 0.2% strain offset fits very well with Hall-Petch behavior observed for Ti-6Al polycrystalline studies.
• The presence of the beta phase in Ti-6242 produces a characteristic length that is related the location of source operation in the alpha phase and the orientation relationship between the alpha and beta phases. This results in a softening effect observed in the stress-strain curves from the orthorhombic short-screw (SS) samples versus the long-screw (LS) samples. This effect should also be present in the cylindrical samples that are smaller than 20µm in diameter, however, more data at the smaller sizes are needed to confirm this explanation.

• At this time it is not clear if/why titanium is affected more by the presence of the gallium compared to nickel and gold. However, the pile-ups observed warrant further detailed study of this effect.
Figure 5.1: SEM image depicting the lathe structure in the large Ti-6242 single colony crystals. The white phase is the beta phase in this back-scattered image.
Figure 5.2: a) Stress-Strain curves illustrating the differences in loading conditions between the PID and OLD control methods. b) the corresponding strain rate data.
Figure 5.3: The slip traces observed in Ti-6Al microcrystals originate at the top and/or bottom contact points as these are areas of incompatibilities and stress concentrations. Typically only one or two slip traces are observed for a given sample.
Figure 5.4: Ti-6Al microcrystal compression results. The yield stresses for all sample sizes, 1-20 μm, are larger than that for bulk samples. There is an observable strengthening effect as sample dimensions are reduced, such that the 1 μm samples are stronger than the 20 μm samples.
Figure 5.5: Strain burst events are found in both Ti-6Al and nickel 1µm microcrystals. However, the characteristics are quite different. Using the same acquisition rates, the nickel microcrystal acquired fewer data points during a burst event compared to the Ti-6Al microcrystals. Indicating that the burst behavior is more controlled/slower in the Ti-6Al microcrystals.
Figure 5.6: Ti-6242 microcrystal compression results from two samples oriented for slip in the a1 Basal direction. Sample #2 contains a large density of polishing induced dislocation content near the surface of the sample, potentially providing an unlimited number of operable sources. In both Sample #1 and Sample #2 there is an observable strength increase in the microcrystals compared to bulk samples, suggesting that source operation is not causing the offset from bulk behavior.
Figure 5.7: Sample #2 contains many polishing induced dislocations near the top surface of the sample. These dislocations should provide an unlimited amount of sources for plasticity to initiate.
Figure 5.8: (a) The stress-strain curve from a 60 µm Ti-6242 microcrystal. A significant deflection in the loading curve is observable which occurs at a stress similar to the proportional limit for bulk samples, as indicated by the arrow. (b) Unloading segments, past the proportional limit, follow the elastic modulas of the material. This observation indicates that this region of the curve is real material behavior and not an artifact from the testing system.
Figure 5.9: The slip traces observed in Ti-6242 microcrystals originate at the top and/or bottom contact points as these are areas of incompatibilities and stress concentrations. There appears to be more observable slip traces than for the Ti-6Al microcrystals, suggesting that the beta phase may be inhibiting dislocation motion, resulting in the activation of more sources.
Figure 5.10: Orthorhombic samples were fabricated to study the effect of sample geometry on the mechanical properties. The arrows indicate the active a1 Burgers vector. Due to the asymmetry of the dislocation loops formed in titanium alloys, sample (b) will contain much long screw segments than in sample geometry (c) which is foreshortened by the surface. These two geometries are termed long-screw (LS) and short-screw (SS), respectively.
Figure 5.11: The flow curves for the Ti-6242 orthorhombic compression microcrystals, indicating that the short-screw (SS) samples are weaker than the long-screw (LS) samples.
Figure 5.12: BF-STEM images taken from a 10 \( \mu \text{m} \) Ti-6242 slip plane foil. Long screw arrays are visible; however, the large density made subsequent analysis difficult.
Figure 5.13: BF-STEM images taken from a 10 μm Ti-6242 slip plane foil. This microcrystal only experienced 0.1% plastic strain, allowing the observation of the very early stages of plasticity.
Figure 5.14: The plastic shear strain associated with the propagation of the dislocation loops was determined by tracing the dislocation line segments and summing the total area swept. The location of the screw segments without a mating screw segment are indicated by the arrows. For these segments, an average area was estimated based on an extrapolation of the observed loops.
Figure 5.15: BF-TEM images taken from a 5 µm Ti-6242 longitudinal foil, such that the Burgers vector is out of the plane of the foil.
Figure 5.16: Higher magnification BF-STEM images taken from the 5 µm Ti-6242 longitudinal foil found in Figure 6.5a. Several screw-character pile-ups are visible at the sample/surface interface.

