MECHANICAL PROPERTIES OF NANOCRYSTALLINE
PLATINUM THIN FILMS

A Dissertation in
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by

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ABSTRACT

Ever since the realization that an increase in grain boundary volume contributes to the strengthening of metals, there has been a drive to reduce the grain size of polycrystalline metals. The creation of materials with finer and finer grain sizes has led to the development of new fabrication techniques, and metals with grain size in the ‘nano’ (~1×10⁻⁹ m) regime are now commonplace. These days, nanocrystalline metals are used in a variety of nonstructural and structural applications. Insuring the durability and reliability of structural, nanograin, metallic films requires an in-depth understanding of their mechanical properties. This study focuses on establishing the mechanical properties of nanocrystalline platinum thin films, with a substantial emphasis on the cyclic fatigue behavior.

Thin film mechanical testing specimens were fabricated of nanocrystalline platinum in two film thicknesses. Various analysis techniques established these films to be composed of fully dense (111) oriented columnar grains roughly 15-35 nm in size of at least 99.99% pure platinum. An annealing process allowed for the modification of the grain morphology such that the columnar grains were reduced to a more polycrystalline morphology; grains were still vertically elongated, but multiple 14-42 nm sized grains were present through the thickness of the annealed films. Creep testing of all free-standing specimens determined that the mechanical properties of the films are not significantly time dependent, in agreement with nanoindentation studies of identical films adhered to a silicon substrate. Tension testing indicated that the films are mechanically robust, with as-received, columnar films having yield and ultimate tensile strengths higher than 1 GPa and a large strain to failure of ~0.03. Annealed films maintained their strength but lost their ductility, displaying a strain to failure of ~0.01, consistent with their altered grain morphology. Scanning and transmission electron transmission based fractography revealed that failure was the result of ductile void-rupture processes and that the grain morphology of these specimens was stable in spite of the high stresses involved.

Fatigue tests were conducted on ~500 nm films with central notches and resulted in a high power law exponent of ~10.5, and a fracture toughness of about ~5 MPa √m. This behavior is more reminiscent of the fatigue behavior of brittle ceramic systems than that of ductile metallic such as the micrograined form of the platinum, which had a power law exponent of
Fractography revealed that the fatigue crack path exhibited two different crack advance modes. At low crack growth rates, grain coarsening and intergranular crack advance dominated while at high crack growth rates, typical ductile transgranular in the absence of grain coarsening dominated, and at intermediate rates, both crack advance modes were witnessed. A large portion of the study was devoted to characterizing the reasons for and mechanisms behind these observations and dependencies on specimen thickness and grain morphology followed using ~1 μm specimens, both columnar and polycrystalline. Further testing of films revealed that the fatigue crack growth rate behavior is largely dictated by specimen thickness, as ~1 μm specimens displayed a much larger range of fatigue crack growth (~20 MPa √m) and a more typical power law exponent of 3.9-4.2. Although the fatigue behavior of the platinum films has a strong dependence on the thickness of the films, the fracture mode in the films did not show the same dependence with the ~1 μm columnar specimens displaying a similar range of the crack growth modes. The polycrystalline samples, however, displayed a shift in the transition from the intergranular mode to the transgranular mode, and thus a link between the crack advance modes and the grain morphology was formed. Finite element modeling of an elastic anisotropic single crystal of platinum was utilized to quantify stresses in the vicinity of crack tips. Shear stress magnitudes along slip directions indicated that through-thickness slip is preferred over in-plane slip under certain conditions, and is dependent on both vicinity to crack tip and grain orientation.
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Chapter 1

Introduction

The first chapter in this dissertation will open with a broad introduction to the world of nanocrystalline metals. The first section of the chapter will begin with a discussion of the Hall-Petch relationship, the driving force to create metals with finer and finer grain size. This relationship’s primary flaw, its implication of indefinite strengthening from an indefinite reduction of grain size has led to the proposal of numerous alternative plastic deformation mechanisms which will be summarized. The importance of understanding the mechanical properties of nanocrystalline systems will be highlighted from both a fabrication and application standpoint. As a result, platinum is selected as an ideal system to study and a discussion of this choice follows. The second section of the chapter will detail the primary focuses of the studies in this work. A discussion of the importance of microstructural stability in any investigated system opens the section. Mechanical properties of a system are then correlated with dependencies on specimen thickness and grain morphology. The section ends with an explanation of how modeling of the system can provide mechanistic insights that are able to expand on experimental work. The final section of the chapter will provide an overview of the structure of the remaining part of the dissertation.

1.1 Nanocrystalline Metals & Thin Films

Typically for metals, plastic deformation mechanisms which operate at room temperature are dominated by processes involving dislocation slip [1-3]. The movement of dislocations through a metal is hindered by any defect in the lattice such as other dislocations, solute atoms, secondary phases, and grain boundaries. As the grain size is decreased, grain boundary volume in the metal increases, reducing dislocation mobility, thereby hindering plasticity and increasing strength. This effect is known as the Hall-Petch (H-P) relationship and has been experimentally shown to follow the relationship in Equation 1:
Equation 1: \( \sigma_y = \sigma_0 + \frac{k}{\sqrt{d}} \)

where \( \sigma_y \) is the yield stress of the polycrystalline metal, \( \sigma_0 \) is the stress required to move a dislocation in a perfect single crystal region, \( k \) is the strengthening coefficient of the metal, and \( d \) is the mean grain diameter [4, 5]. This relationship has been the basis of engineering metals with increased strength by the reduction of their grain size, in some cases to the nanometer scale, for over half a century. However, the fundamental flaw in this relationship is that it inherently suggests that strength increases indefinitely with decreasing grain size. This is a physical impossibility primarily because the strength of a metal cannot exceed the theoretical shear strength of a perfect crystal and amorphous metals, i.e. metals having no discernable long range order and therefore representing a grain size of about zero, are not infinitely strong. Thus, there must be some grain size below which the H-P relationship no longer holds true (Figure 1-1).

Recent works have suggested that there must be a size below which grains can no longer accommodate dislocation motion, multiplication, and pile-up, resulting in a change in the dominant mechanism for plastic deformation when the grain size is reduced past this threshold [6-12]. Metals having grain sizes below such threshold have been experimentally shown to have mechanical properties that deviate from the H-P prediction with some showing an inverse relationship at the smallest grain sizes [13]. Many different alternate plastic deformation mechanisms have been suggested to be operating below the H-P threshold in addition to, or in place of typical slip deformation, including diffusion, grain boundary migration, grain rotation, grain sliding, or some combination of these processes [14-16]. Despite these, some investigations still report mechanical properties of nanocrystalline metals consistent with slip-based deformation [17]. Although the concern regarding this deviation from the known behavior was relegated to the far future when the Hall-Petch relationship was first conceived, modern processing capabilities have made the fabrication of nanocrystalline metals simple and commonplace, resulting in their incorporation into a multitude of applications across numerous fields.

There are several methods for the creation of nanocrystalline materials [18, 19], but the two most common methods of the ‘atom by atom’ transference, most often used in the creation of thin films, are chemical vapor deposition (CVD) and physical vapor deposition (PVD) [19, 20]. Whereas CVD is the process in which a volatile gas phase chemically interacts with the
deposition surface, PVD involves transference from the gas phase to the substrate by physical means (i.e. without chemical interaction). Sputtering is one physical vapor deposition technique in which highly accelerated ions and electrons are made to strike a solid source. This bombardment causes atoms from the solid source to be ejected into the gas phase. Once in the gas phase, atoms are free to interact and settle on surfaces they come in contact with. This method can be precisely controlled by tailoring the amount of material ejected from the source (the sputter yield) by varying the source material, bombarding ion energies and masses and source temperature. Because of the kinetics of particle-particle interaction, virtually any material can be used as a sputtering source. Microstructure can be controlled through the use of masks, movement of the source or target, and the energies related to the deposition impact. This technique is operable at a range of temperatures, creates uniform particle distribution over relatively large areas, and is comparatively cost effective [19]. Most commonly, the result of the sputtering process is a ‘thin film’ composed of the source material; although the thickness is not actually a consideration in the definition of a thin film, typical thin films created through the sputtering process can be as thin as a few nanometers up to several micrometers. There are a number of ways to form ‘bulk nanocrystalline’ metals [21], but more often than in the thin film cases, the end products have been shown to have unstable grain morphologies [22], and any study of their mechanical properties would be complicated by spontaneous and time-dependent processes occurring simultaneously.

Although nanocrystalline metals and thin films are used in a variety of applications including those utilizing them for their ability to modify optical, electrical, chemical, and magnetic properties, they are also often utilized for their mechanical properties. Microelectromechanical systems (MEMS) have been developed in recent years, allowing for the creation of mechanical devices typically on the order of several micrometers. Some of these are sensors as noted previously, but others have novel uses such as gears, actuators and switches [23-28]. One such application is the micromachined radio frequency (RF) microelectromechanical switches [29-31] such as those created by the Army Research Laboratories (ARL) in Adelphi MD [32, 33]. These RF electrical switches are similar to the ones in a typical wall socket, but about 100 times smaller. The ARL switch works by allowing the control of two moveable cantilever arms made from lead zirconate titanate (PZT), which when actuated, move a contact pad so that it closes an electrical circuit (Figure 1-2). In this device, the PZT is stacked between
two layers of nanocrystalline platinum acting as co-planar waveguides for the current and a large portion of the device is free from the substrate. A device’s functionality is heavily reliant on the mechanical and electrical properties of the nanocrystalline platinum thin films, and these properties must remain consistent throughout the service life of the device (ideally millions or billions of cycles). Any instability in the films’ grain morphology for example, a particular concern in nanocrystalline systems, may lead to an early failure of the device. In order to ensure the reliability of these and similar devices, the mechanical properties of the utilized nanocrystalline metals must be known before they are put into service.

Given multiple applications’ reliance on the on nanocrystalline films, there is a need of establishing their material properties, and in particular, their long term viability and response to cyclic (fatigue) loading. In order to establish the mechanical response of nanocrystalline metallic thin films, a model material system must be selected. With the majority of previous work focusing on nickel [7, 24, 34-38] and copper [37, 39-46], it may be wise to select an alternate metallic system, but in order for the studies to complement the previous experimental and modeling work, the selected model system must be sufficiently similar. Thus, the model should be a nanocrystalline, face centered cubic metal, preferably with grain sizes larger than 10 nm (analogous to the modeling work) but smaller than 100 nm (analogous to the nickel work). In order to match the modeling work further, the nanometer sized grains would ideally be columnar [17, 47-49]. In order to reduce environmental effects, such as those of oxide-induced crack closure, specifically mentioned to play a role in the fatigue of nickel [95], selecting a system which is naturally resistant to oxidation would be greatly beneficial. From these few criteria, nanocrystalline platinum was selected. In addition to the aforementioned characteristics, platinum is also a refractory metal, having a melting point of 2041 K [50], and it is already in use in several thin film devices such as those previously mentioned. It is an ideal metallic system with which to establish the fatigue behavior of nanocrystalline metals. The next section will detail the complications in establishing the mechanical properties of nanocrystalline platinum films.
Figure 1-1: A diagram of the relationship between strength or hardness and grain size. Metals having grain sizes larger than the grain size threshold follow the H-P relationship, while metals having grain sizes smaller than this threshold show a behavior that deviates from this relationship in some manner. The amorphous metals represent the strength of a material having a grain size of zero.
Figure 1-2: A microelectromechanical device used as a microscale switch. This device is composed of a stack of thin films (Ti/TiO$_2$/Pt/PZT/Pt) and is mechanically loaded many times over the course of its lifetime.
1.2 Mechanical Properties of Nanocrystalline Metals

Understanding the mechanical properties and the plasticity mechanisms of nanocrystalline metals is vital in the creation of reliable devices which utilize them, especially in applications in which the systems are mechanically loaded. Unfortunately, investigations of these properties are difficult due to multiple aspects unique to nanocrystalline materials. Nanocrystalline systems have been reported to be microstructurally unstable and to have fatigue properties which are dependent on specimen thickness and grain orientation. This section will detail some of the problems exclusive to nanocrystalline systems and will show that nanocrystalline platinum is an ideal system for the investigation of such mechanical properties.

Microstructural stability is required when attempting to correlate a deformation mechanism or mechanical property to specific grain morphologies; if the grain morphology of a system is in flux, no such correlation can be made. The problem is somewhat alleviated when the change in the grain morphology becomes an integral part of the study and results are put in context of such a change. Some investigations have seen evidence for microstructural evolution without the application of any external loading, even at room temperatures [22, 51] but a far greater number of investigations have noted a change in grain morphology as a direct result of mechanical testing. The earliest of the works that noted such response is by Witney et al who conducted tension-tension fatigue on nanocrystalline copper prepared by inert gas condensation [46]. Witney conducted several hundreds of thousands of cycles with stress ranging from 10 MPa to 80% of the yield stress. Witney noted that the cyclic deformation appeared to be largely elastic, despite a permanent strain of about 0.7% and approximately 30% growth in grain size during the test. Since his findings, several others have noted grain coarsening in nanocrystalline copper [52], nickel and nickel-tungsten alloys [53], ultrafinegrained copper [54, 55], and nickel-manganese alloys [15]. The coarsening has been cited as the reason for the observed cyclic softening in nanocrystalline materials [54], and for contributing to crack initiation [15] but the mechanisms for the growth are still unclear. These investigations beg the question of whether or not non-spontaneous morphological evolution in nanocrystalline systems must precede plastic deformation. Nanocrystalline platinum thin films provide an excellent basis for the determination of the coupling of stress and grain coarsening. Despite microstructural stability in response to
tensile and nanoindentation loading conditions, the grain morphology undergoes an evolution in response to fatigue loading conditions [105]. This kind of response allows a focused study, centering on the fatigue properties of a nanocrystalline system, to quantitatively establish which components of the system play a role in the change of the grain morphology.

The specimen thickness has also been shown to play a role in the mechanical response of a system[56]. This becomes particularly noticeable in fatigue behavior of very thin films, when the plastic zone sizes approach the thickness and causes a change in the stress state at the crack tip. The fracture toughness for example, has been shown to be dependent on specimen thickness, increasing to a maximum at some threshold level, but decreasing substantially below such a threshold where thin films would ultimately fit (Figure 1-3). The reason for this correlation between fracture toughness and specimen thickness lies in the region near and ahead of the crack tip known as the plastic zone. The linear elastic approach for the plastic zone size estimate, first conceived by A. A. Griffith in 1920 for brittle materials [57], was expanded upon by G. R. Irwin for ductile materials [58] (see Equations 5 thru 8 in Section 2.3) as an estimate for the zone in the immediate vicinity of a notch or crack in which plasticity is localized. The size of this plastic zone is dependent on the stress state at the crack tip, corresponding to either plane stress, plane strain or some mixed mode. In turn, the stress state at the crack tip has a dependence on the thickness of the specimen and so all the terms are interrelated. An investigation of the mechanical properties of thin films, and in particular the fatigue properties, must account for dependencies of experimental values with thickness. In other words, it is insufficient to measure fatigue behavior of a material system using thin films without investigating multiple thicknesses of aforementioned films. Due to the processing conditions of the platinum films, multiple thicknesses of films can be created which have identical grain morphologies, allowing for direct measurements of the influence of specimen thickness on the measured fatigue behavior of the system.

The causal interpretation of the stress state at the crack tip extends beyond a dependence strictly on specimen thickness. The stress state at the crack tip and the crack path can also be affected by the grain size and grain texture [59, 60]. A simple interpretation of dislocation motion results in dependencies of lattice orientations with respect to the loading axis. Blochwitz et al [61] studied grain orientation effects on the growth of short fatigue cracks in austenitic steels and noted a direct correlation between grain orientation along the crack path and
propagation rates. Another study by Peralta et al [62] studied similar effects in a variety of polycrystalline FCC metallic systems noting that the local orientation near a crack tip can affect the damage accumulation process ahead of the crack and alter its crack path. Both of these studies have noted the propensity for intergranular crack initiation and extension under select conditions, an observation that will become especially important in nanocrystalline materials such as platinum which some modeling studies claim will show a propensity for intergranular crack extension [35, 38, 63, 64]. In order to be able to extend mechanical response findings across multiple grain morphologies, for example from a columnar system to a polycrystalline system, studies must be made of multiple grain morphologies within one system and one specimen thickness.

Of late, modeling of the mechanical response of the systems has become widespread and molecular dynamic simulations [8, 10, 18, 35, 47, 64-70], and finite element models [38, 71-77] have been prominently used to predict and explain the deformation mechanisms of nanocrystalline metals; these models further span from single crystal to bicrystals to polycrystals and from 2-dimensional investigations to 3-dimensional. Considering the dependence of several aspects of the mechanical behavior on non-2D aspects of specimens, i.e. thickness and texture, there is a need for a simple 3D model which would be able to quantify whether inherently 3D aspects such as through-thickness slip play a significant role in the deformation. This sort of model may be able to determine if stresses in the interior of the film, i.e. the midline, are substantially different from stresses on the surface, ascertaining initiation or direction of slip. A similar conclusion can be drawn regarding planar stresses versus stresses on through-thickness slip directions. Such a model would be able to tie together experimental and theoretical results and allow for a complete view of the mechanical behavior in nanocrystalline materials.
Figure 1-3: A schematic of fracture toughness as a function of thickness modified from Broek [59]. $K_{IC}$ reaches a steady state above some threshold ($B_S$), but below some optimal thickness ($B_O$) it begins to drop precipitously. Although the exact thresholds are material specific, nanocrystalline thin films will likely have thicknesses around or below $B_O$. 
1.3 Structure of Dissertation

Chapter 2 will discuss the materials and methods used in this study. The section will open with deposition techniques used in fabricating the test specimens. Characterization techniques used will be detailed, including optical microscopy for inspecting specimen fabrication, transmission electron microscopy (TEM) to determine orientation and grain size, as well as energy dispersive spectroscopy (EDS) and secondary ion mass spectrometry (SIMS) to quantify the relative purity of the films. Further details about the physical specimens such as geometry and physical dimensions will be discussed. The mechanical characterization system used in order to evaluate the mechanical properties of the aforementioned specimens will be fully outlined. The methodologies involved in the reported testing (tension, creep and fatigue) will be listed and the analysis methods used in each case be discussed. Post-testing characterization of the samples, particularly fracture surface analysis by field emission scanning electron microscopy (FE-SEM) and TEM will be discussed. Finally, a finite element modeling of a single crystal thin sheet displaying elastic anisotropic behavior, developed in ANSYS will be detailed.

Chapter 3 will center on mechanical testing of ~500 nm films, and cyclic stress-induced changes within the grain morphology. The chapter will begin by focusing on the microstructural instability in many nanocrystalline metallic systems and the difficulty of correlating stress-induced microstructural changes with those occurring in the absence of stress; one particular study of the nanoindentation of nanocrystalline platinum films on substrate will be emphasized. Experimental testing results, spanning tension, creep, and fatigue testing will be presented. The fatigue behavior of the platinum films will then be examined in the context of the fracture surfaces correlated at given crack growth rates. Given the observations from this series of investigations, possible reasons for this behavior will be discussed and conclusions presented, namely, the need for testing of a substantially different specimen thickness of similar chemistry and grain morphology.

Chapter 4 will elaborate on the conclusions drawn from the study of ~500 nm films, and will summarize numerous articles that highlight a ‘foil effect’, or in essence, dependence of material properties on specimen thickness. In response to this, the study will focus on the mechanical properties of ~1 μm platinum films, having otherwise identical grain morphology as
that of the first study. Again, experimental results will span tension, creep, fatigue testing, and an emphasis on fractography. The results from this section of the study will be closely compared with those from the previous chapter in order to relate the difference in the behavior to specimen thickness. Emphasis will shift to identifying the mechanisms that result in the observed fracture modes, and analyses of damage partitioning, plastic zone sizes, and stress state at the crack tip will result in the identification of two primary proposed mechanisms. It will be noted that the proposed mechanisms were established using 2D models and do not account for dependence of grain morphology and so the need for testing and 3D modeling will be noted.

Chapter 5 will have two major parts: mechanical testing of annealed ~1 μm films having a substantially different texture than as-received films of the same thickness, and a 3D model constructed to quantify stresses near a crack tip. The chapter will open with summary of investigations reporting that mechanical responses of nanocrystalline systems are dependent on grain morphologies. Modeling investigations, both 2D and 3D in nature, will be explored. Again, experimental results will span tension, creep, fatigue testing, and fracture analysis of the new set of annealed films. The results from this section of the study will be closely compared with those from the previous chapter in order to relate the difference in the behavior to grain morphology. The chapter will then shift to discuss a finite element model of a thin sheet displaying elastic anisotropic behavior. The model will examine both planar and through-thickness stresses on slip direction within slip planes and an interpretation based on contributions that grain orientation and texture may have on the mechanical properties of materials will end the discussion.

Chapter 6 will wrap up the dissertation by listing the conclusions of the study and summarizing the results of the various investigations. After a summary of the results from the experimental and modeling investigations, conclusions will be presented regarding the specific factors governing the mechanical behavior of nanocrystalline materials. Conclusions from these studies allow for a discussion of mechanisms that might govern the response of the material system. This final chapter will end a recommendation for future modeling that may help shed further light on the proposed mechanisms.
Chapter 2

Materials & Methods

This chapter will detail the materials and methods used in this study. The first half of the chapter will detail the methods to characterize the materials in this study so that results could be related to fundamental materials science principles and relevant mechanisms. The chapter will open with a detailing of the deposition technique and a post-fabrication annealing process which ultimately produce the characterization specimens used in this study. Evaluation of the physical properties of the finished specimens follows. A discussion of the grain morphology (i.e. texture, grain size, grain aspect ratio etc.) will be followed by an analysis of how the grain morphology is altered by the annealing process. The second half of the chapter will describe the custom-built mechanical characterization system and the testing methods. The testing procedure will be detailed step by step as it makes its way from an unreleased specimen still on the substrate, as it makes its path through mechanical testing and post testing evaluation. The different types of tests used, e.g. tension testing, creep testing, and fatigue testing, will be described and overviews will be given for general testing conditions and parameters used. A large portion of the chapter will focus on the analysis methodologies which allow interpretation of the data resulting from the mechanical testing. The chapter will conclude with post test evaluation techniques, including fracture surface preparation for and characterization by field emission scanning electron microscopy (FE-SEM) and TEM.

2.1 Materials

The mechanical properties of the nanocrystalline platinum thin films were evaluated using specimens developed at the Army Research Laboratory in Adelphi, MD, in two different fabrications runs; the only difference between the two fabrication runs were alterations in specimen features not influencing mechanical properties (i.e. etch hole patterns, taper angles etc.). Fabrication began with a 100 mm diameter single crystal silicon wafer (100) substrate. All
films were sputtered onto the substrate using a Unaxis Clusterline 200 deposition system configured with individual chambers for Ti and Pt deposition at 50°C in order to prevent the formation of platinum silicides by minimizing the temperature’s contribution to diffusion. The first layer deposited onto the silicon substrate was a 15±5 nm thick titanium layer. This layer served as an adhesive layer for the subsequent platinum layers. Following deposition of this layer, a platinum layer of specified thickness was deposited, with a target of either 450 nm or 930 nm layers; hereafter, these specimens will be referred to as ‘~500 nm’ and ‘~1 μm’ for simplicity and to highlight the factor of two in thickness between the films. The blanket films underwent a micromachining process (i.e., resist patterning, development, etching and removal) to pattern the specimens into geometries suited for mechanical testing. Specimens were transported to the Pennsylvania State University by the author while still on the substrate in order to maintain their structural integrity and prevent physical damage during transportation. Prior to testing, a Xactix Xetch system was utilized in order to release the mechanical testing specimens by removing the silicon from underneath them by exposure to XeF₂ gas. The resulting free-standing specimens were connected to the substrate at one end and held at the opposite end by four tethers that were broken manually prior to testing (Figure 2-1). The mechanical testing that relied on specimens described thus far are detailed in Chapter 3 and 4, but Chapter 5 describes the testing conducted on ~1 μm specimens whose grain morphology was altered after fabrication by an annealing process (Figure 2-2). In order to alter the grain morphology in the films after their fabrication, released specimens still on the die were annealed for 6 hours at 500 °C in a Lindberg Type 59344 tube furnace in an inert nitrogen gas environment. The time and temperature conditions were specifically selected so that they were conducive to a change in the grain morphology, but not high enough to allow for diffusion of titanium from the underlying adhesion layer, as confirmed by EDS analysis.