Figure 5.17: Minimal dislocation content was observed below the base of the sample in a few TEM foils.
Figure 5.18: BF-STEM images from a long-screw (LS) TEM foil extracted along the active slip plane. Sources activate at top portion of the foil producing dislocations that can be seen piling-up at the sample surface at the bottom of the foil.
Figure 5.19: BF-STEM images from a short-screw (SS) TEM foil extracted along the active slip plane. Several pile-ups are observed at the exit face.
Figure 5.20: The 0.2% yield stresses for Ti-6Al and Ti-6242 microcrystals are plotted with the yield stresses from previously published FCC microcrystal data. It is apparent from this plot that the increase in strength with decreasing sample size observed in the titanium alloys is not as significant as in the other materials.
Figure 5.21: A higher magnification BF-STEM image from Figure 5.18, highlighting an edge character dislocation pile-up at the exit surface of the microcrystal. This pile-up appears to be related to gallium ion damage caused from the microcrystal fabrication process, evident by the increase in ion damage near the exit surface of the sample, indicated by the arrow.
Figure 5.22: The scaling relationship, $1/D^n$, for the titanium microcrystals is very similar to that observed for polycrystalline Ti-6Al data.
Figure 5.23: The yield stresses from the Ti-6Al data found in Figure 5.20 are recast into a Hall-Petch plot. The H-P slope, k, agrees very well with other published data.
Figure 5.24: The difference in strain rate behavior between a 1 \( \mu \)m and 20 \( \mu \)m microcrystal loaded using the OLD method. The 1 \( \mu \)m sample was able to recover from a burst event, maintaining a constant nominal displacement rate. This was not the case for the 20 \( \mu \)m sample that experienced a dramatic acceleration in strain rate once plasticity begins. The sample continued to deform at this rate until the sample was unloaded.
Figure 5.25: SEM images taken from a (a) 50 µm and two (b)(c) 60 µm samples. In each of the samples, areas of recast are observable such that hardening at these sizes may be a result of the recast layer, the gallium ion damage, or both. Each of these images was taken from the same viewing direction relative to the active Burgers vector.
CHAPTER 6

NICKEL-TITANIUM SHAPE MEMORY ALLOY

6.1 Introduction

Recently much attention has been given to sample size effects associated with dislocation plasticity at sizes below 10 microns. In pure nickel and pure gold, a tremendous strength increase can be achieved by decreasing the sample diameter from 20 microns to sub-micron sizes [7, 27, 28, 55]. It has also been shown, in Chapter 5, that this dramatic increase in strength is not observed in titanium microcrystals that deform via a kink-mode dislocation motion.

NiTi, a shape memory material, undergoes a stress induced martensitic transformation during deformation. Upon unloading, the martensite can transform back to the parent austenite phase, recovering much of the plastic strain. This ability to recover plastic strain is the pseudoelastic effect. Previous evidence indicates that plasticity degrades pseudoelastic effects [49]. If small sample sizes can inhibit plasticity, and raise the yield strengths relative to the transformation stresses, then enhanced pseudoelastic effects may be anticipated. Recently, the pseudoelastic ef-
fect as a function of sample size has been studied by Frick et al. [3] on samples ranging from 200 nm to 2 µm in diameter. The results of this study indicated a loss in pseudoelasticity as the sample dimensions are reduced and are presented in Figure 6.1. The characteristic “knee” shape that occurs during the unloading process is indicative of pseudoelasticity and the transformation back to the parent austenite phase. Apparent in Figure 6.1 is a loss in the ”knee” shape as sample dimensions were reduced from 1,820 nm to 171 nm in diameter.