After the fabrication and release process, all specimens were individually inspected using an optical microscope. Any specimen which appeared flawed, i.e. cracked, broken, bent, dented, malformed, improperly released or otherwise had any other visibly anomalous feature including substantial surface debris, was rejected from mechanical testing; the vast majority of samples did not fall into these categories and were in excellent, optically pristine conditions. The sample surface of as-received specimens was previously investigated using an AFM study [78], and a nominal value of surface roughness, a root mean square value of 2.615 nm over a 1 μm² area in
one sampling was measured. Unlike methods limited to inspecting the specimens’ surface, substantially more information was obtained by inspecting specimen sections thinned down to electron transparency and evaluated using two 200kV JEOL TEM that were outfitted with energy dispersive spectrometers (EDS): a JEM 2010F, equipped with a field-emission electron source and a JEM 2010 equipped with a LaB₆ emitter. Electron transparent samples (both plan-view and cross-sectional) were produced by using conventional mechanical and ion milling techniques [79] and were cleaned using oxygen plasma prior to evaluation to minimize carbon contamination of exposed surfaces. TEM analysis established that the as-received specimens were composed of grains with a strong <111> texture, in agreement with an earlier XRD study [78]. It also revealed that the grain morphology was composed columnar grains, 25±10 nm measured by the line intercept method. Selected area diffraction patterns indicated a lattice spacing of 2.26 Å, matching a (111) structure in the platinum films, consistent with bulk Pt [80]. TEM analysis was also able to confirm that the thickness of specimens was in line with fabrication targets for the two film thicknesses (460 and 940 nm). A similar TEM investigation of the grain morphology of the annealed films revealed that while they maintained approximately the same grain diameter (28±14 nm), they had undergone a significant change in their aspect ratio. Columnar grains in the ~1 μm as-received specimens spanned the entire thickness of the film (Figure 2-3); in the annealed specimens, grains still had an elongated appearance, but multiple grains were stacked on top of each other throughout the thickness (Figure 2-4). Overall, grain height changed from spanning ~1 μm in height in the as-received films, to 55±25 nm in the annealed ones; this is a change in aspect ratio from ~0.027 to ~0.509, or a factor of ~20.

Due to the highly critical role that contaminants play in the inhibition of certain plastic deformation mechanisms [81-83], great care was taken to evaluate the purity of the platinum films. Investigation using energy dispersive spectroscopy (EDS) confirmed that the as-received platinum films were free from contamination both within the grains and at grain boundaries to the detectability limits of the instruments (~0.1 atomic percent) [79], in agreement with an earlier electron energy loss spectrometry (EELS) investigation [78]. Although EDS is a very accurate method of analysis for detecting the presence of elements, secondary ion mass spectrometry (SIMS) has a better resolution [84] and has the distinct advantage of sampling the entirety of the film. Platinum samples were sent to Evans Analytical Group in East Windsor, NJ to acquire concentration depth profiles of all elements present using a Quadrupole Mass Spectrometer.
Because of acquisition area restrictions, only regions that were still adhered to the silicon substrate were investigated – although this had no bearing on the results of the tests, it meant that annealed samples could not be investigated. The SIMS analysis of the ~1 μm as-received specimens echoed conclusions from the EDS and EELS analyses, confirming that the platinum films were free from contamination throughout the entire specimen thickness. The specimen purity of electron transparent sections of ~1 μm annealed specimens were also measured by EDS and confirmed that no contaminants were introduced during the annealing process; SIMS testing could not be conducted due to the difference in chemistry between the unpatterned films on the substrate (required for SIMS evaluation) and the free-standing films not in contact with silicon. So far, no evaluation has been done to measure the orientation in the annealed films.

The geometry of the tested specimens is of crucial importance for both testing conditions and data analysis. The mechanical properties of the platinum films were investigated using sample geometry and testing methods that were established for uniaxial tension-tension of macroscopic specimens in ASTM E 8 [85] with modifications made only to compensate for testing of relevant specimen sizes (Figure 2-1). Gauge widths for specimens used were either, 50, 100, 150 or 200 μm wide, and gauge lengths were either 1.0, 1.3, 1.7 or 2.0 mm long. All mechanical testing was conducted on specimens that were freestanding at one end, and bound to the single crystal silicon substrate at the other. The tensile and creep properties of all thicknesses were measured using constant-width gauge specimens. Fatigue specimens also used the constant-width gauge specimens, but had a single initial obround notch (rectangular with 3 μm semicircular ends) that spanned 33% of the gauge width, allowing for localization of stresses in order to control the fatigue crack initiation site. Two types of notches were used: the ~500 nm employed a central notch, and the ~1 μm films employed an edge notch. In order to create intact specimens that could be prepared for TEM analysis without risk of introducing artifacts from the thinning process, some fatigue tests utilized specimens with arrays of notches with varying lengths (spaced far enough apart to be non-interacting) [86]. In some cases, notches were lithographically patterned and in other cases were created using a Ga⁺ focused ion beam (FIB) system (FEI Quanta 200 3D). Because the damage induced by the focused ion beam was confined to the region immediately adjacent to the notch (~100 nm or less) and the crack extension resolution was five-fold larger, no differences between the fatigue crack growth behavior of the lithographically patterned and FIB machined specimens were observed.
Figure 2-1: A scanning electron micrograph of a ~500 nm fatigue crack growth characterization specimen from the first fabrication run showing (a) the free standing grip section with tethers, (b) the free standing gauge section (200 μm pictured) with central obround slot, and (c) the ‘anchor’ portion attached to the substrate. Tensile characterization specimens lacked the central slot, but were otherwise configured similarly.
Figure 2-2: A scanning electron micrograph of a ~1 μm tension specimen from the second fabrication run showing the specimen as-received (top) and post-anneal (bottom). Notice the only significant change in the outline of the specimen at the free-standing to film-on-substrate interface indicating a weakening in the adhesion at that one locale.
Figure 2-3: (a) Cross-sectional TEM of the full height of the platinum and its 25±10 nm diameter, through-thickness columnar grains. (b) Plan-view TEM of the Pt grains confirming their size and uniform distribution.
Figure 2-4: Cross-sectional TEM of the as-received grain morphology (top) compared to that of the annealed (bottom) grain morphology. Note that the grains have approximately maintained their original diameter and an elongated structure, but no single grain spans the entire thickness of the film.
2.2 Mechanical Testing System

A custom built mechanical testing system was used to characterize the mechanical properties of the nanocrystalline thin films. The testing system comprises of three main parts: a displacement stage to which the substrate-adhered specimen is connected, a load cell connected to the free standing specimen portion, and a camera to image the test in real time. Prior to testing, each specimen was gripped and tested under controlled conditions, while several parameters of interest were monitored and recorded. The following is a detailing of the steps which were followed in order to test each specimen. In following with the description of the system, refer to Figure 2-5 for a basic schematic of the setup.

Prior to testing, specimens selected for tension or creep testing had artificial surface markers added to them via a Magnaflux Developer (SKD-S2) so that strain-induced displacements of the film could be tracked (Figure 2-6). A selected chip containing specimens to be tested was adhered to a custom made aluminum adapter having a 10º tapered end using Superglue®; this adhesive was chosen because it provided a permanent and stiff bond, but could be dissolved at the conclusion of testing using a minute application of acetone. The adapter was in turn connected to a piezoelectric translating stage (PI P620) providing a total of 250 µm of displacement with sub nanometer resolution, in turn mounted on a 3 axis stage capable of tilt, pitch and rotation (Newport PO80N). The displacement stage was controlled by a closed-loop external conditioning box (PI E-665) which allowed digital or manual control of the stage. The control-box was connected to a load control card (National Instruments NI PCI-7340) that allowed for either displacement or force control.

At the other end, a 20 µm tip diameter tungsten needle was affixed to a pin-jack probe holder (American Technologies 745-SAI) using Superglue®. The holder was connected via an adapter to a 50 gram load cell (Sensotec Model 31) capable of force measurements with 0.0005 N resolution. The load cell and attachments sat on top of two stages (Edmund Optics NT56-339, NT55-028) capable of three orthogonal displacements and rotation about the vertical axis. The sample was aligned with the grip system using all the available axes of freedom so that a uniaxial loading mode would result. Ultraviolet (UV) adhesive glue (Dymax OP-24-REV-B) was applied to the tip the needle. It was then lowered on to the free-floating gripping region of the specimen. A hand held UV spot curing system (Electro-Lite ELC-410) was used for 5 minutes to
completely cure the glue. The sample was then realigned by raising the sample to the point where it is flat, resulting in the ability to apply purely tensile forces; this realignment also resulted in the fracture of the 4 temporary tethers with no undue stresses placed on the specimen. Here, an exception is noted for annealed specimens: the annealing process alters the region connecting the specimen to the substrate which results in cohesive failure with the application of very small forces (less than 10% of specimen yield stresses). As a result, the sample was entirely detached from the substrate by the application of such a force, and displaced to the end of the die, where it was lowered onto a flat substrate region, and adhered to the substrate using the UV glue. In these final positions, any motion instruction to the displacement stage would result in the application of uniaxial loading of the specimens and related forces would be directly read by the load cell.

A high resolution color CCD digital camera (Pixelink PL-A776) connected to an image acquisition card (National Instruments NI PCI-1422) which sat on top of two stages (Newport m-562, Newport 813S) and damping rod (Newport 45) so that 5 axes of tilt and translation allowed the camera to be positioned perpendicular to the surface of the gage section of the sample. Long working distance Mitutoyo infinity-corrected long working distance lenses (Edmund Optics NT46), either 20× objectives having a resolution of 0.7 μm, or a 100× objectives having a resolution of 0.4 μm, were used in conjunction to the camera in order to image and record the region of interest. The objective lenses were attached to the camera via an additional stage (PI P-725.2CD) which allowed vertical displacement of the objective lens using a signal sent from an external conditioning box (PI E-665). This attachment allowed the user to change the focus of the objectives whenever necessary without disturbing the system. Illumination for the camera was provided by either a variable intensity coaxial light source with fiber-optic guide (Dolan-Jenner DC950), and/or by secondary oblique light source (Mitutoyo FOI-1). The entire system was situated on top of a bench top vibration isolation system (Minus K BM-4). All electronic instruments were connected to an uninterruptible power source (Tripp-Lite SU3000XL) to prevent power outages from affecting tests or data recording. All testing was conducted in laboratory air (22±2 ºC).

All instruments were controlled by testing software programmed in LabView 7.0. The program controlling tensile tests was based on sending voltage signals to the displacement stage’s conditioning box at quick successive intervals. The conditioning box used the voltage
signals in order to determine a target displacement, and set the voltage required to do so in a closed loop format in real time. This process caused a smooth ramping of the displacement stage away from the load cell, effectively loading the sample in tension. The program was capable of accepting user input for ramp rate, and frequency of imaging. The program recorded load cell output for each displacement increase, along with user specified input. The program controlling fatigue testing ran in force control, taking voltages from the force transducer to calculate appropriate motion of the displacement stage, and allows several user parameters to be entered, including force amplitude, mean force, frequency when cycling, frequency when recording, number of data points to be recorded and frequency of recording of data and images. The creep testing software allowed for a smooth ramping of loads up to a specified load (in much the same manner as a tensile test), held that force constant through load control feedback (in much the same manner as a fatigue test having an amplitude of 0), and then unloaded the sample back to 1% of the maximum load; 1% was used in order to avoid erroneous compressive loading of the samples by the load control software.
Figure 2-5: A basic schematic of the testing system showing the 3 major components of the system, a piezoelectric displacement stage to which the specimen die is affixed, a force transducer connected to the sample via a needle, and a digital microscope capable of imaging and recording the region of interest in real time.
Figure 2-6: (Left) A scanning electron micrograph of a tension specimen after the application of the staining agent. (Right) A higher magnification optical image of the gauge section taken using oblique lighting; the many small features distributed along the specimen were used to track strain using digital image correlation.
2.3 Analysis Methodologies

The raw recorded data (i.e. displacements, forces, and images) produced during the tests allowed for the examination of some of the basic behaviors of the films. Several analysis tools and formulas were used to organize the raw data into constitutive relationships. Analysis of data was largely performed in Excel® 2002 a spreadsheet application from Microsoft. All final curves were graphed and fitted using Levenberg-Marquardt algorithm of version 3.52 of Kaleidograph®, a data analysis and graphic presentation software tool from Synergy Software. The following section will detail how data was analyzed.

All tensile tests were conducted in displacement control, at a displacement rate of 1 μm/s. Due to the uniaxial tension nature of the experiment, stress was calculated by simply dividing the applied force by the cross sectional area of the gauge. Digital image correlation software was used to track displacement of the markers with a strain resolution of 10^{-4} [87]. The yield point (proportional limit) was found by fitting a least-squares linear regression to the first 25% of the data and adding additional data points until the fit correlation value permanently dropped below 0.97. The Young’s modulus was calculated from the slope of the fit prior to the proportional limit.

All creep tests were conducted in load control. Loading and unloading ramps were targeted to match a displacement rate of 1 μm/s. During the ‘holding’ portion of the test, which lasted either 24 or 44 hours, samples were held in load control so that load shedding due to plastic deformation was not a concern. Stresses and strains were calculated in the same fashion as for tensile tests. Creep rate was calculated by simply taking the total accumulated strain and dividing by the time in seconds. When the total accumulated strain was calculated to be ‘zero’, the resolution of the strain-determination technique (10^{-4}) was cited instead.

All fatigue tests were run in load control and targeted to be constant stress amplitude (load ratio \sigma_{\text{min}}/\sigma_{\text{max}}, R = 0.1, sinusoidal, 1 Hz). Images captured for the duration of the test allowed for measurement of crack growth by optical analysis. This method is lens-specific and has a maximum resolution of 4 pixels (2 pixel from each measured end), which at the highest lens objective (100×) correlates to 500 nanometers, close to the resolving power of the lens itself. Images were opened in Photoshop® CS2, and a measurement of crack advance was taken in
pixels, and correlated using a known pixel-meter conversion which was found using a plate stage micrometer (VWR #82026-613) having a 0.05 micrometer resolution. Specimen compliance during fatigue testing was measured by obtaining the slope of a displacement-force plot consisting of 100 points during each cycle. Deviations from linearity in this plot, particularly at low $\Delta K$, may be indicative of contributions from crack closure mechanisms. Previously, a compliance based estimate for crack length was used either in confirmation to or as a substitute for an optical measurement of crack length, however, the scatter in the data only made this technique useful only at the very late stages of crack growth and no values based on this technique were used in this study. More details on the method and reasoning behind this decision is available here [78].

Stress intensity factor, a measure of the driving force of crack advance was found using Equation 2:

$$\Delta K = \Delta \sigma \cdot \sqrt{\pi \cdot a} \cdot f\left(\frac{a}{b}\right)$$

where $a =$ crack length (initially $\frac{1}{2}$ notch width), $b =$ $\frac{1}{2}$ gage width, $\Delta \sigma = \sigma_{\text{max}} - \sigma_{\text{min}}$ as determined from load cell forces and $f\left(\frac{a}{b}\right)$ was found using Equation 3 for a central notch, and Equation 4 for an edge notch, solutions provided by Tada et al [86].

$$f\left(\frac{a}{b}\right) = \left[1 - 0.025 \left(\frac{a}{b}\right)^2 + 0.06 \left(\frac{a}{b}\right)^4 \right]^{\frac{1}{2}} \sec \left(\frac{\pi \cdot a}{2 \cdot b}\right)$$

$$f\left(\frac{a}{b}\right) = \frac{b}{\pi \cdot a} \tan \left(\frac{\pi \cdot a}{4 \cdot b}\right) \left(0.752 + 2.02 \left(\frac{a}{2 \cdot b}\right) + 0.37 \left[1 - \sin \left(\frac{a \pi}{4 \cdot b}\right)\right] \right)$$

Crack growth rates were calculated by dividing the change in the optically measured crack length by the change in cycle (secant method, 3 point, 50% overlap [88]). The fracture toughness, $K_q$, of the material was approximated as the maximum driving force in the cycle that preceded catastrophic failure of the specimen. Monotonic and cyclic plastic zone sizes, for both plane stress and strain were calculated using Equations 5 – 8 [89].

$$r = \frac{1}{\pi} \left(\frac{K_q}{\sigma}\right)^2$$
Equation 6  Monotonic Plastic Zone Size in Plane Strain
\[ r = \frac{1}{3\pi} \left( \frac{K_I}{\sigma_y} \right)^2 \]

Equation 7  Cyclic Plastic Zone Size in Plane Stress
\[ r = \frac{1}{4\pi} \left( \frac{\Delta K_I}{\sigma_y} \right)^2 \]

Equation 8  Cyclic Plastic Zone Size in Plane Strain
\[ r = \frac{1}{12\pi} \left( \frac{\Delta K_I}{\sigma_y} \right)^2 \]

Fractography accounts for a significant amount of information gained from mechanical testing. Two main instruments were used to analyze fracture surfaces, the FE-SEM and the TEM. The early FE-SEM work, on ~500 nm films was accomplished by using JEOL JSM-6700F FE-SEM operating at a range of 5 to 15 kV. This microscope was limited in its tilt capabilities (primarily due to a lack of camera in the chamber), and working distances had to be kept relatively large while tilt was kept relatively minimal. The use of custom-made stubs eased some of the need for tilting, but imaging was still difficult. The switch to using a LEO 1530 FE-SEM, equipped with an in-chamber camera, allowed for smaller working distances, greater tilt, and operation at acceleration voltages ranging from 2 to 5 kV, resulting in a resolution improvement.

TEM analysis was performed on fatigue and fracture crack profiles so that the evolution in the grain morphology could be correlated with the features that were observed on the fracture surfaces. Both arrested and fully propagated fatigue cracks were investigated using the TEM, and special attention was paid to evolution in the grain morphology brought on by the mechanical stresses (i.e. changes in grain size, orientation, and fracture mode). TEM imaging of ~500 nm samples was conducted in a 300kV JEOL 3010 (LaB6), and a 200kV Philips CM200-FEG, and analysis of both as-received and annealed ~1 μm samples was conducted with the previously mentioned TEMs. More details on the sample preparation are found in [90]. In order to measure orientation, the film plane is placed perpendicular to the electron beam by tilting a grain far (~500 μm) from the crack to the <111> zone axis. After doing so, strong diffraction contrast from all of the grains in the BF TEM image is consistent with the entire film having <111> fiber texturing, which was determined via XRD and cross-sectional TEM. Low index diffraction patterns (LIDPs) are collected from the selected grains. The tilts required for orienting the closest LIDP are recorded. The sample preparation and a large part of the analysis were accomplished with help from Daan Hein Alsem, Trevor Clark and Josh Meier (see Acknowledgements).
2.4 Modeling

Finite element analysis (FEA) was conducted using a 3D model incorporating elastic anisotropy created in ANSYS (Version 12.1). The specimen geometry, 100 μm wide, 1000 μm long, 10 μm thick, had an edge crack spanning 33% of the specimen width at its half length (Figure 2-7). This solid was meshed with 8-node element (Solid 185) having three degrees of freedom at each node (x, y, and z). The mesh (Mesh 200) was most refined at the crack tip in order to capture the steep stress gradient associated with that region, fairly dense in areas near the crack tip, and less refined at areas far from the tip. Although symmetry conditions would exist if the model were isotropic, no symmetry conditions were used in order to allow for inspection of crystal anisotropy effects across would-be symmetry planes. A unit stress was applied to the top face of the model, and the bottom face was fixed in both x and y, all consistent with experimental procedures. In the modeled case, the crack plane is the (111), and the crack tip growth direction is any <110> direction. Examination paths were chosen to follow the <110> family of slip directions within the {111} family of closed packed planes of the material modeled and these paths were unique to the material orientation; these paths correspond to the primary slip planes within any FCC system [89]. This allows for inspection of stresses along both in-plane primary slip directions, of which there are 6, and through thickness slip directions, of which there are 3 above the crack plane, and 3 below. Initial focus will be placed on the slip directions ahead of the crack tip, both in- and out-of-plane. The entire script, generated in MATLAB, is available in Appendix A.

It was important to incorporate anisotropy into the model for several reasons, but primarily, it is because platinum is inherently anisotropic [91]; any isotropic 3D model is making an invalid assumption about material properties. In order to the model the orientation-dependent mechanical behavior of grains, the second order elastic stiffness constants of platinum at room temperature [91] associated with typical unit cell axes (listed below) were rotated to new coordinate axes relevant to the texture of the experimental specimens (i.e. <111> oriented).
The anisotropy in platinum is significant: the Zener Ratio, a measure of the elastic anisotropy is 1.59, resulting in Young’s modulus of significantly different values in varying directions, for example 136 GPa along [100], and 210 GPa along [111] [92]. Rotation of the above elastic constants was accomplished by applying a rotation matrix from the original to the new coordinate axes on the 4th order tensors and then reducing back to 2nd order values using a Wolfram Mathematica 7 script; the script is available in full in Appendix B.
Figure 2-7: 3D Finite element model of a thin sheet (left) and a close-up of the mesh configuration near the crack (right).
Chapter 3

Mechanical Properties of ~500 nm Columnar Nanocrystalline Platinum Thin Films

This chapter will detail the mechanical properties of ~500 nm textured, nanocrystalline thin films. In general, there is a fundamental lack of understanding of the relationships between stress, plastic deformation, damage accumulation and microstructural evolution in nanocrystalline metals. The path to identifying and characterizing the roles that these factors play in the mechanical behavior is to identify and characterize a stable, nanograin material under a variety of loading conditions. This chapter will detail results from tensile, creep and fatigue testing. Fractography (using both SEM and TEM) of failure surfaces will follow in order to correlate mechanical behavior to damage accumulation mechanisms. The results are put in context of competing mechanisms, with further testing gearing to explore the cause for mechanisms and the dependency of mechanical behavior on the specimen thickness.

3.1 Introduction

A central challenge to understanding how fatigue damage accumulates in nanograin films has been the limited stability of the structure of the films. In many metallic films (e.g., Ni, Cu, and Ag) the grains spontaneously coarsen (“self annealing”), a phenomenon that can also be driven by stress [93]. Nanocrystalline Ni, for example, has been shown to display a typical power law exponent (between 2 and 3.5) [2, 7], but also grain coarsening in response to cyclic sliding contact testing [8]. However, they have also been shown to creep at room temperature [9] making it difficult to deconvolute the time dependent mechanical responses from the stress and cycle dependent responses. Unlike many nanograin metals, the nanoscale, columnar grain morphology of the Pt films studied in this work are remarkably robust. The grain morphology does not spontaneously change at room temperature or during monotonically increasing tensile or indentation loads, and time-dependency is restricted to a slight anelastic response [96]. As a result, Pt is an ideal system for understanding how cycle-dependent deformation and degradation
occur in pure, textured, face centered-cubic (FCC) films. In the case of columnar, stable, nanoscale grain morphologies evaluated in this work, fatigue degradation at low crack growth rates is intimately linked to cyclic grain coarsening processes where plasticity appears to be dislocation mediated, in spite of the fine grain morphology.

Mechanisms governing plasticity in coarse grained and ‘macroscale’ samples are known to break down when the microstructural features approach the ‘nanoscale’. Understanding the mechanisms governing the mechanical response of nanocrystalline materials would undoubtedly lead to an enhancement of physical properties, but would also provide insight into size and length scale effects in nanoscale specimens and grain morphologies. One of the primary difficulties in establishing these mechanisms is decoupling experimental observation and modeling predictions from the inherent instability of nanograined metals at room temperature, especially in the presence of mechanical stress. This is particularly vital because any grain coarsening that occurs in these materials has the potential to undo the benefits of their initially fine grain size.

Investigations into the fatigue response of nanocrystalline materials are very limited, so there are some important gaps in our understanding of how a cyclic, tensile, and indentation loading modes differ. Despite this, there are a few experimental investigations citing grain coarsening in ultra-fined or nanograin materials in response to fatigue loading. The earliest experiment to report grain coarsening in response to fatigue is by Witney [93], who reported on the microstructural evolution of nanocrystalline copper. Since then, other experimental works involving fatigue on nanocrystalline nickel and nickel-tungsten alloys, ultrafinegrained copper [54, 55], and nickel-manganese alloys [94] have noted grain coarsening. The coarsening has been cited as the reason for the observed cyclic softening in nanocrystalline materials [54], and for contributing to crack initiation [94] but the mechanisms for the growth are still unclear. One investigation, by Zhang [95], reports grain coarsening both at room temperature and cryogenic temperatures, suggesting the growth can be dominated by mechanical factors. Several modeling investigations have suggested possible stress-assisted grain coarsening mechanisms [17, 35, 64, 97, 98], but their mechanisms are varied and difficult to decouple from the room-temperature coarsening response found in many experimental investigations.

In a separate study of the nanocrystalline platinum films used in this study, Romasco [99] studied the mechanical properties of the films via nanoindentation. A series of 10 indents was
made into the platinum films on the silicon substrate from the first fabrication run. Using the Oliver-Pharr analysis, the average plane strain modulus of the blanket films on the silicon substrate was 221±2 GPa, which compares favorably with the 213 GPa predicted by the Vlassak and Nix anisotropic elasticity solution [100]. The average nanoindentation hardness of 7.4±0.1 GPa was consistent with the strength expected of nanocrystalline metallic systems. The regions tested were several millimeters apart, but their individual results have been confirmed by repeat experiments (in separate sessions) within each region. Residual indents resulting from nanoindentation were studied in TEM to confirm the stability of the microstructure in response to compression loads. TEM micrographs reveal no measurable grain coarsening or change to the dislocation density within the interaction volume (Figure 3-1). The tension and indentation results suggest that the films have a stable microstructure even under high loads and are mechanically robust, and as such, make for an excellent system to conduct further mechanical testing.

In general, there is a fundamental lack of understanding of the relationships between stress, plastic deformation, damage accumulation and microstructural evolution in nanocrystalline metals. The path to identifying and characterizing the roles that these factors play in the mechanical behavior is to identify and characterize a stable, nanograin material under a variety of loading conditions. The textured, nanocrystalline platinum films in this work have the requisite stability, and were used to identify the deformation behavior of the films under tensile, indentation, and fatigue loading conditions.
Figure 3-1: Bright field TEM image of a cross section of a residual indent left over from a representative instrumented nanoindentation test of the platinum surface. Note that the microstructure is similar to that of the as-received specimens shown in Figure 2-3 (a), and that there is no measurable amount of grain coarsening within the interaction volume.
3.2 Results and Discussion

Four uniaxial tension tests were performed on platinum films (Figure 3-2) from the second fabrication run. The films displayed a yield strength of 1.5±0.1 GPa, ultimate strength of 1.75±0.05 GPa and had a Young’s modulus of 158±5 GPa. The failure surfaces were inclined ~55º from the tensile loading axis. In comparison, the experimentally measured ultimate stress in bulk, microcrystalline platinum is 145±20 MPa and the Young’s modulus is 171 GPa [50]. The high values of both the yield and ultimate strengths are consistent with the high strength associated with FCC metals with such fine nanoscale microstructure. The Young’s modulus is somewhat low when compared to bulk microcrystalline platinum, but was consistent with the trends in FCC metal films by other researchers [43]. Fracture surfaces of these films displayed a typical transgranular crack path associated with dislocation-mediated plasticity and failure. The plasticity in the films, seen both in the stress-strain curve (a strain of 0.028 to failure) and from the fracture surfaces, is consistent with ductility expected from FCC metals and confirms that the films are not ‘embrittled’ by grain boundary contaminants or voids; comparatively, the strain to failure of bulk microcrystalline platinum is 0.35 [50].

One constant stress creep test was conducted on the ~500 nm platinum film from the second fabrication run. The film was loaded to 1 GPa, representing approximately 65% of the films’ yield stress, and the stress was maintained (in load control), for 24 hours, before being unloaded (Figure 3-3). Strain did not accumulate during the holding phase, and no residual strain was measured after unloading; this is all in confirmation with nanoindentation testing which found that there are is time dependent behavior in the films. After the creep test, the specimen was tested in uniaxial tension in order to confirm that no plastic damage had been incurred by the creep test. Figure 3-4 shows the resulting tension test when compared to the previously discussed tensile tests. The same conclusion was reached by Romasco et al. [99], who tested the time-dependent properties of the films via a series of nanoindentation tests.

Four constant stress amplitude fatigue tests were performed on freestanding notched samples from the first fabrication run. During the fatigue crack growth tests, cracks grew symmetrically from the notches and exhibited straight (i.e., nominally mode I) crack paths, and surface distortions associated with the development of the plastic zone were not observed (Figure
3-3). Final rupture of the specimens occurred on paths that were inclined ~50° from the tensile loading axis after an unknown amount of stable, ductile tearing. The symmetry of the crack extension from both ends allows for reasonable averaging of the two crack lengths. This symmetric growth is also a testament to the uniaxial conditions of the testing setup, as well as the overall uniform material properties of the nanocrystalline platinum.

The measured fatigue crack growth rates as a function of the applied stress intensity factor ranges are shown in (Figure 3-4). An extremely limited range of fatigue crack growth was observed (~2.5 MPa $\sqrt{m}$), and a least squares curve fit of the data to a power law relationship between the fatigue crack growth rate, $da/dN$, and the applied stress intensity factor range, $\Delta K$, (i.e., $da/dN = C(\Delta K)^m$ where $C$ and $m$ are fit parameters) provided a large power law exponent, $m$, which ranged from 7.9 to 15.3. The fracture toughness, $K_q$, ranged from 3.45 MPa $\sqrt{m}$ to 4.88 MPa $\sqrt{m}$. In contrast to bulk microcrystalline metals, the nanograined Pt films in this investigation exhibited fatigue crack growth rate trends that were reminiscent of extrinsically toughened structural ceramics and ordered intermetallics (i.e., $m > 10$). Consistent with this observation, the fracture toughness of the nanograined Pt film was exceptionally low, ~10 times less than the micrograined form of the material [101].

The fatigue crack path in the near-threshold regime (i.e., growth rates below $10^9$ m/cycle) and up to $\sim 2\times10^{-7}$ m/cycle was intergranular (Figure 3-5 left). Images from this region reveal visible grains and secondary cracking. As the cracks grew in length and accelerated to $\sim 3\times10^{-7}$ m/cycle, they gradually transitioned to a transgranular path (Figure 3-5 center). During this transition, a fine ridge parallel to the crack propagation direction developed in the center of the failure surfaces. This relatively short section exhibited a mixture of the features of the neighboring inter- and transgranular regions. The transgranular mode dominated the crack path at growth rates larger than $4\times10^{-7}$ m/cycle (Figure 3-5 right).

The contribution of intrinsic and extrinsic mechanisms to the fatigue crack growth resistance of a material (i.e., mechanisms that operate ahead and in the wake of the crack tip, respectively) can be deduced from the shape of the cracked specimen compliance curves [102, 103]. Deviations from linearity upon partial unloading usually indicate that the crack faces have come into contact and that the effective driving force for fatigue crack growth has been reduced [89]. It is worthwhile to note that the data for coarse grained, bulk Pt published by Speidel was presented in a “closure-corrected” form, and therefore represents the material’s intrinsic
resistance to fatigue crack growth. One cannot help but wonder if the higher fatigue crack growth rate exponent for the textured, nanograined Pt has intrinsic or extrinsic origins. Similarly, the secondary cracking observed in at low fatigue crack growth rates in the Pt films (Figure 3-5 left) could indicate that crack bridging and other shielding mechanisms are important. Crack closure is typically more dominant at low $\Delta K$ and lower load ratios due to the smaller crack opening displacements, so if present it should be easily observed under the testing conditions used in this study. Although significant microcracking was observed, the compliance curves collected during fatigue crack growth in the Pt films were linear for the range of fatigue crack growth rates that were measured [104]. Consequently, extrinsic mechanisms play a minimal role in fatigue crack growth in the Pt films. This observation is in contrast with findings by Hanlon, which alluded to the importance of intrinsic mechanisms in nanocrystalline materials, but no change in power law exponent was observed.

TEM analysis was performed on fatigue and fracture crack profiles so that the evolution in the grain morphology could be correlated with the features that were observed on the fracture surfaces. The transmission electron microscope images from a crack whose growth rates were less than $2 \times 10^{-7}$ m/cycle (i.e., confined to the intergranular region) show clear evidence of increased grain size in the wake and ahead of the crack tip (Figure 3-6) and a tortuous, intergranular path. The grains within $\sim$500 nm of the crack have undergone a nearly 10-fold increase in size when compared to the surrounding material. Moreover, the dislocation density in the coarsened grains is similar to that in the unchanged grains. Selected area diffraction confirmed that the coarsened grains maintained their $\langle 111 \rangle$ orientation after the fatigue crack passed. TEM crack profiles from growth rate regimes where a central ridge is present on the fracture surface (i.e., crack growth rates exceeding $3 \times 10^{-7}$ m/cycle) show no evidence of grain coarsening. Moreover, several grains appear to have been bisected by the crack path, confirming the transgranular nature of the cracking process at these crack growth rates. Collectively, these observations imply that grain growth is primarily a fatigue-driven process that is intrinsic in origin.
Figure 3-2: A stress-strain plot compiling results from four uniaxial tension tests of constant gauge-width samples. The platinum films show a yield strength of \(~1.5\) GPa, and an ultimate strength of \(~1.76\) GPa as well as a substantial amount of plastic deformation prior to failure, all consistent with ductile metallic films. All error is contained within the marker size.
Figure 3-3: A plot of strain as a function of time resulting from a 24-hour constant stress creep test. Although some variability is evident, there is no accumulated strain, confirming that nanocrystalline platinum films do not display time-dependent properties.
Figure 3-4: A stress-strain plot showing results of a tensile test conducted on the specimen that had undergone creep testing (red) compared to those specimens that had not undergone any other testing. Note that the results illustrate that there is no noticeable differences between the two sets of specimens, again confirming that nanocrystalline films do not display time-dependent properties.
Figure 3-5: Optical images acquired during fatigue testing of a nanocrystalline Pt film (test 3) showing (a) the initial obround slot, (b) a crack at 50% of the critical crack size, (c) a crack at 75% of the critical crack size, (d) the sample after fracture.
Figure 3-6: Empirically measured fatigue crack growth behavior of nanograined Pt films (circles) compared to previously published data for micrograined Pt by Speidel (diamonds) [101]. Power law fits of the nanograined Pt indicates a high power law exponent ($m = 10.5$) when compared to the microcrystalline Pt behavior ($m = 3.3$). All error is contained within the marker size.
Figure 3-7: Scanning electron micrographs of a typical Pt film fatigue failure surface in relation to the original sample. As the crack advanced from left to right, the crack propagated via an intergranular path (left). As the fatigue crack growth rate reached $\sim 2 \times 10^{-7}$ m/cycle, the growth mode transitioned to a mixed inter- and transgranular morphology (center). Above $\sim 3 \times 10^{-7}$ m/cycle, the crack path was transgranular (right) with a central ridge that was associated with localized necking.
Figure 3-8: Bright field TEM image of fatigue crack path (ΔK = ~4.5 MPa√m, da/dN = ~1×10⁻⁷ m/cycle) showing effects of stress-assisted grain growth along the intergranular crack path region. Grains coarsened up to 10-fold are found along the crack path. Coarsened grains are also visible ahead of the crack tip at the far right. Note that the apparent bridging of grains along the crack path is an artifact of the slight tilt of the specimen in the TEM. (Arrow denotes crack growth direction)
3.3 Mechanistic Implications

Although the details of the fatigue mechanisms are not completely apparent, the mechanical testing and electron microscopy data presented herein allow us to define their salient features. First, and arguably most important, fatigue crack growth in the platinum films is dominated by cycle-dependent plastic deformation that is mediated by dislocation motion. While the dislocation activity cannot be observed directly, features of the fracture surface make it clear that dislocation motion is important. The ~55.9° inclined fracture surfaces that develop from tensile overload, ductile tearing, and unstable crack growth exhibit a distinctively transgranular appearance. Moreover, the grain structure maintains its nanoscale character, and intergranular voiding that would result from severe grain rotation was not observed. While it was not possible to identify significant changes in dislocation density (not unusual for nanograin metals) or to observe them directly during the degradation process, the inclination of the fracture surface and its morphology are traditional hallmarks of dislocation-based plasticity.

A characteristic feature of textured FCC metal fatigue in nanocrystalline platinum is the evolution of the fatigue crack path from inter- to transgranular. The fatigue failure surfaces at low fatigue crack paths are clearly intergranular. As the fatigue crack growth rate increases, the mode transitions to transgranular and a central “ridge” develops. While this typical feature has not been explicitly noted by other authors (e.g., see Fig 10 of [105]), we have also observed it in 2 µm textured Au films [106]. Given the well-established relationship between dislocation slip and fatigue crack path, it is likely that the evolution of crack path is a natural byproduct of the constrained dislocation slip in the textured film. Initially, dislocation slip is restricted to the best oriented <110> [96] system. As the crack tip stress field becomes more intense, additional transverse planes allow for through-thickness slip of dislocations. This evolution is similar to the plane strain to plane stress transitions that occur in single crystals [75]. While this trend appears in both nano and micrograined textured films, there is an important grain coarsening phenomenon that is enabled by cyclic plastic deformation.

Plastic deformation in metals usually leads to the formation of dislocation networks [89]. Depending on the magnitude of the strain, and the loading type (monotonic or cyclic), the size and arrangements change. Alternating areas of high and low dislocation density form, and the
characteristic patterns of low dislocation density are initially isolated (“cells”) and become interconnected (“labyrinth”) until cracking and decohesion occurs at “ladder-like” persistent slip bands (PSB). In the case of ultrafine and nanograined films, these networks are often not found because they cannot form within a single grain. It is important to note that the absence of these networks does not necessarily mean that dislocation motion does not occur and that (usually) elevated temperature mechanisms such as grain boundary sliding must be active. Instead, the grain boundaries must act as sources and sinks for the dislocations. In the special case of textured FCC films, the angles that arise between adjacent grains are usually low angles. In fact, our TEM evaluations showed that the angle can be so small that it is difficult in many cases to distinguish between grains. In this situation, we postulate that the motion of dislocations allows for the progressive coarsening of the grains. Recall that TEM analysis reveals that a large portion of the crack path is intergranular and that the grain size adjacent to the crack has increased ~10-fold. Moreover, the coarsening is clearly visible ahead of the crack tip and the intergranular fracture surface has through-thickness, linear features that are reminiscent of the original columnar grains. This suggests that clusters of grains consolidate by the annihilation of a portion of the grain boundaries instead of a process which allows larger grains growing at the expense of smaller ones. However, as the crack accelerates, the grain size remains essentially unchanged, even during unstable crack growth. These additional observations provide crucial insight into how fatigue damage occurs.

The combination of fatigue-driven grain coarsening and crack advance can be accommodated by three possible sequences of events. One option would be for coarsening to happen spontaneously after passage of the crack in between the grains. Such a process would be expected to be more extensive when plastic deformation is more severe- such as at high crack growth rates and during tensile overload. Given that the coarsening is observed ahead of the crack tip in the TEM crack profiles and only at low fatigue crack growth rates, it is unlikely that the coarsening and crack growth can be decoupled. This essentially rules out that the underlying mechanisms that are a cyclic analog to self annealing or recrystallization and grain growth at a newly formed free surface. The second option is that the grain coarsening must occur before the crack advances along the grain boundaries. Given the transition to a transgranular path at higher growth rates (i.e., cracking with a notable absence of grain coarsening), this sequence of events is also improbable. Instead, the third sequence is most likely - cyclic crack advance and grain
coarsening must occur simultaneously and likely the two are competing processes. The simultaneous coarsening and crack advance competition allows us to reconcile the experimental data in this study as well as some well-established trends in the literature.

The most likely sequence of events is that cyclic/reverse slip of dislocations near the crack tip causes some grain boundaries (low angle) to be annihilated prior to crack advance during relatively low stresses. The result is effective grain growth that requires cyclic deformation. Moreover, this grain coarsening mechanism will maintain the outer boundary that is made up of a series of columnar grains; this periodicity and distinctive intergranular crack path would appear (consistent with the scanning electron micrographs). The crack will then grow along the weakened grain boundary, probably consistent with criteria such as those developed by Mughrabi [107]. The transition from intergranular to transgranular growth modes is likely due to a competition with a second mechanism; at higher stresses and consequent loss of slip constraints, inclined slip planes can be activated, allowing typical transgranular plasticity to occur. This loss of crack tip constraint (i.e., a plane strain to plane stress transition) would give rise to both a transgranular fracture mode, as well as a central ridge on the fracture surfaces. Moreover, it would also give rise to a transitional region between the two regions in which both mechanisms are operating. Our proposed set of competing mechanisms would explain experimental observation of both the fracture surface and the evolution in microstructure, but does not adequately describe the high power law-exponent and shortened fatigue crack growth range. These two results are most likely a direct result of the thickness of the film, which would explain why other investigations of thicker nanocrystalline FCC metallic systems have not produced a similar response.
3.4 Conclusions

The fatigue behavior of pure, oriented nanocrystalline platinum thin films was evaluated in laboratory air. Tension tests (yield and ultimate tensile stresses of $1.5\pm0.1$ GPa and $1.75\pm0.05$ GPa respectively) showed that the grain structure does not coarsen during tensile loading, a conclusion not unlike that reached by indentation testing of the same films by another investigator [99]. Constant stress amplitude fatigue tests showed an extremely limited range of fatigue crack growth and a large power law exponent, $m$, of $\sim 10.5$. FE-SEM and TEM analyses revealed that cyclic crack advance via a competition between dislocation-mediated grain coarsening (with intergranular cracking) and transgranular crack growth modes. However, the linear unloading compliance curves that were observed in the near threshold regime suggest that the underlying mechanisms are intrinsic in origin.
Chapter 4

The Role of Specimen Thickness on the Mechanical Properties of Nanocrystalline Thin Films

This chapter explores the dependence of the mechanical behavior in nanocrystalline platinum thin films on specimen thickness, and theorizes that two crack growth modes, both dependent on dislocation slip mediated plasticity, operate in conjunction with the stress state at the crack tip. The mechanical properties of ~1 μm thick films are investigated, with analogous tensile, creep and fatigue testing and fracture analysis, and placed in context the results of Chapter 3. Multiple mechanisms are proposed to account for the observations based on an interpretation of the plastic zone size, and the stress state at a crack tip. These mechanisms set the stage for an additional analysis requiring correlation of the mechanical response of the films with grain morphology.

4.1 Introduction

The tendency of nanoscale grains in metals to coarsen at room temperature makes it difficult to deconvolute the stress [52] and temperature [42, 51] contributions to plastic deformation. The problem is even more complex when we consider cyclic plastic deformation and the fatigue damage that it can create [15, 46, 108]. The experiments detailed in the previous chapter have demonstrated that dislocation-mediated, cyclic plastic deformation can lead to significant grain coarsening, even when the nanoscale grains are relatively stable during thermal, tensile, or indentation loading [109]. Moreover, since grain coarsening was restricted to relatively low fatigue crack growth rates, it is clear that grain coarsening is not a prerequisite for crack advance in face centered cubic (FCC) metals. However, the underlying reasons for the reduced fracture toughness and fatigue crack growth resistance are still unclear. In this work we directly link the thickness of the specimen to degraded performance and further clarify the role of dislocation slip in the fatigue and fracture of nanograined metals.
Under appropriate conditions, sputtered platinum can form a mechanically robust, textured, nanoscale grain morphology which is stable even under the high forces associated with nanoindentation and uniaxial tension of thin films [109]. Additionally, surface oxidation and other degradation phenomena are limited because platinum is both a refractory (having a melting point of 2042 K), and a noble metal [50]. Furthermore, reference data of both the bulk microcrystalline form [110], as well as similar FCC nanocrystalline systems [81, 111] is available to serve as points of comparison. These advantages have already resulted in the adaptation of nanocrystalline platinum thin films to be incorporated into small scale devices [32, 33], some of which require the films to be mechanically loaded many times over the lifetime of the device. The fatigue behavior of the nanograin platinum, essential to the long term reliability of such devices, is notably distinct from both its own microcrystalline form as well as other nanocrystalline metallic systems that are otherwise similar to it (as in structure, strength, ductility etc.) (Figure 4-1).

When compared with similar nanocrystalline metals [81, 111], the fatigue crack growth rate behavior of the ~500 nm nanocrystalline platinum films is substantially different. The nanocrystalline platinum fracture toughness is an order of magnitude less than its microcrystalline form [110], and at least a factor of 3 or higher from other forms of nanocrystalline materials [81, 111]. Moreover, platinum’s power law exponent is a factor of 2 to 5 higher than all other investigations, making its fatigue behavior more akin to a ceramic than to otherwise similar FCC metals [112]. The nanograin platinum also displays a peculiar fatigue crack path, transitioning from a grain coarsening coupled intergranular fracture at low crack growth rates to transgranular cracking with no notable change of grain size at the higher rates. In the absence of a time-dependent response, there are several variables that could have a substantial effect on the fatigue crack growth behavior within a single system, most importantly: grain size, texture, and thickness. When comparing the fatigue crack growth behavior of the nanocrystalline system to other nanocrystalline systems, it is obvious that the grain size is not the primary cause of the distinct response. The texturing in the other investigations is somewhat ambiguous; while all the systems shown in Figure 4-1 are FCC in nature, the orientation of the grains is not always well characterized. Thickness is a primary difference between the very thin

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1 Like most metals, the deposition conditions and subsequent heat treatments for platinum thin films can be adjusted to create a wide range of grain morphologies. The stability of a particular processing sequence must be verified experimentally, and less stable films can be fabricated [120].
(\sim 500 \text{ nm}) \text{ platinum films and the other investigations, which span } 100 \mu \text{m to } 270 \mu \text{m} \ [81, 111]. \text{ The complex relationship between the fatigue behavior of a system and the specimen thickness has been explored in the past. Broberg developed a theory to account for the stress state in the region immediately ahead of the crack, noting that this stress state undergoes a significant transformation as the thickness of the material is changed} \ [60]. \text{ Noting a change from plane strain to plane stress as thickness is decreased, Broberg predicts a significantly reduced fracture toughness values for foils and thin films. Broek thoroughly reviews this and several other models on the subject, noting that reduced fracture toughness is a natural result of a transition from in the stress state at the crack tip from plane strain to plane stress} \ [59]. \text{ Cottrell & Reddel echo this conclusion based on their tensile tests of low alloy steels} \ [113]. \text{ By examining the effects of plastic deformation on a layer of ‘brittle lacquer’ places on the surface, their work shows that plastic deformation at the zone ahead of the crack tip is proportional to the sheet thickness. Wang et al. took a less invasive approach by using the digital speckle correlation method at crack tips of copper foils} \ [114]. \text{ Their results experimentally show that fracture toughness is dependent on specimen thickness, but that the relationship is not linear, but rather a function of multiple variables, including the stress state at the crack tip. Schulson and Xu} \ [115] \text{ have experimentally and through finite element modeling shown that the portion of intergranular failure in Ni}_3\text{Al single crystal specimens is directly correlated with the degree of triaxiality at a notch tip; they note that triaxiality increases with thickness, and as such increasing thickness produces a larger fraction of intergranular failure. All of these investigations argue that multiple facets of the fatigue crack growth behavior are tied to the thickness of the specimens, and have experimentally and theoretically shown this for micrograined specimens, but extension of these principles into nanograined specimens has been lacking due to the inherent difficulty of testing such structures, as well as claims of unstable microstructures. Experimental testing of specimens with different film thicknesses, but with an otherwise identical and stable grain morphology, is a unique opportunity to establish the role of specimen thickness in the fatigue crack growth behavior of nanocrystalline platinum. This testing, in conjunction with fractography, will help shed light on the operating mechanisms and their dependence on specimen thickness.}

\text{This chapter will detail an experimental investigation of the mechanical properties of nanocrystalline thin films having a twice the thickness of previous works} \ [109], \text{ but otherwise identical geometry, grain morphology and chemistry. In addition to investigating the role of}
thickness on tensile and time dependent properties, emphasis will be placed on its role in the fatigue crack growth behavior; in this regard, thickness will be examined with respect to fracture toughness, the power law exponent of the crack growth behavior, and the point at which the crack advance mode shifts from grain coarsening coupled intergranular advance to transgranular cracking in the absence of microstructural evolution. In line with all experimental observations, two grain boundary dominated deformation mechanisms are proposed and correlated with specimen thickness and its effects on the loading conditions at the crack tip.
Figure 4-1: Fatigue crack growth rate behavior for multiple material systems. Note the distinctly high power law slope of the nanocrystalline thin film system when compared with its microcrystalline form and other nanocrystalline FCC metals.
4.2 Results and Discussion

The role of film thickness on the mechanical behavior of textured, nanocrystalline platinum thin films was probed through experimental testing. This section will detail results of tension, creep and fatigue testing of ~1 μm thick nanocrystalline platinum films and discuss them in comparison to the previous chapter detailing results of ~500 nm thick films having otherwise identical grain morphology. Analysis of fracture surfaces will investigate whether thickness effects of the mechanical behavior also affects the crack propagation mechanism. In an attempt to explain the effects produced by changing the thickness of the specimen, discussion of damage partitioning as it applies to the fatigue behavior, as well as the dependence of stress state and the plastic zone size ahead of a crack tip on thickness will follow.

4.2.1 Experimental Results

Four uniaxial tension tests were performed on ~1 μm platinum films. The films displayed a yield strength of 1.3±0.1 GPa, an ultimate strength of 1.45±0.05 GPa and had a Young’s modulus of 133±5 GPa (Figure 4-2). When compared with the ~500 nm platinum films of the previous investigation [109], the lower yield and ultimate stresses in the ~1 μm films were also associated with a higher strain to failure, 0.034±0.001 compared to the ~500 nm films which failed at a strain of 0.028±0.001. The elastic modulii of both films are somewhat low when compared to bulk microcrystalline platinum, but are consistent with the trends in FCC metal films by other researchers [43]. The high yield stress and ultimate stresses in the films are consistent with the strength expected from FCC metals with such a fine grain size; despite their high strengths, films retained a large amount of ductility. The ~1 μm specimens had a fracture angle of 48.0±2.4°, compared to ~500 nm specimens which had a fracture angle of 55.9±1.8°. Using Equation 9 [116], the pure tension fracture angle, φ, of a material of planar isotropy (such as ours) can be correlated to the material anisotropy factor Y.

Equation 9: \( \phi = \frac{1}{2} \cos^{-1}(1/(1+2Y)) \)
This factor, $Y$, is simply the calculated ration between width strain to thickness strain, and is therefore indicative of anisotropy within the material. The calculated anisotropy factor for the ~500 nm films is ~0.85, and for the ~1 μm film is ~4.3. This indicates that the thickness of the specimens has a large bearing on the anisotropy of the system, in addition to all other effects. Fracture surfaces of these films displayed a typical transgranular crack path associated with dislocation-mediated plasticity and failure, confirming that the grain boundaries are not embrittled by contaminants or voids (Figure 4-3). Transmission electron microscopy of overloaded regions indicated that no measurable amount of grain coarsening took place, consistent with similar observations made on this system during nanoindentation tests [96].