The microcrystal experiments, discussed previously, coupled with transmission electron microscopy, present a unique opportunity to observe the dislocation interactions and ensembles that are produced across the entire sample cross section. Slip plane TEM foils and longitudinal TEM foil that encompass the entire slip plane and gauge length, respectively, are readily extracted from microcrystals ranging from 1 to 20 µm in diameter. Therefore, the purpose of this study is to utilize TEM to study the martensitic transformation and dislocation ensembles that are produced during the deformation of NiTi microcrystals.

### 6.2 Experimental Procedures

Bulk polycrystalline NiTi bar stock containing 50.7 at.% Ni was heat-treated at 1000°C for 20 hours, in an argon atmosphere, to increase the grain sizes to >300 microns. The samples were then water quenched to minimized the possibility of any meta-stable precipitates, specifically Ni₄Ti₃, from forming.
Figure 6.1: Results published by Frick et al. [3] indicate a loss in the pseudoelastic behavior as sample dimensions were reduced. This is indicated by the loss of a knee during the unloading process.
These polycrystalline samples were cut to button-sized pieces and mechanically parallel polished using an Allied High Tech MultiPrep System to a final surface finish 0.05 \( \mu m \) using colloidal silica. Grain orientations were determined using Electron Backscatter Diffraction (EBSD) on an FEI XL-30 Environmental Scanning Electron Microscope (ESEM). A grain orientation image map (OIM) was produced by rastering the beam across the sample and collecting the EBSD data using TSL software, refer to Figure 6.2. From this OIM, the large grain, indicated by the arrow, was selected such that the loading axis is parallel to the \( \langle 110 \rangle \) direction. This loading direction maximizes the Schmidt factor for \( [100] \) slip on the \( \{100\} \) planes, thereby providing the ideal orientation to study the effect of dislocation motion on the martensitic transformation at small sizes.

Micron-sized compression samples were machined into the \( [110] \) surface normal of the bulk samples using an FEI dual beam focused ion beam (FEI DB 235), according to Uchic et al. [53]. In this grain, two 5 \( \mu m \) and one 20 \( \mu m \) diameter micropillars were fabricated each having an aspect ratio between 2:1 and 3:1. An SEM image from the 20 \( \mu m \) sample prior to testing can be found in Figure 6.3. The circle on the top surface of the pillar is a fiducial mark used during the automated fabrication process.

The samples were uniaxially compressed using an MTS Nano Indenter XP outfitted with a flat diamond indenter tip. To ensure proper sample alignment with the indenter tip, a goniometer stage was used to make fine adjustments. The compression experiments were performed under constant displacement rate loading.
conditions at ambient laboratory temperature. For all compression tests, a nominal strain rate of $10^{-4}$ 1/s was achieved using a proportional-integral-derivative (PID) controller.

Due to the size of the microcrystals, conventional TEM sample preparation techniques were not of use; therefore, TEM samples were extracted with the use of an insitu plucking device, OmniProbe™. Once extracted, additional thinning was performed with the FIB until the samples were electron transparent (<250nm). The foils were extracted along the gauge length of the sample such that the [1 0 0] direction is contained in the foil plane, refer to the illustration in Figure 6.4. All TEM microscopy was performed on a 200 kV FEI/Phillips Tecnai TF20 outfitted with a field-emission electron source utilizing a bright-field-scanning-TEM, the details of which are presented in Chapter 4.