One constant stress creep test was conducted on the ~1 μm film. The specimen was loaded to 1 GPa, approximately 75% of the yield stress, and was held for 44 hours prior to unloading while the strain was measured (Figure 4-4). The test confirmed that the rate of time-dependent plastic deformation was less than $1 \times 10^{-8}$ sec$^{-1}$. This rate of accumulated strain is below the commonly cited creep threshold in bulk microcrystalline materials [117] and supports the idea that the material response is not time dependent. After the conclusion of the creep test, a uniaxial tension test was also conducted on the specimen to confirm that no mechanical behavior has been altered by the creep test. There was no measurable change in the mechanical behavior (similar yield strength, ultimate tensile strength and strain to failure) of the film that had underwent creep testing when compared to similar, untested specimens, again confirming the lack of time dependent deformation in the films.

Three constant stress fatigue tests were performed on ~1 μm specimens. Cracks growing out of the single edge notch in the ~1 μm specimens (Figure 4-5) exhibited straight (i.e., nominally mode I) crack paths similar to the previously investigated ~500 nm specimens [78]. Compliance responses of the ~1 μm films were correlated with crack length, and nonlinearities associated with crack closure were not observed. The measured fatigue crack growth rates as a function of the applied stress intensity factor ranges are shown in Figure 4-6 for both sets of specimens as well as microcrystalline platinum. The ~500 nm specimens displayed an extremely limited range of fatigue crack growth (~2.5 MPa $\sqrt{m}$). A least squares curve fit of the data to a power law relationship between the fatigue crack growth rate, $da/dN$, and the applied stress intensity factor range, $\Delta K$, (i.e., $da/dN = C(\Delta K)^m$ where $C$ and $m$ are fit parameters) provided a large power law exponent, $m$, of about 10.5. The maximum fracture toughness, $K_q$, was about 4.9
MPa \sqrt{m}, \sim 10 \text{ times less than the micrograined form of the material} [101]. The \sim 1 \mu m specimens displayed a larger range of fatigue crack growth (\sim 23 MPa \sqrt{m}) and a power law exponent of 3.9. The maximum fracture toughness, \( K_q \), was about 25.4 MPa \sqrt{m}, only about half of the micrograined form. In perspective, the crack growth behavior of the \sim 1 \mu m specimens was far more similar to the microcrystalline form of the material than to its own thinner form. This behavior shows that thickness has a substantial effect on the fatigue power law exponent, the stress intensity factor range for fatigue, and the estimate of fracture toughness.

The fracture paths of both specimen thicknesses were examined using scanning electron microscopy. Both specimen types exhibited similar fracture paths; Figure 4-7 shows the apparent crack growth rate-dependence of fracture mode in \sim 500 nm films (top) and \sim 1 \mu m films (bottom). The fatigue crack path in the near-threshold regime (i.e., growth rates below \( 10^{-9} \) m/cycle) and up to \sim 2 \times 10^{-7} m/cycle was intergranular (Figure 4-7 left). Images from this region reveal visible grains and secondary cracking. As the cracks grew in length and accelerated to \sim 3 \times 10^{-7} m/cycle, they gradually transitioned to a transgranular path (Figure 4-7 center). During this transition, a fine ridge parallel to the crack propagation direction developed in the center of the failure surfaces. This relatively short section exhibited a mixture of the features of the neighboring inter- and transgranular regions. The transgranular mode dominated the crack path at growth rates higher than \sim 4 \times 10^{-7} m/cycle (Figure 4-7 right). It is known from the assumed crack path in the bulk micrograined form of platinum that the rate at which the intergranular cracking transitions to transgranular cracking is not fixed, however it is now clear that thickness is not a significantly influencing factor.

TEM analysis was performed on fatigue and fracture crack profiles so that the evolution in the grain morphology could be correlated with the features that were observed on the fracture surfaces. The transmission electron microscope images from cracks whose growth rates were less than \sim 2 \times 10^{-7} m/cycle (i.e., confined to the intergranular region) in both \sim 500 nm and \sim 1 \mu m specimens show clear evidence of increased grain size in the crack wake (Figure 4-8) and ahead of the crack tip, and a tortuous, intergranular path. Coarsened grains have undergone a nearly 10-fold increase in size when compared to the as-received grain size which still surrounds them. Dislocations, and dislocation structures such as a dislocation-network (Figure 4-8a) can also be seen in some of the grains, but a detailed study of their prominence has not yet been conducted. Unlike selected area diffractions of coarsened grains in the \sim 500 nm films, which primarily
maintained their <111> orientation, diffraction patterns acquired of coarsened grains in the ~1 μm films indicated that not all maintained their orientation. TEM crack profiles from growth rate regimes where a central ridge is present on the fracture surface (i.e., crack growth rates exceeding $3 \times 10^{-7}$ m/cycle) show no evidence of grain coarsening. Moreover, several grains in this region appear to have been bisected by the crack path, confirming the transgranular nature of the cracking process at these crack growth rates. It is important to note here, that coarsened grains have largely maintained features on their boundaries consistent with the original grain morphology, every 25±10nm. This can also be seen from the on-end fracture surfaces (Figure 4-7 left); even though grains near the fracture path are an order of magnitude larger than the starting grain morphology, the distinct columnar walls of the original morphology are still present. This observation gives some insight into the coarsening mechanism by allowing us to rule out grain growth mechanisms in which grains grow in multiple directions via diffusion-like processes and instead suggest that the mechanism is likely one that involves the motion of certain (i.e. appropriately oriented) grain boundaries.
Figure 4-2: Stress-strain data from uniaxial tension tests compiling previously published results of ~500 nm (black circles) and new results of ~1 μm (blue squares) thick nanocrystalline platinum films. Young’s modulus, yield stress, ultimate tensile stress and ductility all have only a slight dependence on thickness in line with geometric constraint. All error is contained within the marker size.
Figure 4-3: FE-SEM image of a tensile test fracture surface in a ~1 μm thickness specimen. Features indicative of a ductile, void-rupture, transgranular failure can be seen throughout the fracture surface.
Figure 4-4: A plot of strain as a function of time resulting from constant stress creep testing of nanocrystalline platinum thin films: a 24-hour hold at 65% of the yield stress of ~500 nm films (black), and a 44 hour hold at 75% of the yield stress of ~1 μm films (blue). The test confirmed that the rate of time-dependent plastic deformation was less than $1 \times 10^{-8}$ sec$^{-1}$, the commonly cited creep threshold in bulk microcrystalline metals [116].
Figure 4-5: Optical images acquired during fatigue testing of a nanocrystalline Pt specimen showing (a) initial edge notch in a ~1 μm film, (b) a crack at 75% of the critical crack size, and (c) the specimen after failure.
Figure 4-6: Empirically measured fatigue crack growth behavior of nanograind ~1 μm (squares) thick nanocrystalline platinum films compared to previously published data ~500 nm (circles) nanocrystalline films and for micrograined platinum (diamonds) [101]. The power law fit, fatigue cracking range and fracture toughness all have a significant dependence on thickness. All error is contained within the marker size.
Figure 4-7: Scanning electron micrographs of fatigue failure surfaces in ~500 nm Pt film (top) and ~1 μm Pt film (bottom). As the crack advanced from left to right in both cases (arrow), the crack path transitioned from intergranular to transgranular. The similarities in the fracture path illustrate that the same mechanism(s) is/are operating in the films despite their different thickness.
Figure 4-8: Through-thickness transmission electron micrographs of stationary cracks confined to low crack growth rates in (a) ~500 nm and (b) ~1 μm platinum films. Coarsened grains in the immediate vicinity of the crack wake are apparent, while grains further away are not affected.
4.2.2 Damage Partitioning:

Consideration was given to applying a generalized damage partitioning approach to the fatigue behavior of the nanocrystalline platinum. Damage partitioning is a method in which the contributions from multiple mechanisms can be summed up in some manner. As one example, a damage partitioning approach relating to cyclic fatigue combines the contributions of cycle dependent and time dependent crack growth mechanisms into one overall crack growth rate curve [118]. This general approach can provide insight into mechanisms which may be acting dependently, independently, or competing. However, trying to disassemble a fatigue crack growth rate curve into its component curves is not possible without knowledge of individual component behavior; this separation is geometrically feasible in an infinite number of combinations, thus rendering the technique ineffective. Only when information on individualized contributing components comes into light is it possible to gain insight into the individual contributing factor. For example, the power-law behavior of the crack growth rate of either film thickness, lacking curvature at both the threshold and the fast fracture regions, seems to imply at first glance a single mechanism is at play; it would be intuitively (but nonetheless incorrectly) expected that if two or more mechanisms were at play, that some curvature would form from regions of their intersection or overlap. Figure 4-9 illustrates 3 possible configurations in which two mechanisms can be combined such that the overall response is a single linear line; the axes are somewhat irrelevant, but for a close parallel, the Y-axis can be considered the crack growth rate, and X-axis, the stress intensity factor range. Ultimately, it is impossible to take a single behavior curve and separate it into component curves without prior knowledge of those components.
Figure 4-9: Any (a) observed behavior (black) can be deconstructed in a number ways, thus making it impossible to deduce if the component mechanisms (shown in red and blue) are (b) acting independently, (c) dependently, or (d) are competing (shown with an intentional offset).
4.2.3 Thickness Effects:

The stress state at the crack tip (plane strain or plane stress), noted to be correlated with film thickness [59, 60], may serve to explain both the observed reduction in $K_{q}$, and the scaling of the associated power law behavior of the fatigue crack growth. Fractography has shown that intergranular fracture at the early fatigue crack growth stage produces fracture surfaces that have maintained the original film thickness, consistent with plane strain conditions, whereas fracture surfaces produced by transgranular fatigue crack growth or tensile failures show through-thickness necking, consistent with plane stress conditions. Using the ASTM standard shown in Equation 10, the minimum thickness for plane strain conditions shown, $B_{\text{min}}$ for platinum is dependent on $K_{IC}$, the fracture toughness of the material, and $\sigma_y$, the yield stress of the material [119].

\[
\text{Equation 10: } B_{\text{min}} = 2.5 \left( \frac{K_{IC}}{\sigma_y} \right)^{2}
\]

This minimum thickness is on the order of centimeters when using established values for microcrystalline platinum, and on the order of millimeters when using values experimentally measured in this study on nanocrystalline platinum. Although the standard predicts that plane stress conditions will predominate for films in our thickness, the fracture surfaces show evidence that plane stress conditions only develop once the crack growth has transitioned to a transgranular propagation mode. This observation implies that intergranular fracture is associated with a plane strain stress state, whereas the transgranular fracture is associated with a plane stress state. It is also sensible then that a transition between the two would produce a transitional region, displaying some features from both stress states, as is indeed witnessed.

Models predicting a crossover from plane strain to plane stress typically relate the transition to a function of thickness, stating that the ratio of material volume in plane stress compared to plane strain increases as thickness decreases [59]. These models are consistent with a reduced value of fracture toughness at very low thicknesses, when most if not all of the material is experiencing plane stress loading conditions, however, these models do not predict a transition from plane strain to plane stress within a single given thickness. Several possibilities
for the transition from plane strain to plane stress were explored. It is immediately possible to rule out that this transition is entirely dependent on $\Delta K$. This type of behavior would imply that across multiple thicknesses, the transition should appear at the same value of $\Delta K$, which is not the case. A more sensible approach, one that is inherently tied to the conditions associated with the stress state in the material, is to correlate the transition to the plastic zone size. The problem with this approach is that equations for monotonic and cyclic plastic zone sizes are typically planar and calculated for isotropic single crystals without accounting for through-thickness effects. The problem becomes obvious when using anisotropic, polycrystalline or textured materials, and when reducing the thickness of the material to a thin sheet. Possibly the best existing plastic zone size estimate is that put forth by Sobotka & Dodd [77], which uses a non dimensional load parameter shown in Equation 11, as an in-plane measure of the plastic zone size normalized by the thickness.

Equation 11: $\overline{K} = \frac{K_I}{\sigma_0 \sqrt{B}}$

Where $\overline{K}$ is the normalized plastic zone parameter, $K_I$ is the mode I stress intensity factor, $\sigma_0$ is the yield stress, and $B$ is the thickness. This new dimensionless factor was shown to correlate well with a 3D small scale yielding model of a static crack. This factor shares its primary disadvantage with typical plastic zone size estimates – it lacks contributing factor from the materials grain morphology, particularly those that contribute to plasticity mechanisms without affecting the yield stress. In lieu of better models, calculated estimates of plastic zone sizes under all conditions were calculated (Table 5-1) and compared to the thickness of the material, the remaining uncracked ligament ahead of the crack length, and to initiation, transition and fracture conditions. No consistent correlation between any calculated plastic zone size (neither monotonic nor cyclic, under plane stress or plane strain) and the transition region or $K_q$ could be found.

Instead of calculating the relevant length scale in the material, it is possible to quantitatively measure it within the regions at which grain coarsening is occurring. The extent of grain coarsening can provide an experimental measure of the relevant plastic zone in the material, approximately ~500 nm from either side of the crack in both film thicknesses. These direct measurements provide a reasonable estimate for the plastic zone size in the material, however this kind of measurement is limited only to the low crack growth rates in the material corresponding to where coarsening occurs. Although these experiments show that thickness is
not a primary variable in the size of the plastic zone ahead of the crack, estimates of such size utilizing only fracture toughness and yield stress, cannot be the only influencing variables. As multiple forms of plastic deformation in metals are accomplished through slip, variables that can influence slip motion (e.g. grain size and texture) must also be considered.
Table 5-1: Plastic Zone Size Estimates

### ~500 nm:

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<tr>
<th></th>
<th>$\Delta K$ (MPa $\sqrt{m}$)</th>
<th>Dodd’s Parameter (unitless) [77] (Eq. 11)</th>
<th>Plane Stress Monotonic Plastic Zone Size ($\mu$m) (Eq. 5)</th>
<th>Plane Stress Cyclic Plastic Zone Size ($\mu$m) (Eq. 7)</th>
<th>Plane Strain Monotonic Plastic Zone Size ($\mu$m) (Eq. 6)</th>
<th>Plane Strain Cyclic Plastic Zone Size ($\mu$m) (Eq. 8)</th>
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<td>4.19</td>
<td>1.40</td>
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### ~1 $\mu$m:

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<th>Plane Stress Cyclic Plastic Zone Size ($\mu$m) (Eq. 7)</th>
<th>Plane Strain Monotonic Plastic Zone Size ($\mu$m) (Eq. 6)</th>
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4.3 Mechanistic Implications:

A low angle grain boundary can be considered to be an array of dislocations; given this consideration, non-diffusional grain boundary deformation mechanisms can still be discussed under the framework of dislocation slip. There is great appeal in treating grain boundaries as mobile defects whose motion can be described by typical dislocation mechanics, particularly in cases where the mechanical behavior of the material is not time-dependent. It is clear from tensile and high fatigue crack growth rates that typical dislocation-mediated slip can still operate at the nanoscale. It is also clear that under some conditions (i.e. a plane strain stress state at the crack tip), it is not the dominant plasticity mechanism. The mechanism that ultimately describes the deformation process at this condition will be one that leads to both grain coarsening and embrittlement of grain boundaries and must be more active in plane strain than in plane stress. One plasticity mechanism that may be operating at the nanograin length scale is grain boundary migration. In one take on this mechanism, Ovid’ko et al [120] describe the a possible shear-coupled grain boundary migration mechanism (Figure 4-10), resulting in their annihilation and consequent grain coarsening. This grain boundary migration process naturally leaves behind what Ovid’ko terms ‘disinclination quadrupoles’ at the original grain boundary triple junctions (Figure 4-11). Quadrupoles are associated with high local stresses and the generation of nanovoids at stagnant grain boundaries, which subsequently become embrittled. Taken in context with stress states at the crack tip changing as a function of crack length, this theory would certainly support the correlation between grain coarsening by this process, subsequent intergranular cracking at regions of coarsened grains, and a transition to typical dislocation slip failure when grain boundary migration is no longer favored. A second proposed plasticity mode for nanocrystalline materials is grain rotation. Haslam et al. used 2D computational models to investigate the plasticity mechanism in a polycrystal composed of 25 columnar grains with a mean diameter of 15 nm. He found that grain rotation decomposes a grain boundary into multiple but distinct dislocations, which can then move by typical dislocation slip (Figure 4-12). This rotation keeps the unaffected grain boundaries mostly intact, and coarsened grains can maintain their outer boundary shapes. He concludes that grain rotation may be competing with grain boundary migration, and that grain boundary migration is likely dominant. [47]. In general, the
line between grain boundary migration and grain rotation is ambiguous and some modeling investigations consider them to be coupled together or part of a more general mechanism [68]. Although the mechanisms illustrated in these investigations match several of the experimental observations in nanocrystalline platinum, they fail to establish zone size in which they take place, or any relation of such a zone size with respect to a growing fatigue crack. Another substantial drawback to these investigations is the use of planar models, which fail to account for 3-dimensional migration and/or rotation. Although the exact mechanism leading to grain coarsening, rotation, and intergranular failure is not yet conclusive, it is clear that whatever the mechanism may be, it is active only in plane strain loading conditions while typical dislocation slip governs plane stress conditions. Since thickness does not appear to a controlling variable in the determination of the stress state at the crack tip, further experimental work investigating the effects of grain size and/or texture, as well as fully 3D modeling of the grain morphology will shed more light on the fatigue crack propagation mechanism.
Figure 4-10: A modified version of a schematic from [120] illustrating stress-driven migration of grain boundaries. The shear-coupled migration is hampered by surrounding grains. The magnified inset highlights the orientation change resulting from this migration and is analogous to the region depicted in Figure 4-11.
Figure 4-11: A schematic taken directly from [120] depicting a change in grain orientation as a result of shear-coupled grain boundary migration in a nanocrystalline system. The original grains are depicted as a series of directional edge dislocations (left). Motion of a grain boundary through a grain results in an extension of a grain at the expense of the other, leaving behind disinclinations, or quadrupoles (depicted as triangles) at the original triple junctions (right).
Figure 4-12: A schematic taken directly out of [47] depicting the rotation of grains 1 and 25, resulting in the decomposition of the grain boundary dividing them into distinct dislocations which can then migrate and be annihilated at other grain boundaries. Note that their shared grain boundaries with grain 4 appears to have also migrated in the process, though all other boundaries are mostly unaffected.
4.4 Conclusions

When compared with microcrystalline platinum, the fatigue behavior of the ∼500 nm, textured, nanocrystalline platinum thin films showed reduced values of the stress intensity factor range for fatigue and the $K_q$, as well as a high power law exponent of 10.5 [109]. Thickness was suspected to be the root cause of the significantly different response, and ∼1 μm films were tested in order to compare the mechanical behavior. Tensile and creep testing resulted in mechanical properties similar to thinner films: a high yield strength of ∼1.3 GPa, high ultimate tensile strength of ∼1.45 GPa, a strain of ∼0.034 prior to failure, and no time dependency of material properties at room temperature. Fatigue testing produced mechanical behavior far more in line with the microcrystalline form of the material, increasing the stress intensity factor range of the material and increasing the $K_q$ to 25.4 MPa $\sqrt{m}$, while the power law exponent was decreased to 3.9. These results indicate that thickness plays a crucial role in the fatigue behavior of the material. Despite the change in fatigue behavior, the crack growth modes witnessed in the ∼500 nm films, grain coarsening and rotation followed by intergranular failure at low crack growth rates and typical transgranular failure without grain coarsening at higher crack growth rates were also maintained in the ∼1 μm films. This chapter has theorized that the two different growth modes, grain boundary migration and grain rotation, are possible mechanisms which are dominant at plane strain conditions, and typical dislocation slip is dominant at plane stress conditions. Although specimen thickness has a substantial effect on the fatigue behavior of nanocrystalline metallic films, it does not appear to be primary factor in the determination of the stress state at the crack tip or the plastic zone ahead of a loaded crack. The stress state at the crack tip is likely to be more strictly dependent on the texture and grain size of the material and further experimental investigation will pursue this relationship.
Chapter 5
The Role of Grain Morphology on the Mechanical Properties of Nanocrystalline Thin Films

This chapter focuses on the grain morphology dependence of the mechanical behavior of nanocrystalline platinum thin films. Previous chapters established that the fatigue crack advance mode dependence on the stress state at the crack tip, so an alteration of the grain morphology (via an annealing process) allows for a study of the dependence of the stress state at the crack on the grain morphology. This chapter presents results of mechanical (tensile, creep and fatigue) testing of annealed films, and places those results, as well as those stemming from fracture analysis, with those reported on in the previous chapter. Additionally, a finite element model of a single crystal thin sheet is presented. The model is capable of measuring the stresses near a crack tip, and hence predicting whether slip is more likely to occur in plane, or through the thickness of the films.

5.1 Introduction

There is an ever increasing number of experimental [46, 121-124] and modeling [47, 120, 125] investigations which claim that plastic deformation mechanisms in nanocrystalline materials will not be dominated by dislocation slip. Mechanisms purported to take over at such a small size scale are primarily linked to the increasing grain boundary volume, such as grain boundary diffusion, grain boundary migration, and grain rotation. Previous chapters have shown that grain coarsening coupled with intergranular failure occurs at low crack growth rates, but at higher crack growth rates the mechanism transitions to transgranular cracking in the absence of grain coarsening (Figure 5-1) [109]. In light of this, grain boundary mobility and grain rotation were proposed to be competing with the typical dislocation slip mechanism that governs plasticity in typical microcrystalline metals [Section 4.3]. Doubling the thickness of the nanocrystalline films had a significant impact on the fatigue behavior of the films but did not considerably affect the portion of the material that underwent the grain coarsening-coupled
intergranular failure suggesting that while the mechanical behavior may be tied to geometrical factors, the operating plasticity mechanisms are dependent on grain morphology. Since the fracture path in the microcrystalline platinum is transgranular throughout, it is clear that a reduced film thickness cannot be the only factor for conditions promoting intergranular crack propagation. The proposed grain boundary mobility [120] and grain rotation [47] based models were both developed from a 2D perspective. Although a 2D section can represent any planar section of a columnar grain morphology, the mechanisms make isotropic assumptions for the through-thickness deformation, and whether the mechanisms can be extended to reflect non-columnar morphology is uncertain. This investigation takes two approaches in order to resolve this doubt. Experimental testing on nanocrystalline platinum films having non-columnar grain morphology will determine whether fatigue behavior is dependent on a change in the grain morphology, and finite element modeling will examine the dependence of both planar and through-thickness stresses on anisotropy in a fully three-dimensional context. These examinations will allow for both experimental evidence, as well as a mechanistic interpretation of the components influencing fatigue crack advance and stress-induced grain coarsening, thereby enabling a complete mechanistic interpretation of plasticity of nanocrystalline materials and enable extension of principles to multiple metallic systems.

There is increasing evidence that the stress-induced motion of grain boundaries is an integral part of plasticity in ultrafine and nanocrystalline metals, in line with conceptual limitations in dislocations’ mean free path and multiplication probability [16, 121]. Although some experimental investigations have observed such deformation spontaneously at room temperature [51], grain coarsening in nanocrystalline platinum films have only been observed as a result of mechanical loading [109, 122]. Although early investigations reporting stress-induced boundary migration were limited to bicrystals, such as those on Al [126] and Zn [127], numerous experimental investigations now attribute such mechanisms as the cause for stress-induced grain coarsening in the polycrystalline materials [46, 121-124]. Our own earlier investigations on nanocrystalline platinum films of varying thicknesses [Section 4.2.1] noted that under certain fatigue loading conditions, grains near a growing fatigue crack in its early stages coarsen approximately an order of magnitude and cause intergranular crack growth. This crack growth mode, which at higher growth rates transitions to typical transgranular failure in the absence of grain coarsening, was correlated with the stress state at the crack tip. In line with these
observations, both grain boundary rotation, and grain boundary migration were considered as possible mechanisms for the intergranular crack advance [47, 120]. Although the mechanisms governing grain boundary motion are of great importance, a more fundamental concept is whether or not such mechanisms are inherently reliant on the 3D aspects of the system. Based on previous studies on platinum which noted that the specimen thickness was not the dominant factor in the determination of the stress state, texture and grain size are likely to be the dominant influence on the plastic zone size and stress state at the crack tip. This kind of analysis is somewhat contradictory to modeling investigations which have thus far been more focused on a strictly 2D approach to the problem.

The first few investigations of notched single crystals were based on the initial work by Rice [75, 128]. His model is based on the plastic field in the vicinity of the crack tip and utilizes both FCC and BCC systems in tension under plane strain and isotropic conditions. These assumptions lead to identical predictions in both crystal systems, in contrast with experimental works, and notes that future models would ideal incorporate anisotropic conditions, strain hardening or softening, and 3D effects. Indeed, many of the early predictions by Rice were contradictory to experimental results such as those conducted on notched single crystal specimens by Shield [129-131]. Shield compared his results not only to Rice’s model, but also to 2D finite element modeling solutions by Mohan et al. [132] and Cuitino and Ortiz [133], none of which were in agreement. Cuitino and Ortiz later noted that the plane strain assumptions cannot be valid, due to the large differences in stress states between the surfaces and internal sections and have since constructed a 3D model to account for this [134]. Although 2D models do have a solid basis for interpretation of conditions at a notch tip, their limited consideration of the degree freedom brought on by a consideration of the third special dimension carry with them significant disadvantages. For instance, particular slip plane stresses cannot be compared on planes which are isotropic, or with any slip non-planar slip planes. Also, any noted grain rotation or coarsening is strictly planar, but only as an artifact of the modeling technique, not the mechanism itself. Due to their 2D nature, assumptions must be made of the texture of the material, and any 3D texture in a material is essentially nullified, allowing no conclusions to be drawn regarding its importance.

There are 3D models that have attempted to expand on previously planar analysis. Sobotka & Dodd [77] created a 3-D finite element model of a crack in an elastic-plastic isotropic
material loaded in tension. Their model, which focused primarily on the plastic zone near a crack tip showed some significant differences between the surfaces and midline of the specimens. The study also found differences in the zone shape between plane strain conditions, which overlapped with the crack wake, and plane stress conditions, which were confined to the regions ahead of the crack; these findings suggest that if the loading conditions were dependent on a feature in the microstructure, the crack advance mode could be different between the two loading conditions. The development of plane strain conditions at a crack tip under certain conditions may help to explain why coarsening and intergranular failure are not observed during tensile testing or fatigue conditions in which only plane stress loading exists. Arakere et al [71] used a 3D model on an FCC material, but also accounted for material anisotropy when looking at the stress fields ahead of a notch. By accounting the crystal orientation with respect to the loading conditions, he was able to map out which slip systems are activated near the presence of a notch. He also noted that resolved shear stresses at the midplane were ‘consistently higher’ than at the surface, implying that slip is likely to originate from the specimen’s midplane and progress to the surface. Arakere stresses the importance of accounting for both elastic anisotropy as well as 3D effects when modeling slip activation. Schulson and Xu [115] used finite element modeling of a notched elastic-plastic single crystal which displays a work hardening behavior in an effort to match experimental observations in notched specimens of polycrystalline boron-doped nickel aluminide (Al3Ni). Their model correlates experimental intergranular failure with theoretical stress triaxiality (plane strain loading conditions), and likewise, experimental transgranular fracture with theoretical plane stress conditions. Although 3D models offer a more complete view of system, the added complexity and computational power associated with the additional dimension may not be warranted if a 2D model can adequately predict the material response. This question is particularly relevant in columnar microstructures where a 2D view of the microstructure is a fair descriptor of any planar section of the microstructure. There is a need for a simple 3D model of a columnar structure, preferably in a system which is perfectly plastic (so that strain hardening and/or softening is not relevant) which can quantify whether the added complexity provides any information which cannot be gleaned, calculated or predicted from a 2D model of the same system. Nanocrystalline platinum is the ideal material of choice for such a model: specimens can be columnar or their texture modified by annealing, tension testing shows an elastic-perfectly plastic response, they have stable grain morphology and a well characterized chemistry.
This chapter details experimental results from mechanical testing of nanocrystalline platinum thin films having a grain morphology significantly different from the columnar films previously tested. This change in the grain morphology is linked with both a change in the uniaxial tension response of the films, as well as a change in the fatigue crack advance modes, despite no significant change in their overall fatigue crack growth behavior. This experimental study is supplemented by a simple 3D model of a mechanical characterization testing specimen. The elastic and anisotropic model of the system unambiguously shows that a 3D analysis of a system, even in columnar structures, is necessary in order to capture activation of through thickness slip systems which are dominant at given crystal orientations and account for anisotropic behavior in the system.
Figure 5-1: Empirically measured fatigue crack growth behavior of nanograinised ~500 nm (circles), and ~1 μm (squares) thick nanocrystalline platinum films compared to previously published data for micrograined Pt (diamond) [101]. Markers in red correspond to intergranular failure, purple to transitional failure, and blue to transgranular failure. The power law fit, fatigue cracking range and fracture toughness all have a significant dependence on thickness. All error is contained within the marker size.
5.2 Results and Discussion

In order to be able to extend observations and mechanistic interpretations from nanocrystalline platinum films with a columnar grain structure to other nanocrystalline grain morphologies, the role of grain morphology must be established. Experimental testing of columnar films which had undergone an annealing process to alter their grain morphology to a non-columnar nature allowed for direct comparisons to be made between films in which the grain morphology was the only primary difference. Three uniaxial tension tests were performed on the annealed films and compared to four tests on the as-received specimens. The columnar ~1 μm films displayed a yield strength of 1.3±0.1 GPa, an ultimate strength of 1.45±0.05 GPa and had a Young’s modulus of 133±5 GPa. The annealed films displayed a yield strength of 1.2±0.1 GPa, an ultimate strength of 1.41±0.05 GPa and had a Young’s modulus of 145±5 GPa (Figure 5-2). The non-columnar films had a fracture angle of 47.2±1.0º from the tensile loading axis, resulting in a similar anisotropy factor (Based on Equation 9 in Section 4.3) as those of the columnar films which fractured at an angle of 48.0±2.4º. The most contrasting difference between the two films was the strain to failure: 0.034±0.001 for the as-received specimens and 0.013±0.003 for the annealed specimens. These results indicate that ductility in the platinum films may have been derived from through-thickness deformation; such deformation would be more limited as the aspect ratio of the grains increased. Finite element modeling will examine this relationship in detail at regions nearest crack tips in order to confirm that through-thickness slip can indeed be dominant over planar slip. Both films displayed a typical transgranular crack path associated with dislocation-mediated plasticity and failure, confirming that the grain boundaries were not embrittled by contaminants or voids, neither prior nor post-annealing.

Nanoindentation testing by Romasco et al [99], as well as creep testing on the columnar ~500 nm and ~1 μm films revealed that the mechanical properties of the nanocrystalline films were not time-dependent. In order to verify that the lack of time-dependency of the mechanical properties was not tied to the films’ grain morphology, a 24 hour long creep test was conducted on an annealed, non-columnar sample. In a similar fashion to creep testing conducted on the as-received ~1 μm specimens (Section 4.2), the film was loaded to 1 GPa, approximately 75% of its yield strength (Figure 5-3). The test confirmed that the rate of time-dependent plastic
deformation was less than $1 \times 10^{-8}$ sec$^{-1}$. This rate of accumulated strain is often the creep threshold in bulk microcrystalline materials [117] and supports the idea that the material response is not time dependent. After the conclusion of the creep testing, a uniaxial tension test was also conducted on the specimen to confirm that no properties were altered due to the creep test. There was no measurable change in the mechanical behavior (similar yield strength, ultimate tensile strength and strain to failure) of the film that had underwent creep testing when compared to similar, untested specimens, again confirming the lack of time-dependent deformation in the films.

Prior testing indicated that the fatigue behavior of the platinum films has a strong dependence on specimen thickness [Section 4.2.1]; however, the crack advance mode did not share this dependence, and was theorized to be associated more directly with the stress state at the crack tip and should be associated with the grain morphology. Three fatigue tests were performed on the annealed specimens and compared to the three performed on the columnar specimens in order to verify this relationship. Cracks growing out of the single edge notch in the annealed specimens exhibited a straight (i.e., nominally mode I) crack paths, and surface distortions associated with the development of the plastic zone were not observed. Compliance-based measurement of crack closure revealed that crack closure is not a significant influence on the fatigue crack growth behavior to any measurable amount. The measured fatigue crack growth rates as a function of the applied stress intensity factor ranges are shown in Figure 5-4 for both sets of specimens. The columnar ~1 μm specimens displayed a power law exponent of 3.9 and a maximum fracture toughness, $K_q$, was about 25.4 MPa $\sqrt{m}$. The annealed specimens showed only minor differences, having a power law exponent of 4.2 and a fracture toughness of 17.8. These observations show that texture in the material plays only a minor role in the fatigue behavior of a system, despite a factor of 2-3 reduction in strain to failure as measured by tension testing.

The similarity in the fatigue crack growth behavior confirms a primary dependence on specimen thickness, but does not readily reveal the effects that a change in the grain morphology had on the system. The competition between the crack growth modes and its relationship to grain morphology are particularly important. In order to evaluate these effects, the fracture paths of the annealed specimens were examined using scanning electron microscopy and compared to previously attained micrographs of the as-received specimens. Both specimen types exhibited
similar fracture paths; Figure 5-5 shows the cracks paths in the as-received films (top) and the annealed films (bottom). Although both sets of films exhibit a similar transition from an intergranular crack path to a transgranular crack path, the location of the transition (i.e. the \( \Delta K \) and growth rate) are distinct. Figure 5-6 shows the fatigue crack growth rates of the two films with an intentional abscissa offset to facilitate comparisons. In the as-received specimens, the fatigue crack path in at crack growth rates up to \( \sim 2 \times 10^{-7} \text{ m/cycle} \) was intergranular (Figure 5-5 left). Images from this region reveal visible through-thickness, columnar features and secondary cracking. As the cracks grew in length and accelerated to \( \sim 3 \times 10^{-7} \text{ m/cycle} \), they gradually transitioned to a transgranular path (Figure 5-5 center). During this transition, a fine ridge parallel to the crack propagation direction developed in the center of the failure surfaces. This relatively short section exhibited a mixture of the features of the neighboring inter- and transgranular regions. The transgranular mode dominated the crack path at growth rates higher than \( \sim 4 \times 10^{-7} \text{ m/cycle} \) (Figure 5-5 right). The same crack path as found in the annealed films, but the growth rates associated with the mode transitions are not the same. Intergranular cracking is restricted to crack growth rates below \( \sim 3 \times 10^{-8} \text{ m/cycle} \), and the transition region is significantly shorter; transgranular cracking begins at \( \sim 5 \times 10^{-8} \text{ m/cycle} \). It is clear that the change in texture caused by the annealing process has affected the stress state at the crack tip, and in turn, the crack propagation mode, without significantly affecting the fracture toughness or the \( K_q \).
Figure 5-2: A stress-strain plot compiling results from uniaxial tension tests of ~1 μm as-received (blue) and annealed (orange) nanocrystalline platinum films. Annealed films show only very minor differences in elastic modulii, yield stresses, and ultimate stresses, but ductility is substantially reduced. All error is contained within the marker size.
Figure 5-3: A stress-strain plot compiling results from constant stress creep tests of ~1 μm as-received (blue) and annealed (orange) nanocrystalline platinum films. In both cases, specimens were loaded to 75% of the yield stress, and displayed no time-dependent properties.
Figure 5-4: Empirically measured fatigue crack growth behavior of the as-received (blue squares) and annealed (orange squares) nanograin ~1 μm thick platinum. Although annealing the films had a substantial effect on the ductility of the films in tension, it does not have a major effect on the fatigue behavior. All error is contained within the marker size.
Figure 5-5: Scanning electron micrographs of fatigue failure surfaces in as-received (top) and annealed (bottom) nanograin platinum. As the crack advanced from left to right in both cases, the crack path transitioned from intergranular to transgranular. The similarities in the fracture path illustrate that the same mechanism(s) is/are operating in the films despite a change in thickness.
Figure 5-6: The fatigue crack growth behavior of as-received (left) and annealed (right) nanocrystalline platinum films plotted with an intentional offset in the x-axis. With the offset in place, it is clear that even though the films show similar fatigue behavior, the transition in the fatigue crack growth mode is shifted to lower growth rates as a result of a change in texture. All error is contained within the marker size.
5.3 **Modeling:**

Tension testing experimentally showed that ductility is hindered when grain boundary area is increased through the thickness of the sample (as indicated by the increase of the grains’ aspect ratio). This limitation on ductility also appears to favor a plane stress state at the crack tip, making grain coarsening-coupled intergranular failure less favored during cyclic crack advance. This is consistent with the increased availability of suitably oriented slip systems near the crack tip. Finite element modeling of an anisotropic elastic body has the capacity to predict the magnitude of shear stresses placed on close-packed directions within close-packed planes. Examination paths were chosen to follow the <110> family of slip directions within the \{111\} family of closed packed planes of the material modeled and these paths were unique to the material orientation; these paths correspond to the primary slip planes within any FCC system [89]. In the modeled case, the crack plane is the (111), and the crack tip growth direction is any <110> direction. This allows for inspection of stresses along both in-plane primary slip directions, as well as through-thickness ones. In the first case, magnitudes of in plane slip at different sections of the model (i.e. top surface, midline, etc.) were compared when a [110] direction was directly ahead of the crack; this configuration leads to a symmetric stress distribution across the slip direction. The left portion of Figure 5-7 shows the initial design of the model: a primary slip direction within the (111) plane pointing directly ahead of the crack tip, perpendicular to the loading axis. The red, blue and green lines correspond to layers within the model, i.e. that top, midline, and bottom surface respectively and are consistent with the Figure 5-8. The right portion of the figure shows the shear stress plot resulting from the loading conditions. Note the 4-fold shear stress distribution emanating from the crack tip with symmetric concentrations at ±~30°, and ±~105° from the direction perpendicular to the loading axis. Figure 5-8 shows results of the shear stress magnitude along a slip plane perpendicular to the loading axis, directly ahead of the crack tip, as a function of distance from the crack tip normalized by the specimen thickness. The plot shows that the magnitude of the shear stresses is virtually identical (less than 1% variation) along the entire thickness of the specimen. This observation is in contrast with findings by Arakere et al [71], and implies that it is not possible to predict a which position in-plane slip will initiate at within the sample.
Although this kind of information is useful given the experimental observations, it would be more apt to compare the magnitude of shear stress on one in-plane slip direction to a through-thickness slip direction. This second type of analysis directly leads to visualization of bias in the crack tip stress field and allows for a discussion of whether through-thickness slip is a contributing factor. Note that this type of visualization is not possible from a 2D model. Figure 5-9 illustrates two cases which illustrate the relationship between in-plane and through-thickness slip, as well as the dependence of this relationship on anisotropy. The two cases showcased were chosen such that the in-plane slip directions passed through a high (Case 1) and low (Case 2) region of shear.

Figure 5-10 shows the magnitude of the resolved shear stress on two through thickness slip directions ahead of the crack tip, normalized by the magnitude of the shear stress on the nearest surface (in plane) slip direction, plotted as a function of the distance from the crack tip normalized by the specimen thickness. These plots show that the magnitude of shear stress on through-thickness slip directions can be many times the magnitude of the surface slip directions, and that this ratio is highly sensitive to the orientation of the crystal with respect to the loading axis. These findings suggest that at areas nearest notch, through thickness slip may initiate prior to planar slip and then be overtaken by planar slip as the distance from the notch grows. These results confirm experimental results which indicated that through-thickness slip play an important role in the ductility of the system. Similar examinations were conducted on slip directions in the crack wake. In the cases in which the in plane slip direction was oriented at 105º and 135º, through thickness slip was still dominant in regions closest to the crack tip, but preference quickly shifted to in-plane deformation. The results indicate that an anisotropy consideration is crucial in the evaluation of the material response, and as such, the grain morphology of a system has pronounced effects on the plasticity mechanisms operating near a crack tip. What this model fails to capture is the plastic response of the system, and as such, cannot impart significant conclusions regarding the cyclic or monotonic plastic zone size or stress state near the crack tip. This can only be captured by a fully plastic-anisotropic model which will be the focus of future studies.
Figure 5-7: (Left) a schematic of the 3D model configuration used. The red, blue and green lines correspond to layers within the model, i.e. that top, midline, and bottom surface respectively and are consistent with the Figure 7. (Right) A shear stress distribution plot of the top surface of the model showing a 4-fold stress distribution. The distributions are only symmetric as shown when the elastic constants are oriented at specific directions such that shown to the left. The color scheme is consistent with Figure 5-8.
Figure 5-8: Finite element modeling results showing the magnitude of resolved shear stress along a [110] on a (111) for the top surface, half thickness, and the bottom surface as a function of the distance from the crack tip normalized by the specimen thickness. The close agreement of the stresses in all three layers shows that planar stresses in 2D models can be extended to 3D.
Figure 5-9: (Left) a schematic of the 3D model configuration used. Red lines indicate planar slip directions, and blue lines indicate the nearest through-thickness slip direction. Solid lines belong to Case 1 and dashed lines belong to Case 2. (Right) Planar view of the two cases, note that blue lines are projections onto the surface, whereas the actual measured response is through-thickness. The solid / dashed scheme is consistent with Figure 5-10.
Figure 5-10: Finite element modeling results showing the magnitude of resolved shear stress along a through-thickness slip direction (blue) normalized by the magnitude of shear stress of the nearest planar slip direction (red) as a function of the distance from the crack tip normalized by the specimen thickness. Results are shown in a specimen with a planar slip direction pointed 60 degrees from the loading axis (left) and 30 degrees from the loading axis (right).
5.4 Conclusions

The fatigue behavior of nanocrystalline platinum films has been previously found to have a significant dependence on thickness [Section 4.2.1], but the crack advance mode was independent of thickness. The texture of the films, i.e. the vertical to horizontal aspect ratio of the grain size, has been hypothesized to be a significant factor in determining the stress state at the crack tip, and as a result, the crack advance mode. ~1 µm thick nanocrystalline films with columnar grains annealed for 6 hours at 500 ºC in order to produce a non-columnar grain morphology. Tension, creep and fatigue testing was carried out on these tests and the results compared to the as-received columnar films. Texture in the films was shown to have a substantial effect on the ductility of metal under uniaxial tension. The reduction of the aspect ratio is likely to have limited dislocation motion due to the increase in the overall number of grain boundaries. This change in texture did not significantly alter the yield or ultimate tensile strength. A reduction in texture did not significantly affect the fatigue behavior of the material. As-received and annealed films had nearly identical fracture toughness and power law slope, confirming previous conclusions that the fatigue behavior is primarily dictated by the thickness of the specimen. In contrast, the change in texture produced a major affect on the stress state at the crack tip, directly affecting the competition between grain-boundary dominated plasticity and typical dislocation motion. The overall change in texture resulted in a change in a shift in the transition point from an intergranular to transgranular fatigue cracking mode. In order to quantify the contribution of deformation along through-thickness slip-directions, a finite element model examined the dominance of slip in planar and through-thickness directions. A strictly planar examination showed that stresses were approximately the same between top surface, midline and bottom surface of the model, suggesting that it is not possible to determine whether slip initiates at surfaces or from the midline. However, model showed that shear stresses in slip directions along through thickness slip planes can be higher than shear stresses on planar slip planes, especially in close proximity to the crack tip, and this dominance had a large dependence on anisotropy. The modeling results highlight the necessity of considering 3-dimensional aspects of the grain morphology and accounting for anisotropy. Although grain morphology has been experimentally and computationally shown to affect not only ductility in tension testing but also the cyclic crack extension mode, an elastic model cannot capture the relevant size scales
associated with this dependence. In order to properly predict the dependence of plastic deformation mechanisms on grain morphology, a 3D anisotropic model must be constructed, and such a model will be the focus of a future study.
Chapter 6

Summary

This final chapter of the dissertation presents a summary of results and conclusions from the study of the mechanical behavior of nanocrystalline platinum thin films. Mechanical testing and finite element modeling were performed on sputtered, thin film specimens after a microstructural evaluation to characterize their purity, texture, and crystallography. Mechanical testing results, including tensile, creep and fatigue testing and fractographic analyses will be listed first. Insights from a 3D elastic, anisotropic finite element model of the system will be detailed last.

1. Four uniaxial tension tests were performed on ~500 nm films. The films displayed a yield strength of 1.5±0.1 GPa, ultimate strength of 1.75±0.05 GPa, strain to failure of 0.034±0.001 and had a Young’s modulus of 158±5 GPa. The failure surfaces were inclined 55.9±1.8º from the tensile loading axis. An additional four uniaxial tension tests were performed on ~1 μm platinum films and these films displayed a yield strength of 1.3±0.1 GPa, an ultimate strength of 1.45±0.05 GPa, strain to failure of 0.028±0.001, and had a Young’s modulus of 133±5 GPa. The failure surfaces were inclined 48.0±2.4º from the tensile loading axis, indicating a change in the anisotropy factor. These results indicate that manufactured, as-received samples are strong and ductile, consistent with behavior expected from nanocrystalline FCC metals, and in line with results obtained through nanoindentation of films on substrate. Three uniaxial tension tests were conducted on ~1 μm films that had undergone a 500 ºC anneal for 6 hours. Annealed films displayed a yield strength of 1.2±0.1 GPa, an ultimate strength of 1.41±0.05 GPa, strain to failure of 0.013±0.003, and a Young’s modulus of 145±5 GPa. The failure surfaces were inclined 47.2±1.0º from the tensile loading axis, resulting in a similar anisotropy factor as those of the as-received films. These results indicate that although there is some small dependence of the mechanical behavior of specimen thickness, there is a significantly larger dependence between ductility and grain morphology in the
nanocrystalline films. Fracture surfaces from all tensile tests displayed ductile, dimple-void rupture features consistent with their mechanical properties.

2. A creep test was conducted on each of the three platinum films. Creep tests on the ~500 nm, and the annealed ~1 μm films lasted 24 hours, and the creep tests on the ~1 μm as-received specimen lasted 44 hours. In all cases, no time-dependent behavior was observed, with all films experiencing a strain rate of less than $1 \times 10^{-8}$ sec$^{-1}$. Again, this observation is consistent with independent testing of rate-dependent response in the films by nanoindentation. Tensile testing of films following the creep test produced a tensile response similar to that of specimens that had not undergone creep testing, providing a third confirmation of the lack of time-dependent behavior. Fracture surfaces from post-creep tension test fracture surfaces closely resembled fracture surfaces from tensile failures in specimens that had not undergone creep testing, i.e. features consistent with ductile dimple-void rupture failure.

3. Constant stress amplitude tests were conducted on notched specimens. Four such tests on ~500 nm films with central notches resulted in a power law exponent of ~10.5, and a fracture toughness of about 4.88 MPa $\sqrt{m}$. This behavior is more reminiscent of the fatigue behavior of brittle ceramic systems than that of ductile metals (previous studies on micrograined platinum established a power law exponent of ~3.3 and approximately an order of magnitude greater fracture toughness than the nanograin form). Differences between the bulk and thin film forms were theorized to be caused by the small specimen thickness. This was confirmed when three fatigue tests conducted on ~1 μm specimens displayed a larger range of fatigue crack growth (~23 MPa $\sqrt{m}$) and a power law exponent of 3.9. The maximum fracture toughness, $K_{\text{q}}$, was about 25.4 MPa $\sqrt{m}$, only about half of the micrograined form. This behavior shows that thickness has a substantial effect on the fatigue power law exponent, the stress intensity factor range for fatigue, and the estimate of fracture toughness. In line with observation, fatigue testing of annealed films, having the same ~1 μm thickness but a different grain morphology produced similar fatigue behavior: a power law exponent of 4.2 and a fracture toughness of 17.8 MPa $\sqrt{m}$. 
4. Although the fatigue behavior of the platinum films has a strong dependence on the thickness of the films, the fracture mode in the films did not show the same dependence. In the ~500 nm specimens, the fatigue crack path in the near-threshold regime (i.e., growth rates below $10^{-9}$ m/cycle) and up to $\sim 2 \times 10^{-7}$ m/cycle was intergranular. FE-SEM images from this region reveal visible grains and secondary cracking. As the cracks grew in length and accelerated to $\sim 3 \times 10^{-7}$ m/cycle, they gradually transitioned to a transgranular path. During this transition, a fine ridge parallel to the crack propagation direction developed in the center of the failure surfaces and dominated the crack path at growth rates larger than $4 \times 10^{-7}$ m/cycle. TEM images from the intergranular regions revealed that grains nearest the crack path had coarsened up to an order of magnitude, whereas grains near the crack at transgranular paths had not undergone coarsening (and had in fact been severed by the advancing crack). Although changing the specimen thickness had produced a large effect on the power law exponent and the fracture toughness of the specimens, the same fracture modes were exhibited at similar crack growth rates in the ~1 μm specimens. The fracture mode was theorized to have a dependence on the stress state at the crack tip, influenced directly by the grain morphology of the specimen, and annealed ~1 μm specimens were tested. Fracture surfaces from these tests produced a shift in the fracture modes (with otherwise little effect on the fatigue behavior). In the annealed films, the intergranular cracking is restricted to crack growth rates below $3 \times 10^{-8}$ m/cycle, and the transition region is significantly shorter, giving way to transgranular cracking at about $5 \times 10^{-8}$ m/cycle.

5. Finite element models of a single crystal thin sheet specimen displaying anisotropic, elastic behavior were constructed to examine the relationship between shear stresses on in plane and through-thickness slip directions. This model showed that shear stresses along in plane slip directions were approximately equal at specimens’ surface and interior. It also showed that shear stresses on through-thickness slip directions can exceed shear stresses on planar slip directions, and that the dominance of one over the other is dependent on grain orientation.
The studies presented in this dissertation have uncovered several relationships between mechanical properties of nanocrystalline platinum films and the variables influencing them. Specimen thickness has been shown to affect the fatigue crack growth behavior significantly, with a reduction of thickness below ~1 μm correlated with a reduction of fracture toughness and an increase in the power law exponent but specimens with a thickness greater than ~1 μm maintain roughly the same fatigue behavior as the bulk. The cyclic crack advance modes have been theorized to be dependent on the stress state at the crack tip, with intergranular failure in conjunction with grain coarsening occurring at plane strain conditions, and transitioning to plane stress conditions resulting in typical transgranular failure without grain morphology evolution; the stress states are in turn dependent on the grain morphology, with columnar and non-columnar films influencing the stress states differently due to variance in through-thickness slip. A system sufficiently random, such as the bulk microcrystalline system, would not display intergranular cracking, consistent with observations of both bulk, and various nanocrystalline systems.