6.3 Results

6.3.1 NiTi Microcrystal Compression Results

The NiTi microcrystal compression results, presented in Figure 6.5 are indicative of pseudoelastic behavior given by the flag shaped hysteresis. In all tests, there appears to be a small upper yield point followed by a plateau and subsequent hardening. The transformation stress for both of the 5 µm samples and the 20 µm sample occurs ~625 MPa, in good agreement with bulk single crystal compression results for the same ⟨1 1 0⟩ orientation published by Gall et al. [87]. The moduli are similar in value, however, the proportional limit, the lowest stress at which plas-
ticity begins, is separated by 200 MPa or more. The microcrystals exhibit a much
sharper elastic/transformation transition than the bulk behavior. This absence of
a micro-strain regime indicates little or no plasticity prior to the transformation.
Furthermore, the hardening behavior observed in the microcrystal experiments is
very different to that observed by Gall. In the bulk specimen, there is no hardening
(possibly softening) out to \(\sim 10\%\) strain; however, the 5 \(\mu\)m sample (that experi-
enced one cycle) began to harden at only 2.5\% strain and continues to harden out to
strains of 12\%, see Figure 6.5d. Frick et al. \[3\] observed similar hardening behavior
in microcrystals smaller than 2 \(\mu\)m and suggested that this may be due to gallium
ion damage caused during the fabrication of the compression specimens.

The amount of plastic strain recovered from the reverse transformation, is
presented in Figure 6.6 as the percentage of plastic strain recovered from the maxi-
mum plastic strain observed for each respective sample. The 5 \(\mu\)m samples exhibit
a smaller recovery percentage compared to the 20 \(\mu\)m sample; however, the 5 \(\mu\)m
samples experienced a larger plastic strain. Based on the argument that plasticity
retards the transformation, this result is to be expected.

6.3.2 NiTi TEM Results

TEM foils were extracted from both of the 5 \(\mu\)m samples, such that the Burgers
vectors for the four possible slip systems, \([\overline{1}00](010)\), \([0\overline{1}0](100)\), \([0\overline{1}0](101)\) and
\([\overline{1}00](10\overline{1})\), are contained in the foil plane. Each of the samples experienced the
same total strain level with the only difference being the number of cycles. This
allows for a direct comparison between the number of loading cycle and the evolved dislocation substructure. TEM images collected using BF-STEM are presented in Figure 6.7 for both of the 5 µm samples. A band of remnant dislocation structure is apparent in both samples, extending from the upper-left corner of the foil and continuing to the bottom-right corner of the foil, ending near the base of the sample. This region is most likely the region that was martensitically transformed during loading, but has since transformed back to austenite as diffraction studies indicate. The diffraction patterns were taken from various locations in each of the foils and in all cases, no residual martensite was found. The dislocation density at the top of the foils is much greater that at the bottom of the foil, suggesting that the transformation likely initiated at the upper surface. This is not surprising since even a slight misalignment between the indenter and the pillar, combined with the geometry of the sample, produce stress concentrations at the corners.

Higher magnification images, found in Figure (6.8a, 6.8c), indicate that several dislocation line directions are present; there are those related to the dislocations found inside the transformation zone which run vertically, as well as two more found outside of this zone. In several instances, the line direction outside of the transformation is bent to then match the observed line directions found inside the transformation zone, refer to Figure 6.8c.

Conventional dislocation analysis was performed, including invisibility conditions, to determine the Burgers vectors for these dislocations. Images used for this analysis are found in Figure 6.8. These results indicate that all dislocations found
inside and outside of the transformation zone satisfy an invisibility condition using $g = [\{1 \, 0 \, 0\}]$. By tilting away from the $(0 \, 0 \, 1)$ zone, it was determined that the dislocations outside of the transformation zone lie on the $(1 \, 0 \, 1)$ plane and are therefore, of type $a\{0 \, 1 \, 0\}(1 \, 0 \, 1)$. This result is rather surprising, since the Schmidt factors for $\langle 1 \, 0 \, 0 \rangle\{1 \, 0 \, 0\}$ and $\langle 1 \, 0 \, 0 \rangle\{1 \, 1 \, 0\}$ type slip are 0.5 and 0.35, respectively. Hence, we are observing activity associated with the lower Schmidt factor system. Furthermore, the line directions for the $a\{0 \, 1 \, 0\}(1 \, 0 \, 1)$ type dislocations are not pure screw character; these dislocations take on a mixed character configuration, apparent in Figure 6.8c.