The mechanical behavior of the films appears to be a competition between two plasticity mechanisms. The first mechanism is the same slip-mediated deformation that is responsible for plasticity in bulk, macrocrystalline materials. Despite the grain size being on the order of just a few nanometers, evidence from experimental testing and fracture testing suggests that the tension and higher rates of cyclic crack advance occur as a result of dislocation motion and interaction. This mode is dominant at high stresses and is correlated with plane stress conditions at crack tips. The second mechanism dictating the mechanical behavior of the films has been attributed to grain boundary deformation mechanisms. This mechanism has yet to be observed in-situ, but evidence derived from fractography, such as intergranular failure and grain coarsening, makes such a mechanism likely. Two versions of such grain boundary dominated deformation have been proposed in the literature: the first is a grain boundary migration mechanism put forth by Ovid’ko et al, and the second is a grain rotation and subsequent grain boundary decomposition mechanism put forth by Haslam et al. In order to be able to proceed and determine the precise mechanisms more definitively and be able to extend the findings herein to other metallic systems, either in-situ TEM experiments of electron transparent thin films, or 3-dimensional molecular dynamics simulation such as Bishop’s [66] (currently in progress at Georgia Tech) are recommended.
Bibliography


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Appendix A

MATLAB Script for ANSYS Finite Element Modeling

clear all;
close all;

% Variable Definitions
% W: width of plate
% L: length of plate
% halflength: half the length of the plate
% a: crack length
% W_a: remaining (uncracked) width ligament
% SA: Inward applied pressure (negative for outwardly applied)
% MESHTIP: variable fineness of mesh around crack tip

% Set geometry (dimensions in micrometers)
W = 100;
L = 1000;
halflength = L/2;
a = 30;
W_a = W - a;
X_1=a/2;
X_2=a;
X_3=W_a/4+a;
X_4=W_a/2+a;
X_5=3*W_a/4+a;

Y_1=halflength+7.5;
Y_2=halflength+15;
Y_3=halflength+30;
Y_4=halflength+37.5;
Y_5=halflength-7.5;
Y_6=halflength-15;
Y_7=halflength-30;
Y_8=halflength-37.5;

if (a <= W_a)
    MESHTIP = a/20;
else
    MESHTIP = W_a/20;
end;

% Set Solution Parameters
SA = -1E-12;

% Set output file name
filename='EdgeCrackedSheet3D.log';

fid=fopen(filename, 'w');
% Initial Setup
fprintf(fid, 'finish\n');
fprintf(fid, 'KEYW,PR_SGUI,1\n');
fprintf(fid, '/CLEAR,START\n');
fprintf(fid, 'input,start21i,ans,/gpfs/apps/x86_64-rhel5/ansys/12.1.1/v121(ansys/apdl/ ,\n'); % version specific startup file
fprintf(fid, '/UNITS, SI\n');
fprintf(fid, 'K,1,0,0,,\n');
fprintf(fid, strcat('K,2,', num2str(W), ',0,, \n'));
fprintf(fid, strcat('K,3,', num2str(W), ',', num2str(halflength), ',,, \n'));
fprintf(fid, strcat('K,4,', num2str(W), ',', num2str(L), ',,, \n'));
fprintf(fid, strcat('K,5,', num2str(a), ',', num2str(L), ',,, \n'));
fprintf(fid, strcat('K,6,0,, num2str(L),,, \n'));
fprintf(fid, strcat('K,7,0,, num2str(halflength),,, \n'));
fprintf(fid, strcat('K,8,, num2str(X_2),,, num2str(halflength),,, \n'));
fprintf(fid, strcat('K,9,0,, num2str(halflength),,, \n'));
fprintf(fid, strcat('K,10,, num2str(a),,, num2str(Y_5),,, \n'));
fprintf(fid, strcat('K,11,, num2str(X_3),,, num2str(Y_6),,, \n'));
fprintf(fid, strcat('K,12,, num2str(X_4),,, num2str(Y_5),,, \n'));
fprintf(fid, strcat('K,13,, num2str(X_4),,, num2str(Y_1),,, \n'));
fprintf(fid, strcat('K,14,, num2str(X_3),,, num2str(Y_2),,, \n'));
fprintf(fid, strcat('K,15,, num2str(X_2),,, num2str(Y_1),,, \n'));
fprintf(fid, strcat('K,16,, num2str(X_5),,, num2str(Y_6),,, \n'));
fprintf(fid, strcat('K,17,, num2str(W),,, num2str(Y_5),,, \n'));
fprintf(fid, strcat('K,18,, num2str(W),,, num2str(Y_1),,, \n'));
fprintf(fid, strcat('K,19,, num2str(X_5),,, num2str(Y_2),,, \n'));
fprintf(fid, strcat('K,20,, num2str(X_1),,, num2str(Y_2),,, \n'));
fprintf(fid, strcat('K,21,0,, num2str(Y_1),,, \n'));
fprintf(fid, strcat('K,22,0,, num2str(Y_5),,, \n'));
fprintf(fid, strcat('K,23,, num2str(X_1),,, num2str(Y_6),,, \n'));
fprintf(fid, strcat('K,24,, num2str(W*5),,, num2str(L*25),,, \n')); % unused
fprintf(fid, strcat('K,25,, num2str(W*5),,, num2str(L*75),,, \n')); % unused
fprintf(fid, strcat('K,26,, num2str(X_1),,, num2str(Y_3),,, \n'));
fprintf(fid, strcat('K,27,0,, num2str(Y_4),,, \n'));
fprintf(fid, strcat('K,28,, num2str(X_2),,, num2str(Y_4),,, \n'));
fprintf(fid, strcat('K,29,, num2str(X_3),,, num2str(Y_3),,, \n'));
fprintf(fid, strcat('K,30,, num2str(X_4),,, num2str(Y_4),,, \n'));
fprintf(fid, strcat('K,31,, num2str(X_5),,, num2str(Y_3),,, \n'));
fprintf(fid, strcat('K,32,, num2str(W),,, num2str(Y_4),,, \n'));
fprintf(fid, strcat('K,33,, num2str(X_1),,, num2str(Y_7),,, \n'));
fprintf(fid, strcat('K,34,0,, num2str(Y_8),,, \n'));
fprintf(fid, strcat('K,35,, num2str(X_2),,, num2str(Y_8),,, \n'));
fprintf(fid, strcat('K,36,, num2str(X_3),,, num2str(Y_7),,, \n'));
fprintf(fid, strcat('K,37,, num2str(X_4),,, num2str(Y_8),,, \n'));
fprintf(fid, strcat('K,38,, num2str(X_5),,, num2str(Y_7),,, \n'));
fprintf(fid, strcat('K,39,, num2str(W),,, num2str(Y_8),,, \n'));
fprintf(fid, strcat('K,40,0,0,10,\n'));
fprintf(fid, strcat('K,41,, num2str(W),,, 0,10,\n'));
fprintf(fid, strcat('K,42,, num2str(W),,, num2str(halflength),,, 10,\n'));
fprintf(fid, strcat('K,43,, num2str(W),,, num2str(L),,, 10,\n'));
fprintf(fid, strcat('K,44,, num2str(a),,, num2str(L),,, 10,\n'));
fprintf(fid, strcat('K,45,0,, num2str(L),,, 10,\n'));
fprintf(fid, strcat('K,46,0,, num2str(halflength),,, 10,\n'));
fprintf(fid, strcat('K,47,, num2str(X_2),,, num2str(halflength),,, 10,\n'));
fprintf(fid, strcat('K,48,0,, num2str(halflength),,, 10,\n'));
fprintf(fid, strcat('K,49,, num2str(a),,, num2str(Y_5),,, 10,\n'));
fprintf(fid, strcat('K,50,', num2str(X_3), ',\', num2str(Y_6), ',10, \n'));
fprintf(fid, strcat('K,51,', num2str(X_4), ',\', num2str(Y_5), ',10, \n'));
fprintf(fid, strcat('K,52,', num2str(X_4), ',\', num2str(Y_1), ',10, \n'));
fprintf(fid, strcat('K,53,', num2str(X_3), ',\', num2str(Y_6), ',10, \n'));
fprintf(fid, strcat('K,54,', num2str(X_2), ',\', num2str(Y_1), ',10, \n'));
fprintf(fid, strcat('K,55,', num2str(X_5), ',\', num2str(Y_6), ',10, \n'));
fprintf(fid, strcat('K,56,', num2str(N), ',\', num2str(Y_5), ',10, \n'));
fprintf(fid, strcat('K,57,', num2str(N), ',\', num2str(Y_1), ',10, \n'));
fprintf(fid, strcat('K,58,', num2str(X_5), ',\', num2str(Y_2), ',10, \n'));
fprintf(fid, strcat('K,59,', num2str(X_1), ',\', num2str(Y_2), ',10, \n'));
fprintf(fid, strcat('K,60,0,\', num2str(Y_1), ',10, \n'));
fprintf(fid, strcat('K,61,0,\', num2str(Y_5), ',10, \n'));
fprintf(fid, strcat('K,62,\', num2str(X_1), ',\', num2str(Y_6), ',10, \n'));
fprintf(fid, strcat('K,63,\', num2str(N*.5), ',\', num2str(L*.25), ',10, \n'));
fprintf(fid, strcat('K,64,\', num2str(N*.5), ',\', num2str(L*.75), ',10, \n'));
fprintf(fid, strcat('K,65,\', num2str(X_1), ',\', num2str(Y_3), ',10, \n'));
fprintf(fid, strcat('K,66,0,\', num2str(Y_4), ',10, \n'));
fprintf(fid, strcat('K,67,\', num2str(X_2), ',\', num2str(Y_4), ',10, \n'));
fprintf(fid, strcat('K,68,\', num2str(X_3), ',\', num2str(Y_4), ',10, \n'));
fprintf(fid, strcat('K,69,\', num2str(X_4), ',\', num2str(Y_4), ',10, \n'));
fprintf(fid, strcat('K,70,\', num2str(X_5), ',\', num2str(Y_4), ',10, \n'));
fprintf(fid, strcat('K,71,\', num2str(N), ',\', num2str(Y_4), ',10, \n'));
fprintf(fid, strcat('K,72,\', num2str(X_1), ',\', num2str(Y_7), ',10, \n'));
fprintf(fid, strcat('K,73,0,\', num2str(Y_8), ',10, \n'));
fprintf(fid, strcat('K,74,\', num2str(X_2), ',\', num2str(Y_8), ',10, \n'));
fprintf(fid, strcat('K,75,\', num2str(X_3), ',\', num2str(Y_8), ',10, \n'));
fprintf(fid, strcat('K,76,\', num2str(X_4), ',\', num2str(Y_8), ',10, \n'));
fprintf(fid, strcat('K,77,\', num2str(X_5), ',\', num2str(Y_8), ',10, \n'));
fprintf(fid, strcat('K,78,\', num2str(N), ',\', num2str(Y_8), ',10, \n'));
fprintf(fid, strcat('L,1,2\n'));
fprintf(fid, strcat('L,2,3\n'));
fprintf(fid, strcat('L,3,4\n'));
fprintf(fid, strcat('L,4,5\n'));
fprintf(fid, strcat('L,5,6\n'));
fprintf(fid, strcat('L,6,7\n'));
fprintf(fid, strcat('L,7,8\n'));
fprintf(fid, strcat('L,8,9\n'));
fprintf(fid, strcat('L,9,1\n'));
fprintf(fid, strcat('L,8,3\n'));
fprintf(fid, strcat('L,10,11\n'));
fprintf(fid, strcat('L,11,12\n'));
fprintf(fid, strcat('L,12,13\n'));
fprintf(fid, strcat('L,13,14\n'));
fprintf(fid, strcat('L,14,15\n'));
fprintf(fid, strcat('L,15,8\n'));
fprintf(fid, strcat('L,16,17\n'));
fprintf(fid, strcat('L,17,18\n'));
fprintf(fid, strcat('L,18,19\n'));
fprintf(fid, strcat('L,19,13\n'));
fprintf(fid, strcat('L,20,21\n'));
fprintf(fid, strcat('L,21,7\n'));
fprintf(fid, strcat('L,22,9\n'));
fprintf(fid, strcat('L,10,11\n'));
fprintf(fid, strcat('L,11,12\n'));
fprintf(fid, strcat('L,12,13\n'));
fprintf(fid, strcat('L,13,14\n'));
fprintf(fid, strcat('L,14,15\n'));
fprintf(fid, strcat('L,15,8\n'));
fprintf(fid, strcat('L,16,17\n'));
fprintf(fid, strcat('L,17,18\n'));
fprintf(fid, strcat('L,18,19\n'));
fprintf(fid, strcat('L,19,13\n'));
fprintf(fid, strcat('L,20,21\n'));
fprintf(fid, strcat('L,21,7\n'));
fprintf(fid, strcat('L,22,9\n'));
fprintf(fid, 'L,       20,      26\n'); % Line 29
fprintf(fid, 'L,       26,      27\n'); % Line 30
fprintf(fid, 'L,       27,      21\n'); % Line 31
fprintf(fid, 'L,       26,      28\n'); % Line 32
fprintf(fid, 'L,       28,      29\n'); % Line 33
fprintf(fid, 'L,       29,      14\n'); % Line 34
fprintf(fid, 'L,       29,      30\n'); % Line 35
fprintf(fid, 'L,       30,      31\n'); % Line 36
fprintf(fid, 'L,       31,      19\n'); % Line 37
fprintf(fid, 'L,       31,      32\n'); % Line 38
fprintf(fid, 'L,       32,      18\n'); % Line 39
fprintf(fid, 'L,       23,      33\n'); % Line 40
fprintf(fid, 'L,       33,      34\n'); % Line 41
fprintf(fid, 'L,       34,      22\n'); % Line 42
fprintf(fid, 'L,       33,      35\n'); % Line 43
fprintf(fid, 'L,       35,      36\n'); % Line 44
fprintf(fid, 'L,       36,      11\n'); % Line 45
fprintf(fid, 'L,       36,      37\n'); % Line 46
fprintf(fid, 'L,       37,      38\n'); % Line 47
fprintf(fid, 'L,       38,      16\n'); % Line 48
fprintf(fid, 'L,       38,      39\n'); % Line 49
fprintf(fid, 'L,       39,      17\n'); % Line 50
fprintf(fid, 'L,       1,       34\n'); % Line 51
fprintf(fid, 'L,       2,       39\n'); % Line 52
fprintf(fid, 'L,       27,      6\n'); % Line 53
fprintf(fid, 'L,       32,      4\n'); % Line 54
fprintf(fid, 'L,       40,      41\n'); % Line 55
fprintf(fid, 'L,       41,      42\n'); % Line 56
fprintf(fid, 'L,       42,      43\n'); % Line 57
fprintf(fid, 'L,       43,      44\n'); % Line 58
fprintf(fid, 'L,       44,      45\n'); % Line 59
fprintf(fid, 'L,       45,      46\n'); % Line 60
fprintf(fid, 'L,       46,      47\n'); % Line 61
fprintf(fid, 'L,       47,      48\n'); % Line 62
fprintf(fid, 'L,       48,      40\n'); % Line 63
fprintf(fid, 'L,       47,      49\n'); % Line 64
%
%Grains
fprintf(fid, 'L,       47,      49\n'); % Line 65
fprintf(fid, 'L,       49,      50\n'); % Line 66
fprintf(fid, 'L,       50,      51\n'); % Line 67
fprintf(fid, 'L,       51,      52\n'); % Line 68
fprintf(fid, 'L,       52,      53\n'); % Line 69
fprintf(fid, 'L,       53,      54\n'); % Line 70
fprintf(fid, 'L,       54,      47\n'); % Line 71
fprintf(fid, 'L,       51,      55\n'); % Line 72
fprintf(fid, 'L,       55,      56\n'); % Line 73
fprintf(fid, 'L,       56,      57\n'); % Line 74
fprintf(fid, 'L,       57,      58\n'); % Line 75
fprintf(fid, 'L,       58,      52\n'); % Line 76
fprintf(fid, 'L,       54,      59\n'); % Line 77
fprintf(fid, 'L,       59,      60\n'); % Line 78
fprintf(fid, 'L,       60,      46\n'); % Line 79
fprintf(fid, 'L,       49,      62\n'); % Line 80
fprintf(fid, 'L,       62,      61\n'); % Line 81
fprintf(fid, 'L,       61,      48\n'); % Line 82
fprintf(fid, 'L,       59,      65\n'); % Line 83
fprintf(fid, 'L,       65,      66\n'); % Line 84
fprintf(fid, 'L, 66, 60\n'); % Line 85
fprintf(fid, 'L, 65, 67\n'); % Line 86
fprintf(fid, 'L, 67, 68\n'); % Line 87
fprintf(fid, 'L, 68, 53\n'); % Line 88
fprintf(fid, 'L, 68, 69\n'); % Line 89
fprintf(fid, 'L, 69, 70\n'); % Line 90
fprintf(fid, 'L, 70, 58\n'); % Line 91
fprintf(fid, 'L, 70, 71\n'); % Line 92
fprintf(fid, 'L, 71, 57\n'); % Line 93
fprintf(fid, 'L, 62, 72\n'); % Line 94
fprintf(fid, 'L, 72, 73\n'); % Line 95
fprintf(fid, 'L, 73, 61\n'); % Line 96
fprintf(fid, 'L, 72, 74\n'); % Line 97
fprintf(fid, 'L, 74, 75\n'); % Line 98
fprintf(fid, 'L, 75, 50\n'); % Line 99
fprintf(fid, 'L, 75, 76\n'); % Line 100
fprintf(fid, 'L, 76, 77\n'); % Line 101
fprintf(fid, 'L, 77, 55\n'); % Line 102
fprintf(fid, 'L, 77, 78\n'); % Line 103
fprintf(fid, 'L, 78, 56\n'); % Line 104
fprintf(fid, 'L, 40, 73\n'); % Line 105
fprintf(fid, 'L, 41, 78\n'); % Line 106
fprintf(fid, 'L, 66, 45\n'); % Line 107
fprintf(fid, 'L, 71, 43\n'); % Line 108
fprintf(fid, 'L, 1, 40\n'); % Line 109
fprintf(fid, 'L, 2, 41\n'); % Line 110
fprintf(fid, 'L, 3, 42\n'); % Line 111
fprintf(fid, 'L, 4, 43\n'); % Line 112
fprintf(fid, 'L, 5, 44\n'); % Line 113
fprintf(fid, 'L, 6, 45\n'); % Line 114
fprintf(fid, 'L, 7, 46\n'); % Line 115
fprintf(fid, 'L, 8, 47\n'); % Line 116
fprintf(fid, 'L, 9, 48\n'); % Line 117
fprintf(fid, 'L, 10, 49\n'); % Line 118
fprintf(fid, 'L, 11, 50\n'); % Line 119
fprintf(fid, 'L, 12, 51\n'); % Line 120
fprintf(fid, 'L, 13, 52\n'); % Line 121
fprintf(fid, 'L, 14, 53\n'); % Line 122
fprintf(fid, 'L, 15, 54\n'); % Line 123
fprintf(fid, 'L, 16, 55\n'); % Line 124
fprintf(fid, 'L, 17, 56\n'); % Line 125
fprintf(fid, 'L, 18, 57\n'); % Line 126
fprintf(fid, 'L, 19, 58\n'); % Line 127
fprintf(fid, 'L, 20, 59\n'); % Line 128
fprintf(fid, 'L, 21, 60\n'); % Line 129
fprintf(fid, 'L, 22, 61\n'); % Line 130
fprintf(fid, 'L, 23, 62\n'); % Line 131
fprintf(fid, 'L, 24, 63\n'); % Line 132 - unused
fprintf(fid, 'L, 25, 64\n'); % Line 133 - unused
fprintf(fid, 'L, 26, 65\n'); % Line 134
fprintf(fid, 'L, 27, 66\n'); % Line 135
fprintf(fid, 'L, 28, 67\n'); % Line 136
fprintf(fid, 'L, 29, 68\n'); % Line 137
fprintf(fid, 'L, 30, 69\n'); % Line 138
fprintf(fid, 'L, 31, 70\n'); % Line 139
fprintf(fid, 'L, 32, 71\n'); % Line 140
fprintf(fid, 'L, 33, 72\n'); % Line 141
fprintf(fid, 'L, 34, 73\n'); % Line 142
fprintf(fid, 'L, 35, 74\n'); % Line 143
fprintf(fid, 'L,       36,      75\n'); % Line 144
fprintf(fid, 'L,       37,      76\n'); % Line 145
fprintf(fid, 'L,       38,      77\n'); % Line 146
fprintf(fid, 'L,       39,      78\n'); % Line 147

%     Create Areas from Lines - Start with bottom surfaces
fprintf(fid, 'FLST,2,5,4\n');
fprintf(fid, 'FITEM,2,7\n');
fprintf(fid, 'FITEM,2,17\n');
fprintf(fid, 'FITEM,2,23\n');
fprintf(fid, 'FITEM,2,24\n');
fprintf(fid, 'FITEM,2,25\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,7,4\n');
fprintf(fid, 'FITEM,2,11\n');
fprintf(fid, 'FITEM,2,12\n');
fprintf(fid, 'FITEM,2,13\n');
fprintf(fid, 'FITEM,2,14\n');
fprintf(fid, 'FITEM,2,15\n');
fprintf(fid, 'FITEM,2,17\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,6,4\n');
fprintf(fid, 'FITEM,2,24\n');
fprintf(fid, 'FITEM,2,29\n');
fprintf(fid, 'FITEM,2,30\n');
fprintf(fid, 'FITEM,2,31\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,27\n');
fprintf(fid, 'FITEM,2,28\n');
fprintf(fid, 'FITEM,2,32\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,27\n');
fprintf(fid, 'FITEM,2,28\n');
fprintf(fid, 'FITEM,2,41\n');
fprintf(fid, 'FITEM,2,42\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,6,4\n');
fprintf(fid, 'FITEM,2,26\n');
fprintf(fid, 'FITEM,2,40\n');
fprintf(fid, 'FITEM,2,43\n');
fprintf(fid, 'FITEM,2,44\n');
fprintf(fid, 'FITEM,2,45\n');
fprintf(fid, 'FITEM,2,12\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,6,4\n');
fprintf(fid, 'FITEM,2,15\n');
fprintf(fid, 'FITEM,2,22\n');
fprintf(fid, 'FITEM,2,37\n');
fprintf(fid, 'FITEM,2,36\n');
fprintf(fid, 'FITEM,2,35\n');
fprintf(fid, 'FITEM,2,34\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,6,4\n');
fprintf(fid, 'FITEM,2,45\n');
fprintf(fid, 'FITEM,2,46\n');
fprintf(fid, 'FITEM,2,47\n');
fprintf(fid, 'FITEM,2,48\n');
fprintf(fid, 'FITEM,2,18\n');
fprintf(fid, 'FITEM,2,13\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,37\n');
fprintf(fid, 'FITEM,2,21\n');
fprintf(fid, 'FITEM,2,39\n');
fprintf(fid, 'FITEM,2,38\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,37\n');
fprintf(fid, 'FITEM,2,21\n');
fprintf(fid, 'FITEM,2,39\n');
fprintf(fid, 'FITEM,2,38\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,9,4\n');
fprintf(fid, 'FITEM,2,41\n');
fprintf(fid, 'FITEM,2,43\n');
fprintf(fid, 'FITEM,2,44\n');
fprintf(fid, 'FITEM,2,46\n');
fprintf(fid, 'FITEM,2,47\n');
fprintf(fid, 'FITEM,2,49\n');
fprintf(fid, 'FITEM,2,52\n');
fprintf(fid, 'FITEM,2,1\n');
fprintf(fid, 'FITEM,2,51\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,10,4\n');
fprintf(fid, 'FITEM,2,30\n');
fprintf(fid, 'FITEM,2,32\n');
fprintf(fid, 'FITEM,2,33\n');
fprintf(fid, 'FITEM,2,35\n');
fprintf(fid, 'FITEM,2,36\n');
fprintf(fid, 'FITEM,2,38\n');
fprintf(fid, 'FITEM,2,54\n');
fprintf(fid, 'FITEM,2,4\n');
fprintf(fid, 'FITEM,2,5\n');
fprintf(fid, 'FITEM,2,53\n');
fprintf(fid, 'AL,P51x\n');