6.3.3 SEM Imaging of 20 µm #1 Following 4 Loading Cycles

Due to the minimal amount of non-recoverable strain found in the 5 µm samples, slip traces were not discernable using SEM imaging techniques. Therefore, correlations will be drawn based on SEM images from the 20 µm sample which experienced 4 cycles and contained approximately 8% of non-recoverable strain. Images were acquired from four different rotations in the SEM, these images are found in Figure 6.9. The arrow indicates the foil normal direction $[0 \, 0 \, 1]$ and the solid line indicates the location and orientation of the foils that were extracted from the 5 µm samples. Figure 6.9a is very close to the same viewing direction that the TEM foils were imaged from in Figures 6.7 and 6.8. There appears to be a correlation with the transformation zone from the TEM foils and the slip traces observed in Figure (6.9a 6.9c). This suggests that the transformation is occurring in a
projected direction parallel to the foil normal, [0 0 1], and along the planes depicted in the SEM images as slip traces. This is visible in Figure 6.9d, by which there is an overall displacement parallel to the [0 0 1], however, there is no resolved shear stress on either the [0 0 1]{1 0 0} or [0 0 1]{1 1 0} given the loading direction of [0 1 1]. Therefore, this displacement can only be achieved by a phase transformation.

6.4 Discussion

The results presented by Frick et al. in Figure 6.1 for [1 1 1] microcrystals, indicate a loss in pseudoelasticity for sample dimensions smaller than 200nm. For the sample dimensions explored in this work (5µm/20µm), no such size effect was observed. The loading curves for the [1 1 1] microcrystals exhibit a more gradual systematic ”take-up” to reach fully elastic behavior compared to the [1 1 0] microcrystals in this study. This difference may be attributed to surface flatness at the top surface of the sample or poor sample alignment, as bending issues become more pronounced at smaller sizes. Also, in this study a goniometer stage was utilized to make fine adjustments to achieve proper alignment. Additionally, the [1 1 0] compression results, from this study, exhibit a much sharper elastic/transformation transition and a more pronounced back-transformation upon unloading compared to the [1 1 1] results published by Frick et al. This result is surprising based on the aging treatment performed on the [1 1 1] microcrystals, producing semi-coherent Ti<sub>3</sub>Ni<sub>4</sub> precipitates, which have been shown to assist in the martensitic transformation. One would expect the aged microstructure to exhibit a sharper
elastic/transformation transition and more pronounced back-transformation. However, variations in Ti$_3$Ni$_4$ precipitate sizes may produce internal stresses variations causing a more gradual elastic/transformation transition as transformations occur at different external stresses. Furthermore, these differences may also be attributed to possible bending effects, suggested by the soft elastic moduli observed for several samples found in Figure 6.1. Although the difference in loading directions between the two sets of data may also be contributing these differences. The TEM results presented in this chapter indicate that dislocations prefer the $\langle 100 \rangle \{110\}$ slip system, resulting in Schmidt factors of 0.46 and 0.35 for the [111] and [110] microcrystals, respectively. The difference between these two Schmidt factors may be large enough to induce plasticity prior to the transformation stress, resulting in a more gradual transition from elastic to in-elastic behavior. As mentioned previously, dislocation content decreases the pseudoelastic effect by inhibiting the transformation back to austenite. The increase in the Schmidt factor is likely to produce more dislocations that contribute to the overall deformation process, resulting in a less pronounced pseudoelastic effect compared to the [110] microcrystals.

The relationship between plasticity and the martensitic phase transformation is not well understood. However, coupling microcrystal experiments with TEM provides a unique method enabling properties to be directly correlated with transformational associated plasticity.
6.5 Conclusions

Microcrystal compression specimens (5 µm and 20 µm) were fabricated from a large [1 1 0] grain from a polycrystalline sample. Utilizing TEM techniques, the substructure evolution was studied as a function of loading cycles. The results from this study indicate that:

- At the sizes explored, there is no evidence to suggest a loss in pseudoelastic behavior as observed by Frick et al. for microcrystals smaller than 200nm.