% % Top Surfaces
fprintf(fid, 'FLST,2,5,4\n');
fprintf(fid, 'FITEM,2,61\n');
fprintf(fid, 'FITEM,2,71\n');
fprintf(fid, 'FITEM,2,77\n');
fprintf(fid, 'FITEM,2,78\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,5,4\n');
fprintf(fid, 'FITEM,2,62\n');
fprintf(fid, 'FITEM,2,65\n');
fprintf(fid, 'FITEM,2,80\n');
fprintf(fid, 'FITEM,2,81\n');
fprintf(fid, 'FITEM,2,82\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,7,4\n');
fprintf(fid, 'FITEM,2,65\n');
fprintf(fid, 'FITEM,2,66\n');
fprintf(fid, 'FITEM,2,67\n');
fprintf(fid, 'FITEM,2,68\n');
fprintf(fid, 'FITEM,2,69\n');
fprintf(fid, 'FITEM,2,70\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,78\n');
fprintf(fid, 'FITEM,2,83\n');
fprintf(fid, 'FITEM,2,84\n');
fprintf(fid, 'FITEM,2,85\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,77\n');
fprintf(fid, 'FITEM,2,94\n');
fprintf(fid, 'FITEM,2,95\n');
fprintf(fid, 'FITEM,2,96\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,6,4\n');
fprintf(fid, 'FITEM,2,83\n');
fprintf(fid, 'FITEM,2,77\n');
fprintf(fid, 'FITEM,2,70\n');
fprintf(fid, 'FITEM,2,88\n');
fprintf(fid, 'FITEM,2,87\n');
fprintf(fid, 'FITEM,2,86\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,5,4\n');
fprintf(fid, 'FITEM,2,83\n');
fprintf(fid, 'FITEM,2,81\n');
fprintf(fid, 'FITEM,2,82\n');
fprintf(fid, 'FITEM,2,86\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,6,4\n');
fprintf(fid, 'FITEM,2,80\n');
fprintf(fid, 'FITEM,2,94\n');
fprintf(fid, 'FITEM,2,97\n');
fprintf(fid, 'FITEM,2,98\n');
fprintf(fid, 'FITEM,2,99\n');
fprintf(fid, 'FITEM,2,66\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,6,4\n');
fprintf(fid, 'FITEM,2,88\n');
fprintf(fid, 'FITEM,2,69\n');
fprintf(fid, 'FITEM,2,76\n');
fprintf(fid, 'FITEM,2,91\n');
fprintf(fid, 'FITEM,2,90\n');
fprintf(fid, 'FITEM,2,89\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,6,4\n');
fprintf(fid, 'FITEM,2,67\n');
fprintf(fid, 'FITEM,2,99\n');
fprintf(fid, 'FITEM,2,100\n');
fprintf(fid, 'FITEM,2,101\n');
fprintf(fid, 'FITEM,2,102\n');
fprintf(fid, 'FITEM,2,72\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,91\n');
fprintf(fid, 'FITEM,2,75\n');
fprintf(fid, 'FITEM,2,93\n');
fprintf(fid, 'FITEM,2,92\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,102\n');
fprintf(fid, 'FITEM,2,103\n');
fprintf(fid, 'FITEM,2,104\n');
fprintf(fid, 'FITEM,2,73\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,9,4\n');
fprintf(fid, 'FITEM,2,95\n');
fprintf(fid, 'FITEM,2,97\n');
fprintf(fid, 'FITEM,2,98\n');
fprintf(fid, 'FITEM,2,100\n');
fprintf(fid, 'FITEM,2,101\n');
fprintf(fid, 'FITEM,2,103\n');
fprintf(fid, 'FITEM,2,106\n');
fprintf(fid, 'FITEM,2,55\n');
fprintf(fid, 'FITEM,2,105\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,10,4\n');
fprintf(fid, 'FITEM,2,84\n');
fprintf(fid, 'FITEM,2,86\n');
fprintf(fid, 'FITEM,2,87\n');
fprintf(fid, 'FITEM,2,89\n');
fprintf(fid, 'FITEM,2,90\n');
fprintf(fid, 'FITEM,2,92\n');
fprintf(fid, 'FITEM,2,108\n');
fprintf(fid, 'FITEM,2,58\n');
fprintf(fid, 'FITEM,2,59\n');
fprintf(fid, 'FITEM,2,107\n');
fprintf(fid, 'AL,P51x\n');

% Vertical Areas
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,1\n');
fprintf(fid, 'FITEM,2,110\n');
fprintf(fid, 'FITEM,2,55\n');
fprintf(fid, 'FITEM,2,109\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,2\n');
fprintf(fid, 'FITEM,2,111\n');
fprintf(fid, 'FITEM,2,56\n');
fprintf(fid, 'FITEM,2,110\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,3\n');
fprintf(fid, 'FITEM,2,112\n');
fprintf(fid, 'FITEM,2,57\n');
fprintf(fid, 'FITEM,2,111\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,4\n');
fprintf(fid, 'FITEM,2,113\n');
fprintf(fid, 'FITEM,2,58\n');
fprintf(fid, 'FITEM,2,112\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,5\n');
fprintf(fid, 'FITEM,2,114\n');
fprintf(fid, 'FITEM,2,59\n');
fprintf(fid, 'FITEM,2,113\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,6\n');
fprintf(fid, 'FITEM,2,115\n');
fprintf(fid, 'FITEM,2,60\n');
fprintf(fid, 'FITEM,2,114\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,7\n');
fprintf(fid, 'FITEM,2,116\n');
fprintf(fid, 'FITEM,2,61\n');
fprintf(fid, 'FITEM,2,115\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,8\n');
fprintf(fid, 'FITEM,2,117\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,9\n');
fprintf(fid, 'FITEM,2,109\n');
fprintf(fid, 'FITEM,2,63\n');
fprintf(fid, 'FITEM,2,117\n');
fprintf(fid, 'AL,P51x\n');

fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,10\n');
fprintf(fid, 'FITEM,2,111\n');
fprintf(fid, 'FITEM,2,64\n');
fprintf(fid, 'FITEM,2,116\n');
fprintf(fid, 'AL,P51x\n');

% Grain 1
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,17\n');
fprintf(fid, 'FITEM,2,123\n');
fprintf(fid, 'FITEM,2,71\n');
fprintf(fid, 'FITEM,2,116\n');
fprintf(fid, 'AL,P51x\n');

fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,23\n');
fprintf(fid, 'FITEM,2,128\n');
fprintf(fid, 'FITEM,2,77\n');
fprintf(fid, 'FITEM,2,123\n');
fprintf(fid, 'AL,P51x\n');

fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,24\n');
fprintf(fid, 'FITEM,2,129\n');
fprintf(fid, 'FITEM,2,78\n');
fprintf(fid, 'FITEM,2,128\n');
fprintf(fid, 'AL,P51x\n');

% Grain 2
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,11\n');
fprintf(fid, 'FITEM,2,118\n');
fprintf(fid, 'FITEM,2,65\n');
fprintf(fid, 'FITEM,2,116\n');
fprintf(fid, 'AL,P51x\n');

fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,26\n');
fprintf(fid, 'FITEM,2,131\n');
fprintf(fid, 'FITEM,2,80\n');
fprintf(fid, 'FITEM,2,118\n');
fprintf(fid, 'AL,P51x\n');

fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,27\n');
fprintf(fid, 'FITEM,2,130\n');
fprintf(fid, 'FITEM,2,81\n');
fprintf(fid, 'FITEM,2,131\n');
fprintf(fid, 'AL,P51x\n');

fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,28\n');
fprintf(fid, 'FITEM,2,117\n');
fprintf(fid, 'FITEM,2,82\n');
fprintf(fid, 'FITEM,2,130\n');
fprintf(fid, 'AL,P51x\n');

% Grain 3
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,12\n');
fprintf(fid, 'FITEM,2,119\n');
fprintf(fid, 'FITEM,2,66\n');
fprintf(fid, 'FITEM,2,118\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,13\n');
fprintf(fid, 'FITEM,2,120\n');
fprintf(fid, 'FITEM,2,67\n');
fprintf(fid, 'FITEM,2,119\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,14\n');
fprintf(fid, 'FITEM,2,121\n');
fprintf(fid, 'FITEM,2,68\n');
fprintf(fid, 'FITEM,2,120\n');
fprintf(fid, 'AL,P51x\n');

fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,15\n');
fprintf(fid, 'FITEM,2,122\n');
fprintf(fid, 'FITEM,2,69\n');
fprintf(fid, 'FITEM,2,121\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,16\n');
fprintf(fid, 'FITEM,2,123\n');
fprintf(fid, 'FITEM,2,70\n');
fprintf(fid, 'FITEM,2,122\n');
fprintf(fid, 'AL,P51x\n');

% Grain 4
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,18\n');
fprintf(fid, 'FITEM,2,124\n');
fprintf(fid, 'FITEM,2,72\n');
fprintf(fid, 'FITEM,2,120\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,19\n');
fprintf(fid, 'FITEM,2,125\n');
fprintf(fid, 'FITEM,2,73\n');
fprintf(fid, 'FITEM,2,124\n');
fprintf(fid, 'AL,P51x\n');

fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,20\n');
fprintf(fid, 'FITEM,2,126\n');
fprintf(fid, 'FITEM,2,74\n');
fprintf(fid, 'FITEM,2,125\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,21\n');
fprintf(fid, 'FITEM,2,127\n');
fprintf(fid, 'FITEM,2,75\n');
fprintf(fid, 'FITEM,2,126\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,22\n');
fprintf(fid, 'FITEM,2,121\n');
fprintf(fid, 'FITEM,2,76\n');
fprintf(fid, 'FITEM,2,127\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,29\n');
fprintf(fid, 'FITEM,2,134\n');
fprintf(fid, 'FITEM,2,83\n');
fprintf(fid, 'FITEM,2,128\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,30\n');
fprintf(fid, 'FITEM,2,135\n');
fprintf(fid, 'FITEM,2,84\n');
fprintf(fid, 'FITEM,2,134\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,40\n');
fprintf(fid, 'FITEM,2,141\n');
fprintf(fid, 'FITEM,2,94\n');
fprintf(fid, 'FITEM,2,131\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,41\n');
fprintf(fid, 'FITEM,2,142\n');
fprintf(fid, 'FITEM,2,95\n');
fprintf(fid, 'FITEM,2,141\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,34\n');
fprintf(fid, 'FITEM,2,137\n');
fprintf(fid, 'FITEM,2,40\n');
fprintf(fid, 'FITEM,2,140\n');
fprintf(fid, 'FITEM,2,94\n');
fprintf(fid, 'FITEM,2,131\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,42\n');
fprintf(fid, 'FITEM,2,142\n');
fprintf(fid, 'FITEM,2,95\n');
fprintf(fid, 'FITEM,2,141\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,130\n');
fprintf(fid, 'FITEM,2,96\n');
fprintf(fid, 'FITEM,2,142\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,34\n');
fprintf(fid, 'FITEM,2,137\n');
fprintf(fid, 'FITEM,2,88\n');
fprintf(fid, 'FITEM,2,122\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,33\n');
fprintf(fid, 'FITEM,2,136\n');
fprintf(fid, 'FITEM,2,87\n');
fprintf(fid, 'FITEM,2,137\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,32\n');
fprintf(fid, 'FITEM,2,134\n');
fprintf(fid, 'FITEM,2,86\n');
fprintf(fid, 'FITEM,2,136\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,43\n');
fprintf(fid, 'FITEM,2,143\n');
fprintf(fid, 'FITEM,2,97\n');
fprintf(fid, 'FITEM,2,141\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,44\n');
fprintf(fid, 'FITEM,2,144\n');
fprintf(fid, 'FITEM,2,98\n');
fprintf(fid, 'FITEM,2,143\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,37\n');
fprintf(fid, 'FITEM,2,139\n');
fprintf(fid, 'FITEM,2,91\n');
fprintf(fid, 'FITEM,2,127\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,36\n');
fprintf(fid, 'FITEM,2,138\n');
fprintf(fid, 'FITEM,2,90\n');
fprintf(fid, 'FITEM,2,139\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,35\n');
fprintf(fid, 'FITEM,2,137\n');
fprintf(fid, 'FITEM,2,89\n');
fprintf(fid, 'FITEM,2,138\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,42\n');
fprintf(fid, 'FITEM,2,142\n');
fprintf(fid, 'FITEM,2,96\n');
fprintf(fid, 'FITEM,2,140\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,43\n');
fprintf(fid, 'FITEM,2,143\n');
fprintf(fid, 'FITEM,2,97\n');
fprintf(fid, 'FITEM,2,141\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,44\n');
fprintf(fid, 'FITEM,2,144\n');
fprintf(fid, 'FITEM,2,98\n');
fprintf(fid, 'FITEM,2,143\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,36\n');
fprintf(fid, 'FITEM,2,138\n');
fprintf(fid, 'FITEM,2,90\n');
fprintf(fid, 'FITEM,2,139\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,35\n');
fprintf(fid, 'FITEM,2,137\n');
fprintf(fid, 'FITEM,2,89\n');
fprintf(fid, 'FITEM,2,138\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,42\n');
fprintf(fid, 'FITEM,2,142\n');
fprintf(fid, 'FITEM,2,96\n');
fprintf(fid, 'FITEM,2,140\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,43\n');
fprintf(fid, 'FITEM,2,143\n');
fprintf(fid, 'FITEM,2,97\n');
fprintf(fid, 'FITEM,2,141\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,44\n');
fprintf(fid, 'FITEM,2,144\n');
fprintf(fid, 'FITEM,2,98\n');
fprintf(fid, 'FITEM,2,143\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,36\n');
fprintf(fid, 'FITEM,2,138\n');
fprintf(fid, 'FITEM,2,90\n');
fprintf(fid, 'FITEM,2,139\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,35\n');
fprintf(fid, 'FITEM,2,137\n');
fprintf(fid, 'FITEM,2,89\n');
fprintf(fid, 'FITEM,2,138\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,42\n');
fprintf(fid, 'FITEM,2,142\n');
fprintf(fid, 'FITEM,2,96\n');
fprintf(fid, 'FITEM,2,140\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,43\n');
fprintf(fid, 'FITEM,2,143\n');
fprintf(fid, 'FITEM,2,97\n');
fprintf(fid, 'FITEM,2,141\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,44\n');
fprintf(fid, 'FITEM,2,144\n');
fprintf(fid, 'FITEM,2,98\n');
fprintf(fid, 'FITEM,2,143\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,36\n');
fprintf(fid, 'FITEM,2,138\n');
fprintf(fid, 'FITEM,2,90\n');
fprintf(fid, 'FITEM,2,139\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,35\n');
fprintf(fid, 'FITEM,2,137\n');
fprintf(fid, 'FITEM,2,89\n');
fprintf(fid, 'FITEM,2,138\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,42\n');
fprintf(fid, 'FITEM,2,142\n');
fprintf(fid, 'FITEM,2,96\n');
fprintf(fid, 'FITEM,2,140\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,43\n');
fprintf(fid, 'FITEM,2,143\n');
fprintf(fid, 'FITEM,2,97\n');
fprintf(fid, 'FITEM,2,141\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,44\n');
fprintf(fid, 'FITEM,2,144\n');
fprintf(fid, 'FITEM,2,98\n');
fprintf(fid, 'FITEM,2,143\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,36\n');
fprintf(fid, 'FITEM,2,138\n');
fprintf(fid, 'FITEM,2,90\n');
fprintf(fid, 'FITEM,2,139\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,35\n');
fprintf(fid, 'FITEM,2,137\n');
fprintf(fid, 'FITEM,2,89\n');
fprintf(fid, 'FITEM,2,138\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,46\n');
fprintf(fid, 'FITEM,2,145\n');
fprintf(fid, 'FITEM,2,100\n');
fprintf(fid, 'AL,P51x\n');

fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,47\n');
fprintf(fid, 'FITEM,2,146\n');
fprintf(fid, 'FITEM,2,101\n');
fprintf(fid, 'AL,P51x\n');

fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,48\n');
fprintf(fid, 'FITEM,2,124\n');
fprintf(fid, 'AL,P51x\n');

fprintf(fid, '% Grain 11
');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,39\n');
fprintf(fid, 'FITEM,2,140\n');
fprintf(fid, 'FITEM,2,93\n');
fprintf(fid, 'AL,P51x\n');

fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,38\n');
fprintf(fid, 'FITEM,2,139\n');
fprintf(fid, 'FITEM,2,92\n');
fprintf(fid, 'AL,P51x\n');

fprintf(fid, '% Grain 12
');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,50\n');
fprintf(fid, 'FITEM,2,147\n');
fprintf(fid, 'FITEM,2,104\n');
fprintf(fid, 'AL,P51x\n');

fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,49\n');
fprintf(fid, 'FITEM,2,147\n');
fprintf(fid, 'FITEM,2,103\n');
fprintf(fid, 'AL,P51x\n');

fprintf(fid, '% Grain 13
');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,51\n');
fprintf(fid, 'FITEM,2,142\n');
fprintf(fid, 'FITEM,2,105\n');
fprintf(fid, 'AL,P51x\n');

fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,52\n');
fprintf(fid, 'FITEM,2,146\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FITEM,2,110\n');
fprintf(fid, 'AL,P51x\n');

% Grain 14
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,53\n');
fprintf(fid, 'FITEM,2,114\n');
fprintf(fid, 'FITEM,2,107\n');
fprintf(fid, 'FITEM,2,135\n');
fprintf(fid, 'AL,P51x\n');
fprintf(fid, 'FLST,2,4,4\n');
fprintf(fid, 'FITEM,2,54\n');
fprintf(fid, 'FITEM,2,112\n');
fprintf(fid, 'FITEM,2,108\n');
fprintf(fid, 'FITEM,2,140\n');
fprintf(fid, 'AL,P51x\n');

% Make Volumes From Areas
% Grain 1
fprintf(fid, 'FLST,2,7,5,ORDE,5\n');
fprintf(fid, 'FITEM,2,1\n');
fprintf(fid, 'FITEM,2,15\n');
fprintf(fid, 'FITEM,2,35\n');
fprintf(fid, 'FITEM,2,39\n');
fprintf(fid, 'FITEM,2,-42\n');
fprintf(fid, 'VA,P51X\n');

% Grain 2
fprintf(fid, 'FLST,2,7,5,ORDE,5\n');
fprintf(fid, 'FITEM,2,2\n');
fprintf(fid, 'FITEM,2,16\n');
fprintf(fid, 'FITEM,2,36\n');
fprintf(fid, 'FITEM,2,43\n');
fprintf(fid, 'FITEM,2,-46\n');
fprintf(fid, 'VA,P51X\n');

% Grain 3
fprintf(fid, 'FLST,2,9,5,ORDE,6\n');
fprintf(fid, 'FITEM,2,3\n');
fprintf(fid, 'FITEM,2,17\n');
fprintf(fid, 'FITEM,2,39\n');
fprintf(fid, 'FITEM,2,43\n');
fprintf(fid, 'FITEM,2,47\n');
fprintf(fid, 'FITEM,2,-51\n');
fprintf(fid, 'VA,P51X\n');

% Grain 4
fprintf(fid, 'FLST,2,8,5,ORDE,5\n');
fprintf(fid, 'FITEM,2,4\n');
fprintf(fid, 'FITEM,2,18\n');
fprintf(fid, 'FITEM,2,49\n');
fprintf(fid, 'FITEM,2,52\n');
fprintf(fid, 'FITEM,2,-56\n');
fprintf(fid, 'VA,P51X\n');

% Grain 5
fprintf(fid, 'FLST,2,6,5,ORDE,5\n');
fprintf(fid, 'FITEM,2,5\n');
fprintf(fid, 'FITEM,2,19\n');
fprintf(fid, 'FITEM,2,41\n');
fprintf(fid, 'FITEM,2,57\n');
fprintf(fid, 'FITEM,2,-59\n');
fprintf(fid, 'VA,P51X\n');

%Grain 6
fprintf(fid, 'FLST,2,6,5,ORDE,5\n');
fprintf(fid, 'FITEM,2,6\n');
fprintf(fid, 'FITEM,2,20\n');
fprintf(fid, 'FITEM,2,45\n');
fprintf(fid, 'FITEM,2,60\n');
fprintf(fid, 'FITEM,2,-62\n');
fprintf(fid, 'VA,P51X\n');

%Grain 7
fprintf(fid, 'FLST,2,8,5,ORDE,7\n');
fprintf(fid, 'FITEM,2,7\n');
fprintf(fid, 'FITEM,2,21\n');
fprintf(fid, 'FITEM,2,57\n');
fprintf(fid, 'FITEM,2,40\n');
fprintf(fid, 'FITEM,2,51\n');
fprintf(fid, 'FITEM,2,63\n');
fprintf(fid, 'FITEM,2,-65\n');
fprintf(fid, 'VA,P51X\n');

%Grain 8
fprintf(fid, 'FLST,2,8,5,ORDE,7\n');
fprintf(fid, 'FITEM,2,8\n');
fprintf(fid, 'FITEM,2,22\n');
fprintf(fid, 'FITEM,2,47\n');
fprintf(fid, 'FITEM,2,44\n');
fprintf(fid, 'FITEM,2,60\n');
fprintf(fid, 'FITEM,2,66\n');
fprintf(fid, 'FITEM,2,-68\n');
fprintf(fid, 'VA,P51X\n');

%Grain 9
fprintf(fid, 'FLST,2,8,5,ORDE,7\n');
fprintf(fid, 'FITEM,2,9\n');
fprintf(fid, 'FITEM,2,23\n');
fprintf(fid, 'FITEM,2,63\n');
fprintf(fid, 'FITEM,2,50\n');
fprintf(fid, 'FITEM,2,56\n');
fprintf(fid, 'FITEM,2,69\n');
fprintf(fid, 'FITEM,2,-71\n');
fprintf(fid, 'VA,P51X\n');

%Grain 10
fprintf(fid, 'FLST,2,8,5,ORDE,7\n');
fprintf(fid, 'FITEM,2,10\n');
fprintf(fid, 'FITEM,2,24\n');
fprintf fid(f, 'FITEM,2,52\n');
fprintf(fid, 'FITEM,2,48\n');
fprintf(fid, 'FITEM,2,68\n');
fprintf(fid, 'FITEM,2,72\n');
fprintf(fid, 'FITEM,2,-74\n');
fprintf(fid, 'VA,P51X\n');

%Grain 11
fprintf(fid, 'FLST,2,6,5,ORDE,6\n');
fprintf(fid, 'FITEM,2,11\n');
fprintf(fid, 'FITEM,2,25\n');
fprintf(fid, 'FITEM,2,69\n');
fprintf(fid, 'FITEM,2,55\n');
fprintf(fid, 'FITEM,2,75\n');
fprintf(fid, 'FITEM,2,76\n');
fprintf(fid, 'VA,P51X\n');

% Grain 12
fprintf(fid, 'FLST,2,6,5,ORDE,6\n');
fprintf(fid, 'FITEM,2,12\n');
fprintf(fid, 'FITEM,2,26\n');
fprintf(fid, 'FITEM,2,53\n');
fprintf(fid, 'FITEM,2,74\n');
fprintf(fid, 'FITEM,2,78\n');
fprintf(fid, 'FITEM,2,77\n');
fprintf(fid, 'VA,P51X\n');

% Grain 13
fprintf(fid, 'FLST,2,11,5,ORDE,11\n');
fprintf(fid, 'FITEM,2,13\n');
fprintf(fid, 'FITEM,2,27\n');
fprintf(fid, 'FITEM,2,29\n');
fprintf(fid, 'FITEM,2,80\n');
fprintf(fid, 'FITEM,2,78\n');
fprintf(fid, 'FITEM,2,73\n');
fprintf(fid, 'FITEM,2,67\n');
fprintf(fid, 'FITEM,2,66\n');
fprintf(fid, 'FITEM,2,61\n');
fprintf(fid, 'FITEM,2,79\n');
fprintf(fid, 'VA,P51X\n');

% Grain 14
fprintf(fid, 'FLST,2,12,5,ORDE,12\n');
fprintf(fid, 'FITEM,2,14\n');
fprintf(fid, 'FITEM,2,28\n');
fprintf(fid, 'FITEM,2,32\n');
fprintf(fid, 'FITEM,2,33\n');
fprintf(fid, 'FITEM,2,81\n');
fprintf(fid, 'FITEM,2,58\n');
fprintf(fid, 'FITEM,2,65\n');
fprintf(fid, 'FITEM,2,64\n');
fprintf(fid, 'FITEM,2,71\n');
fprintf(fid, 'FITEM,2,70\n');
fprintf(fid, 'FITEM,2,76\n');
fprintf(fid, 'FITEM,2,82\n');
fprintf(fid, 'VA,P51X\n');

% Set Model Constraints 1
fprintf(fid, 'ET,1,SOLID185\n');

% Set Model Constraints 2
fprintf(fid, 'ET,2,SOLID185\n');

% Enter Anisotropic Elastic Constants in Stiffness Form for [1, -1, 0] pointing at 0 degrees: (-90 degrees offset)
fprintf(fid, 'TB,ANEL,1,1,21,0,\n');
fprintf(fid, 'TBTEMP,0\n');
fprintf(fid, 'TBDATA,1,0.384725,0.231726,0.231726,0,0,0\n');
fprintf(fid, 'TBDATA,7,0.375226,0.241224,0,0,0.0134331,0.375226\n');
fprintf(fid, 'TBDATA,13,0,0,0.0134331,0.0670008,0.0134331,0\n');
fprintf(fid, 'TBDATA,19,0.0575021,0,0.0575021,,\n!*\n');

% Enter Anisotropic Elastic Constants in Stiffness Form for [1, -1, 0] pointing at 30 degrees: (-60 degrees offset)
fprintf(fid, 'TB,ANEL,1,1,21,0,\n');
fprintf(fid, 'TBTEMP,0\n');
fprintf(fid, 'TBDATA,1,0.384725,0.231726,0.231726,0,0,0\n');
% fprintf(fid, 'TBDATA,7,0.375226,0.241224,0,0.0134331,0,0.375226\n');
% fprintf(fid, 'TBDATA,13,0,-0.0134331,0,0.0670008,0,0.0134331\n');
% fprintf(fid, 'TBDATA,19,0.0575021,0,0.0575021,,\n!*
');

% Enter Anisotropic Elastic Constants in Stiffness Form for [1,-1,0]
% pointing at 60 degrees: (-30 degrees offset)
% fprintf(fid, 'TB,ANEL,1,1,21,0,\n');
% fprintf(fid, 'TBTEMP,0\n');
% fprintf(fid, 'TBDATA,1,0.384725,0.231726,0.231726,0,0,0\n');
% fprintf(fid, 'TBDATA,7,0.375226,0.241224,0,-0.0134331,0.0134331,0.375226\n');
% fprintf(fid, 'TBDATA,13,0,0,0.0134331,0.0670008,0.0134331,0\n');
% fprintf(fid, 'TBDATA,19,0.0575021,0,0.0575021,,\n!*
');
% Enter Anisotropic Elastic Constants in Stiffness Form for [1,-1,0]
% pointing at 102 degrees: (12 degrees offset)
% fprintf(fid, 'TB,ANEL,1,1,21,0,\n');
% fprintf(fid, 'TBTEMP,0\n');
% fprintf(fid, 'TBDATA,1,0.384725,0.231726,0.231726,0,0,0\n');
% fprintf(fid, 'TBDATA,7,0.375226,0.241224,0,-0.0134331,0.00789578,0.375226\n');
% fprintf(fid, 'TBDATA,13,0,0.0108676,-0.00789578,0.0670008,-0.00789578,-0.0108676\n');
% fprintf(fid, 'TBDATA,19,0.0575021,0,0.0575021,,\n!*
');
% Enter Anisotropic Elastic Constants in Stiffness Form for [1,-1,0]
% pointing at 132 degrees: (42 degrees offset)
% fprintf(fid, 'TB,ANEL,1,1,21,0,\n');
% fprintf(fid, 'TBTEMP,0\n');
% fprintf(fid, 'TBDATA,1,0.384725,0.231726,0.231726,0,0,0\n');
% fprintf(fid, 'TBDATA,7,0.375226,0.241224,0,-0.00789578,0.0108676,0.375226\n');
% fprintf(fid, 'TBDATA,13,0,-0.00789578,-0.0108676,0.0670008,-0.00789578,-0.0108676\n');
% fprintf(fid, 'TBDATA,19,0.0575021,0,0.0575021,,\n!*
');

fprintf(fid, 'VSEL,S,VOLU,,1,14,1,0 \n');
fprintf(fid, 'VATT,1,,, \n');
%fprintf(fid, 'VSEL,S,VOLU,,4,14,1,0 \n');
%fprintf(fid, 'VATT,2,,, \n');
fprintf(fid, 'VSEL,ALL \n');

% Mesh it!