- The compression results indicate a sharp elastic/transformation transition, suggesting that little plasticity is occurring prior to the transformation.

- Dislocations outside of the transformation zone are of type $a[0\overline{1} 0](1 0 \overline{1})$ and the dislocations inside the transformation zone observe the same invisibility conditions. However, the line directions between the two are very different.

- SEM observations from the 20 µm sample, after 4 cycles and 8% non-recoverable strain, indicate an overall displacement parallel to the $[0 0 \overline{1}]$ direction. This displacement must be caused by the martensitic transformation, due to the fact that there is no resolved shear stress in this direction given the loading direction of $[\overline{1} \overline{1} 0]$. 
Figure 6.2: Orientation Image Map (OIM) indicating the $\langle 110 \rangle$ grain used for the fabrication of the NiTi microcrystals.
Figure 6.3: SEM image taken from the 20µm diameter NiTi microcrystal prior to deformation
Figure 6.4: A schematic illustrating the geometry of the TEM foils extracted from the NiTi microcrystals, such that the entire gauge length is contained in the foil, as well as the [100] direction.
Figure 6.5: Stress-strain curves from the NiTi microcrystals compared to the bulk.
Figure 6.6: The percentage of plastic strain recovered based on the maximum plastic strain experienced by the respective sample is plotted as a function of sample size. The 5 µm samples exhibit a smaller recovery percentage compared to the 20 µm sample; however, the 5 µm samples experienced a larger amount of total plastic strain.
Figure 6.7: TEM images taken from the 5μm microcrystals.
Figure 6.8: TEM images indicating the invisibility criterion for all dislocations found in the foil. It was determined that the dislocations outside of the transformation zone are $a[0\overline{1}0](10\overline{1})$. (a) $g=[0\overline{1}0]$ (b) $g=[\overline{1}00]$ (c) $g=[0\overline{1}0]$ (d) $g=[\overline{1}00]$
Figure 6.9: SEM images taken from the 20 μm sample, which experienced 4 cycles and contained approximately 8% of non-recoverable strain. The arrow indicates the foil normal direction [0 0 1] and the solid line indicates the location and orientation of the foils that were extracted from the 5 μm samples. (a) represents a similar viewing direction as observed from the TEM images in Figures 6.7 and 6.8.
CHAPTER 7

SUMMARY

Microcrystal compression studies on pure nickel, titanium and nickel-titanium were performed to explore sample size effects at the micrometer scale. The results suggest the dislocation micro-mechanisms, inherent to each material, contribute to different sample size effects. In nickel, an obstacle controlled material, an increase in the dislocation density was observed at smaller samples sizes. However, the hardening behavior associated with such densities was insufficient in explaining the observed flow stresses based on a Taylor based model. Furthermore, the contribution from a source hardening mechanism, coupled with the forest hardening behavior, was also unable to entirely account for the large stresses. This result suggests the possibility that a change in the dislocation forest strength may be occurring at small sizes, resulting in an increase in the flow stresses. Further studies using dislocation dynamic simulations are needed to support this hypothesis.

The single phase, Ti-6Al, titanium microcrystals exhibit a size effect that is very different than that observed in nickel. Nickel microcrystals follow the scaling
relationship $1/D^n$, where $n$ is reported as 0.6 to 0.7. Using this same scaling relationship, $n$ values of $\sim 0.08$ were determined for Ti-6Al and Ti-6242 microcrystals, indicating the differences between bowing- and kink-mode materials at small size scales. The possibility that ion damage may be contributing to the size effect in titanium is supported by the following observations.

- Many dislocation pile-ups, both screw and edge character, are observed in TEM foils extracted from the titanium microcrystals.

- The scaling relationship for the Ti-6Al microcrystals follow a Hall-Petch relationship, similar to polycrystalline Ti-6Al.

- Bulk flow stresses are still not observed in the $60\mu$m microcrystals. However, the proportional limits at this size are very similar to that in bulk samples, suggesting that source operation is not a contributing factor to the higher flow stresses.

- Ti-6242 Sample #2 was "seeded" with polishing induced dislocation content near the top surface, potentially providing an infinite number of dislocation sources. An offset from bulk behavior is still observed in microcrystals tested from this sample, further suggesting that source operation is not the cause.
- The small-strained, 10µm, sample shows an offset from bulk behavior at only 0.1% plastic strain. The planarity and shape of the dislocation arrays suggest that forest-type hardening behavior is not contributing to the offset from bulk flow stresses.

Unfortunately, the presence of gallium seems to have tainted the fundamental aspects related to dislocation micro-mechanisms as a function of size for kink-mode materials. Therefore, fundamental comparisons between bowing-mode and kink-mode materials at the micron size scale are difficult with the present data set.

The nickel-titanium microcrystals deform differently compared to the bowing- and kink-mode materials. Instead of dislocations gliding across a slip plane to induce a shape change, a reversible martensitic phase transformation occurs, contributing to the pseudoelastic behavior. As such, these microcrystal exhibit no size effect related to the transformation stress for the sample sizes tested. However, differences are observed in the shape of the flow curves between the microcrystals and bulk samples. First, the elastic/transformation transition is much sharper for the microcrystals, suggesting that little plasticity is occurring prior to the transformation. Furthermore, the microcrystals exhibit hardening behavior, following the transformation stress, that is much more pronounced than bulk behavior. A similar hardening behavior was observed by Frick et al. in [1 1 1] microcrystals. They suggested that this may be due to gallium ion damage caused during the fabrication of the compression specimens. TEM investigations indicates that dislocations outside of the transformation zone are of type a[0 T 0](1 0 T) and the dislocations inside
the transformation zone observe the same invisibility conditions. However, the line directions between the two are very different. The relationship between plasticity and the martensitic phase transformation is not well understood. However, coupling microcrystal experiments with TEM provides a unique method enabling properties to be directly correlated with transformational associated plasticity.

Regarding FIB induced ion damage. The results presented for the titanium microcrystals suggest that a strengthening effect is occurring as a result of this phenomena. However, this does not seem to be occurring in the nickel and Ni-Ti microcrystals, as indicated by the observed bulk flow stresses in the 20µm samples. At the present time it is unclear why this would be different between the two materials that deform plasticly via dislocation motion. However, one possibility may be related to an asymmetric strain field produced by the crystal structure and SRO in the titanium microcrystals, resulting in a more dramatic strengthening effect for the titanium alloys.
CHAPTER 8

FUTURE WORK

• The fabrication of titanium microcrystals using a different process is necessary to determine if ion damage is contributing to an increase in strength. One possibility may be laser fabrication. Another option would be to load a Ti-6Al sample past the proportional limit, but prior to the upper yield point and look for pile-ups in a slip plane TEM foil.

• Since remnants of a recast layer were found on the 50/60µm Ti-6242 microcrystals, another 60µm sample should be fabricated and tested. If the characteristics of the flow curve are similar to the samples with the recast, then this is very good evidence that gallium ion damage is a strong barrier to dislocation motion.

• TEM analysis on the ion damage layer to determine the nature of the strain-fields associated with gallium ions in nickel and titanium. This could reveal the difference in hardening behavior between the nickel and titanium microcrystals.
• Dislocation dynamic simulations should be performed on virtual nickel micro-
crystals, incorporating the TEM results discussed in chapter 4 to determine
the nature of forest junction formation and hardening at the micron size scale.

• The fabrication of NiTi microcrystals smaller than 5µm are needed to study
the transformation stress and subsequent hardening behavior at small sizes.
Coupling TEM with these results, insights into the relationship between plasticity and the transformation may be achieved.
APPENDIX A

RATE SENSITIVITY IN α1 BASAL Ti-6242 MICROCRYSTALS

The strain rate sensitivity exponent was measured using data acquired from several 7.5 µm Ti-6242 microcrystals. These samples were tested under PID control, with strain rates of $5.5 \times 10^{-3}$, $1.0 \times 10^{-4}$ and $1.2 \times 10^{-5}$. The results are presented in Figure A.1. The stresses at 1% plastic strain were selected from each of their respective stress-strain curves and plotted as a function of strain rate. From this plot, A.1c, it was determined that the strain rate sensitivity exponent is 0.025. However, the result from this study should be taken cautiously. As illustrated in the previous sections of this dissertation, the small size scale of these experiments produce a substantial amount of scatter in the data for any given sample size. I have tried my best to minimize the variability in the testing conditions by testing these samples on the same nano-indenter and without removing the sample prior to any test. That being said, the measured rate sensitivity exponent is very comparable to a value of 0.01 measured by Neeraj et al. [84] for polycrystalline Ti-6242.
Figure A.1: The strain rate sensitivity exponent was determined by testing four 7.5µm Ti-6242 microcrystals under PID control and varying the strain rate for each.
APPENDIX B

Ti-6242 MICROCRYSTAL RESULTS FROM ORIENTATIONS OTHER THAN a1 BASAL

The early work on Ti-6242 microcrystals consisted of fabricating the samples from the "butt-ends" of previously deformed micro-tensile bars. A schematic is presented in Figure B.1. This provided the ideal scenario for studying the tension-compression asymmetry observed in many titanium alloys. The butt-ends of these sample bars were far away from the active gauge length of the samples, such that they did not experience any deformation prior to the microcrystal fabrication. The orientations used for this study were: a2 basal, a3 basal, a1 prism, a2 prism, and a3 prism. The results from this work are presented in Figure B.2. The yield points, plotted as critical resolved shear stresses (CRSS’s), are compared to results published for bulk compression [90] and micro-tension experiments [44]. It is apparent that the strengths achieved for the microcrystals with basal orientations are larger than bulk compression experiments. However, similar trends are apparent, resulting from the orientation relationship between the alpha and beta phases.
The microcrystals results presented above should be taken with a grain of salt. For all orientations, other than a1 Basal, each point in Figure B.2 reflect a single experiment. The repeatability is still an open question. The microcrystal samples used for this study were not fabricated using the lathe automation script. Therefore, these samples are not as "clean" as the a1 Basal samples that utilized the automation and image recognition. This should reflect as a substantial amount of scatter in the data from sample to sample at the same sample size and orientation. Furthermore, these microcrystals were tested without the use of the goniometer stage, such that sample alignment may not be optimal.
Figure B.1: (a) A schematic illustrating the manor from which the microcrystals were fabricated into the "butt-ends" of the microtensile specimens. (b) SEM image showing the microcrystals fabricated into the five orientations.
Figure B.2: The titanium CRSS values are plotted with the results from bulk compression and micro-tension experiments.
APPENDIX C

LATTICE ROTATIONS ACROSS A NICKEL DISLOCATION BRAID

Utilizing EF-CBED and a Cold-Stage, lattice rotations caused from edge-character dislocation braids were studied using higher-order-laue-zone (HOLZ) measurements. Figure C.1 contains images from the TEM foil used for this study. The TEM foil was extracted parallel to the loading direction with the primary Burgers vector out of the plane of the foil. The lattice rotation was determined by collecting an EF-CBED image from various locations on either side of the dislocation braid. These locations are found in Figure C.1. A cross was then placed at the intersection of two HOLZ lines from the EF-CBED image, this is indicated in Figure C.2. When these intersection points were overlaid onto the same image, the average lattice rotation was determined to be ∼9 mRad. As one would suspect, the direction of rotation is perpendicular to the line direction of the edge components.
Figure C.1: (a) BF-STEM images taken from a TEM foil extracted from a 20 µm nickel microcrystal, parallel to the loading direction, with the primary Burgers vector out of the plane of the foil. (b) An enlarged view of the dislocation braid used for this study. The points correspond to the locations where a CBED pattern was collected.
Figure C.2: CBED patterns taken from the 114 zone axis. (a) A cross is placed at the intersection of two HOLZ lines. (b) The crosses from all measurements are overlaid onto one image. From this image, the average lattice rotation was found to be $\sim 9$ mRad.
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