% Set Mesh Model
fprintf(fid, 'ET,3,MESH200\n');
fprintf(fid, 'KEYOPT,3,1,6\n');
fprintf(fid, 'KEYOPT,3,2,0\n');
fprintf(fid, 'TYPE, 3\n');
fprintf(fid, 'MAT, 1\n');
fprintf(fid, 'REAL, 0\n');
fprintf(fid, 'ESYS, 0\n');
fprintf(fid, 'SECNUM, \n !* \n');

fprintf(fid, 'FLST,2,12,5,ORDE,2\n');
fprintf(fid, 'FITEM,2,15 \n');
fprintf(fid, 'FITEM,2,-26 \n');
fprintf(fid, 'AESIZE,P51X,2,\n');
fprintf(fid, 'FLST,2,2,5,ORDE,2\n');
fprintf(fid, 'FITEM,2,27 \n');
fprintf(fid, 'FITEM,2,28 \n');
fprintf(fid, 'AESIZE,P51X,8,\n');
fprintf(fid, strcat('KSCON, 47,', num2str(MESHTIP), ', 0, 12, , \n'));
fprintf(fid, 'MSHAPE,0,2D \n');
fprintf(fid, 'MSHKEY,0 \n !* \n');
% Set Forces & Displacements
% Restrict X, Y and Z motion of bottom
fprintf(fid, '/SOL\n');
fprintf(fid, 'FLST,2,1,5,ORDE,1\n');
fprintf(fid, 'FITEM,2,29 \n');
fprintf(fid, '/GO\n');
fprintf(fid, 'DA,P51X,ALL,0\n');
% Apply unit force (pressure) to top
fprintf(fid, 'FLST,2,2,5,ORDE,2\n');
fprintf(fid, 'FITEM,2,32 \n');
fprintf(fid, 'FITEM,2,-33 \n');
fprintf(fid, '/GO \n');
fprintf(fid, strcat('SFA,P51X,1,PRES,', num2str(SA), ' \n'));
fprintf(fid, '/STATUS,SOLU\n');

% Restrict X motion of top
fprintf(fid, 'FLST,2,2,5,ORDE,2\n');
fprintf(fid, 'FITEM,2,32 \n');
fprintf(fid, 'FITEM,2,-33 \n');
fprintf(fid, '/GO\n');
fprintf(fid, 'DA,P51X,UX,0\n');
fprintf(fid, '/STATUS,SOLU\n');

% Solve
fprintf(fid, 'SOLVE\n');

% Postprocessor
fprintf(fid, '/POST1\n');

% % Top Surface - Planar Slip
% fprintf(fid, 'PATH,SLIP1,2,30,500,\n');
% fprintf(fid, 'PPATH,1,0,30,500,5,0,\n');
% fprintf(fid, 'PPATH,2,0,100,500,5,0,\n');
% fprintf(fid, 'AVPRIN,0, ,\n');
% fprintf(fid, 'PDEF,SLIP1XY,S,XY,AVG\n');
% fprintf(fid, '/PBC,PATH, ,1\n');
% fprintf(fid, 'PLPAGM, SLIP1XY, 200, 'NODE' \n');
% fprintf(fid, 'PATH,SLIP1 \n');
% fprintf(fid, 'PRPATH,SLIP1XY \n');
% % Midline
% fprintf(fid, 'PATH,SLIP2,2,30,500,\n');
% fprintf(fid, 'PPATH,1,0,30,500,5,0,\n');
% fprintf(fid, 'PPATH,2,0,100,500,5,0,\n');
% fprintf(fid, 'AVPRIN,0, ,\n');
% fprintf(fid, 'PDEF,SLIP2XY,S,XY,AVG\n');
% fprintf(fid, '/PBC,PATH, ,1\n');
% fprintf(fid, 'PLPAGM, SLIP2XY, 200, 'NODE' \n');
% fprintf(fid, 'PATH,SLIP2 \n');
% fprintf(fid, 'PRPATH,SLIP2XY \n');
% % Bottom Surface
% fprintf(fid, 'PATH,SLIP3,2,30,500,\n');
% fprintf(fid, 'PPATH,1,0,30,500,5,0,\n');
% fprintf(fid, 'PPATH,2,0,100,500,5,0,\n');
% fprintf(fid, 'AVPRIN,0, ,\n');
% fprintf(fid, 'PDEF,SLIP3XY,S,XY,AVG\n');
% fprintf(fid, '/PBC,PATH, ,1\n');
% fprintf(fid, 'PLPAGM, SLIP3XY, 200, 'NODE' \n');
% fprintf(fid, 'PATH,SLIP3 \n');
% fprintf(fid, 'PRPATH,SLIP3XY \n');
% % Top Surface - Planar Slip @ 30 Deg
% fprintf(fid, 'PATH,SLIP1,2,30,577,\n');
% fprintf(fid, 'PPATH,1,0,30,500,10,0,\n');
% fprintf(fid, 'PPATH,2,0,100,500,10,0,\n');
% fprintf(fid, 'AVPRIN,0, ,\n');
% fprintf(fid, 'PDEF,SLIP1XY,S,XY,AVG\n');
% fprintf(fid, '/PBC,PATH, ,1\n');
% fprintf(fid, 'PLPAGM, SLIP1XY, 200, ''NODE'\n');
% fprintf(fid, 'PATH,SLIP1 \n');
% fprintf(fid, 'PRPATH,SLIP1XY \n');
%
% % Through Thickness Slip @ 0 Deg
% fprintf(fid, 'PATH,SLIP2,2,30,76,\n');
% fprintf(fid, 'PPATH,1,0,30,500,10,0,\n');
% fprintf(fid, 'PPATH,2,0,33.54,500,0,0,\n');
% fprintf(fid, 'AVPRIN,0, ,\n'!*
');
% fprintf(fid, 'PDEF,SLIP2XZ,S,XZ,AVG\n');
% fprintf(fid, '/PBC,PATH, ,1\n'!*
');
% fprintf(fid, 'PLPAGM, SLIP2XZ, 200, ''NODE'' \n');
% fprintf(fid, 'PATH,SLIP2 \n');
% fprintf(fid, 'PRPATH,SLIP2XZ \n');
%
% % Top Surface - Planar Slip @ 60 Deg
% fprintf(fid, 'PATH,SLIP1,2,30,1334,\n');
% fprintf(fid, 'PPATH,1,0,30,500,10,0,\n');
% fprintf(fid, 'PPATH,2,0,100,673.14,10,0,\n');
% fprintf(fid, 'AVPRIN,0, ,\n'!*
');
% fprintf(fid, 'PDEF,SLIP1XY,S,XY,AVG\n');
% fprintf(fid, '/PBC,PATH, ,1\n'!*
');
% fprintf(fid, 'PLPAGM, SLIP1XY, 200, ''NODE'' \n');
% fprintf(fid, 'PATH,SLIP1 \n');
% fprintf(fid, 'PRPATH,SLIP1XY \n');
%
% % Through Thickness Slip @ 30 Deg
% fprintf(fid, 'PATH,SLIP2,2,30,76,\n');
% fprintf(fid, 'PPATH,1,0,30,500,10,0,\n');
% fprintf(fid, 'PPATH,2,0,33.066,501.77,0,0,\n');
% fprintf(fid, 'AVPRIN,0, ,\n'!*
');
% fprintf(fid, 'PDEF,SLIP2XZ,S,XZ,AVG\n');
% fprintf(fid, '/PBC,PATH, ,1\n'!*
');
% fprintf(fid, 'PLPAGM, SLIP2XZ, 200, ''NODE'' \n');
% fprintf(fid, 'PATH,SLIP2 \n');
% fprintf(fid, 'PRPATH,SLIP2XZ \n');
%
% % Top Surface - Planar Slip @ 102 Deg
% fprintf(fid, 'PATH,SLIP1,2,30,1030,\n');
% fprintf(fid, 'PPATH,1,0,30,500,10,0,\n');
% fprintf(fid, 'PPATH,2,0,0.641.14,10,0,\n');
% fprintf(fid, 'AVPRIN,0, ,\n'!*
');
% fprintf(fid, 'PDEF,SLIP1XY,S,XY,AVG\n');
% fprintf(fid, '/PBC,PATH, ,1\n'!*
');
% fprintf(fid, 'PLPAGM, SLIP1XY, 200, ''NODE'' \n');
% fprintf(fid, 'PATH,SLIP1 \n');
% fprintf(fid, 'PRPATH,SLIP1XY \n');
%
% % Through Thickness Slip @ 72 Deg
% fprintf(fid, 'PATH,SLIP2,2,30,76,\n');
% fprintf(fid, 'PPATH,1,0,30,500,10,0,\n');
% fprintf(fid, 'PPATH,2,0,31.094,503.367,0,0,\n');
% fprintf(fid, 'AVPRIN,0, ,\n'!*
');
% fprintf(fid, 'PDEF,SLIP2XZ,S,XZ,AVG\n');
% fprintf(fid, '/PBC,PATH, ,1\n'!*
');
% fprintf(fid, 'PLPAGM, SLIP2XZ, 200, ''NODE'' \n');
% fprintf(fid, 'PATH,SLIP2 \n');
% fprintf(fid, 'PRPATH,SLIP2XZ \n');
%
% % Top Surface - Planar Slip @ 142 Deg
% fprintf(fid, 'PATH,SLIP1,2,30,320,\n');
% fprintf(fid, 'PPATH,1,0,30,500,10,0,\n');
% fprintf(fid, 'PPATH,2,0,0,533.32,10,0,\n');

% fprintf(fid, 'AVPRIN,0, ,\n ');% fprintf(fid, 'PDEF,SLIP1XY,S,XY,AVG\n');% fprintf(fid, '/PBC,PATH, ,1\n ');% fprintf(fid, 'PLPAGM, SLIP1XY, 200, 'NODE' \n');% fprintf(fid, 'PATH,SLIP1 \n');% fprintf(fid, 'PRPATH,SLIP1XY \n');% % % Through Thickness Slip @ 102 Deg% fprintf(fid, 'PATH,SLIP2,2,30,76,\n');% fprintf(fid, 'PPATH,1,0,30,500,10,0,\n');% fprintf(fid, 'PPATH,2,0,29.264,503.54,0,0,\n');% fprintf(fid, 'AVPRIN,0, ,\n ');% fprintf(fid, 'PDEF,SLIP2XZ,S,XZ,AVG\n');% fprintf(fid, '/PBC,PATH, ,1\n ');% fprintf(fid, 'PLPAGM, SLIP2XZ, 200, 'NODE' \n');% fprintf(fid, 'PATH,SLIP2 \n');% fprintf(fid, 'PRPATH,SLIP2XZ \n');% fprintf(fid, 'FINISH \n');% Hooray - Done.
fclose('all');
Appendix B

Mathematica Script for Elastic Constant Reorientation

RotationOnSecondOrderStiffness_mps_ab_v6
2011.01.13
v 6

Created by Melissa Stegman, edited by Amber Romanco

Program takes original ([100],[010],[001])] orthogonal axes and rotates to a new set of orthogonal axes (which must be known and input as new1, new2, & new3). The rotation matrix, αij is developed from the direction cosines (cos(ij)). It is then rotated within a plane by specifying which plane to rotate in and the angle to be rotated by.

1. The rotation matrix αij is fed into the α matrix that allows for rotation of the stiffness matrix via matrix math & without expansion to its full 81 term form. αij terms are then rotated via the α matrix. This is the first rotation, and the first new basis. (The principal crystallographic axes are the original basis - (1,0,0), (0,1,0), (0,0,1))

   → α_{ii} = \alpha_{i1} = \alpha_{i1} + (1 - \delta_{i1}) \alpha_{i1} \alpha_{i1}
   \rightarrow α_{i1} = \alpha_{ij} = \alpha_{ij} + (1 - \delta_{ij}) \alpha_{ij} \alpha_{ij}
   \rightarrow (\alpha) = (a) \cdot \text{Transpose}(\alpha)

In the program, it is listed as

\[ a_{ij} = a_{ij} \cdot \text{Transpose}(a) \]

2. An in-plane rotation is then done to the first NEW basis. This rotation is defined by the angle \( \theta \), and the axis is defined as the new x axis = rotationAxis=1 (New1→[1,0,0]), the new y axis = rotationAxis=2 (New2→[0,1,0]), or the new z axis = rotationAxis=3 (New3→[0,0,1]). A new α matrix is then developed using the method above. This α matrix is then multiplied by the stiffness matrix for the first new basis.

   → (\alpha) = (\alpha) \cdot \text{Transpose}(\alpha)

In the program, it is listed as

\[ a_{ij} = a_{ij} \cdot \text{Transpose}(a) \]

Note: If crystal symmetry states that two basis should be the same, then they should have the same stiffness matrix.

Miscellaneous notes:

\[ (\alpha) = \text{Transpose}(\alpha)^{-1} \cdot \alpha \cdot (\alpha)^{-1} \]

\[ \alpha_{ij} = \alpha_{ij} \cdot \text{Transpose}(\alpha)^{-1} \]

\[ (\alpha) = \text{Transpose}(\alpha) \cdot \alpha \cdot \text{Transpose}(\alpha) \]

\[ \alpha_{ij} = \alpha_{ij} \cdot \text{Transpose}(\alpha) \]

\[ (\alpha) = \alpha \cdot \text{Transpose}(\alpha)^{-1} \cdot \alpha \]

\[ \alpha_{ij} = \alpha_{ij} \cdot \alpha \cdot \text{Transpose}(\alpha)^{-1} \]

\[ (\alpha) = \alpha^{-1} \cdot \alpha \cdot \text{Transpose}(\alpha)^{-1} \]

New in v6 → v6 is the first working version of the program. All other versions were beta tests. No new changes.
Inputting parameters in program -- all input parameters are in this cell.

```plaintext
ćeOriginal -100, axes - no need to change.

ćeOriginal = (1 0 0.0
0 1 0
0 0 1);

ćeDefine the new basis you want to determine the constitutive behavior in,
New1 is new [100] axis, New2 is new [010] axis, and New3 is new [001] axis.
New1 = Normalize[{1, 1, 1}];
New2 = Normalize[{1, -1, 0}];
New3 = Normalize[Cross[New1, New2]]; (*New3 = Normalize[{1, 1, 1}];*)
New = {New1, New2, New3};
ćeDefine the plane to rotate within after the new basis is found/axis to rotate around:
1 is yz plane, about the New1 vector; 2 is the zx plane, about the New2 vector;
3 is the xy plane, about the New3 vector.*
rotationAxis = 1;
ćeDefine the angle to rotate within the new basis, from the z axis for 1,
axis for 2 and y axis for 3 - input in degrees, converts to radians!!!
ćeθ = 60 Degree;

MatrixForm[New]

Performing first rotation of original stiffness matrix to first new basis

ćeCreating aij matrix from cosθi, where
coesθi = xi . xi', where xi is from original orthonormal matrix and xi' is from new
orthonormal matrix -- ie. cosθi = [100].new1, cosθ2 = [010].new3
aij = Table[ćeOriginal [[ i ]]. New[[ i ]], { i, 1, 3}, { j, 1, 3}];
MatrixForm[aij]

ćeFloating rotation to check proper rotation obtained; magenta point is origin [0,0,0],
green is [111] in respective axis system.
ćegr = {Cuboid[], AbsolutePointSize[10], Opacity[1], {Black, Point[{0, 0, 0}]}.
{Red, Point[{1, 0, 0}]}-{Blue, Point[{0, 1, 0}]}-{Green, Point[{0, 0, 1}]};
Graphics3D[{Opacity[.35], Blue, gr}, GeometricTransformation[{Opacity[.85], Red, gr, aij}],
Boxed -> False]

ćeCreating a matrix to do matrix manipulation to rotate -- does not require expansion
of aij to aijkl
ćeLarge = Table[ćeaij[[ i, k] aij[[ j, l]] = (1 - KroneckerDelta[k, l]) aij[[ i, j]] aij[[ k, l]], { i, 1, 3},
{ j, 1, 3}, { k, 1, 3}, { l, 1, 3}];
ćeα =
(0 0 0 0 0
0 0 0 0 0
0 0 0 0 0
0 0 0 0 0
0 0 0 0 0
0 0 0 0 0
0 0 0 0 0
0 0 0 0 0
0 0 0 0 0)
```
For [i = 1, i ≤ 3, i++, For [j = 1, j ≤ 3, j++, For [k = 1, k ≤ 3, k++, For [l = 1, l ≤ 3, l++,
    If [i = j, m = 1,
        If [k = 2 & j] = 3, m = 1,
        If [k = 1 & j] = 3, m = 4,
        If [k = 1 & j - 2, m = 6,
            If [k = 1 & j = 1, n = 5,
                If [k = 2 & j = 1, m = 6]]]]]]];
If [k = 1, n = k,
    If [k = 2 & k = 3, n = 4,
        If [k = 1 & k = 3, n = 5,
            If [k = 1 & k = 2, n = 6,
                If [k = 1 & k = 1, n = 4,
                    If [k = 2 & k = 1, n = 6]]]]]]];
MatrixForm[a]

(* Creating a^-1 matrix to do matrix manipulation to rotate -- does not require expansion
  of cij to cijkl *)

inv = Table[a[i, j], {i, 1, 3}, {j, 1, 3}];

inv = Table[1, {i, 1, 3}, {j, 1, 3}];

MatrixForm[inv]

For [i = 1, i ≤ 3, i++, For [j = 1, j ≤ 3, j++, For [k = 1, k ≤ 3, k++, For [l = 1, l ≤ 3, l++,
    If [i = j, m = 1,
        If [k = 2 & j] = 3, m = 1,
        If [k = 1 & j] = 3, m = 4,
        If [k = 1 & j - 2, m = 6,
            If [k = 1 & j = 1, n = 5,
                If [k = 2 & j = 1, m = 6]]]]]]];
If [k = 1, n = k,
    If [k = 2 & k = 3, n = 4,
        If [k = 1 & k = 3, n = 5,
            If [k = 1 & k = 2, n = 6,
                If [k = 1 & k = 1, n = 4,
                    If [k = 2 & k = 1, n = 6]]]]]]];
MatrixForm[inv]
(Definition of second order elastic constants (cij))

\[
\begin{pmatrix}
346.73 \times 10^{-3} & 250.723 \times 10^{-3} & 250.723 \times 10^{-3} & 0 & 0 & 0 \\
250.723 \times 10^{-3} & 346.73 \times 10^{-3} & 346.73 \times 10^{-3} & 0 & 0 & 0 \\
250.723 \times 10^{-3} & 250.723 \times 10^{-3} & 346.73 \times 10^{-3} & 0 & 0 & 0 \\
0 & 0 & 0 & 76.4994 \times 10^{-3} & 0 & 0 \\
0 & 0 & 0 & 0 & 76.4994 \times 10^{-3} & 0 \\
0 & 0 & 0 & 0 & 0 & 76.4994 \times 10^{-3}
\end{pmatrix}
\]

(Transforming cij to cijP using a matrix *)

\[
\text{cijP} = \text{a.cij}.\text{Transpose}[\text{a}];
\]

For[i = 1, i <= 6, i++], For[j = 1, j <= 6, j++],

If[Abs[cijP[i,j]] < 1 \times \text{10}^{-20}, cijP[i,j] = 0]]]; (*eliminating rounding errors*)

MatrixForm[cijP]

This part of the program takes the new basis (New), and rotates it around one of the new vectors (New1 = (1,0,0), New2 = (0,1,0), New3 = (0,0,1)). This is so misorientations of \( \theta \) within a plane can be examined in ANSYS by giving a separate set of stiffness matrices.

(Rotation about the axis in the new basis*)

(Defining 2nd rotation matrix)

If[rotationAxis == 1,

\[
cij2 = \begin{pmatrix}
1 & 0 & 0 \\
0 & \cos[\theta] & -\sin[\theta] \\
0 & \sin[\theta] & \cos[\theta]
\end{pmatrix},
\]

If[rotationAxis == 2, cij2 = \begin{pmatrix}
\cos[\theta] & 0 & -\sin[\theta] \\
0 & 1 & 0 \\
\sin[\theta] & 0 & \cos[\theta]
\end{pmatrix}]

If[rotationAxis == 3, cij2 = \begin{pmatrix}
\cos[\theta] & -\sin[\theta] & 0 \\
\sin[\theta] & \cos[\theta] & 0 \\
0 & 0 & 1
\end{pmatrix}]]];

MatrixForm[cij2]

(Plotting 2nd rotation to check proper rotation obtained; magenta point is origin \( [0,0,0] \),
green is \( [111] \) in respective axis system*)

gv = \{Cuboid[], \text{AbsolutePointSize}[10], \text{Opacity}[1], \text{Black}, \text{Point}[[0,0,0]]\},

\{Red, \text{Point}[[1,0,0]], \text{Blue}, \text{Point}[[0,1,0]], \text{Green}, \text{Point}[[0,0,1]]\};

Graphics3D[{{\text{Opacity}[.35], \text{Blue}, gv}, \text{GeometricTransformation}[\text{Opacity}[.05], \text{Red}, gv], cij2]],

Boxed \rightarrow \text{False}

(Creating 2nd \( a \) matrix to do matrix manipulation to rotate 2nd time -- does not require expansion of ci to cijk*)

\[
a2 = \text{Table}[cij2[[i, j]] + (1 - \text{KroneckerDelta}[k, l]) cij2[[i, k]], \{i, 1, 3\}, \{j, 1, 3\}, \{k, 1, 3\}, \{l, 1, 3\}];
\]

\[
a2 = \begin{pmatrix}
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix}
\]
For[1 = 1, 1 \leq 3, 1++], For[j = 1, j \leq 3, j++], For[k = 1, k \leq 3, k++], For[l = 1, l \leq 3, l++]

If[i == j, m = i, 
If[i == 2 \&\& j == 3, m = 4, 
If[l == 1 \&\& j == 3, m = 5, 
If[l == 1 \&\& j == 2, m = 6, 
If[j == 3 \&\& j == 2, m = 4, 
If[l == 1 \&\& j == 1, m = 5, 
If[l == 2 \&\& j == 1, m = 6]])]]]]];

If[k == 1, n = k, 
If[k == 2 \&\& l == 3, n = 4, 
If[k == 1 \&\& l == 3, n = 5, 
If[k == 1 \&\& l == 2, n = 6, 
If[k == 3 \&\& l == 2, n = 4, 
If[k == 3 \&\& l == 1, n = 5, 
If[k == 2 \&\& l == 1, n = 6]])]]]]];

a2[[m, n]] = aLarge2[[i, j, k, l]]];

MatrixForm[a2]

(*Creating 2nd α⁻¹ matrix to do matrix manipulation to rotate 2nd time -- does not require expansion of cij to cijkl*)

aInverseLarge2 =

aLarge2 = Table[a[i, j], {i, 1, 3}, {j, 1, 3}];

aInverse2 = Table[0, {i, 1, 3}, {j, 1, 3}];

For[1 = 1, 1 \leq 3, 1++], For[j = 1, j \leq 3, j++], For[k = 1, k \leq 3, k++], For[l = 1, l \leq 3, l++]

If[i == j, m = i, 
If[i == 2 \&\& j == 3, m = 4, 
If[i == 1 \&\& j == 3, m = 5, 
If[i == 1 \&\& j == 2, m = 6, 
If[i == 3 \&\& j == 2, m = 4, 
If[i == 3 \&\& j == 1, m = 5, 
If[i == 2 \&\& j == 1, m = 6]])]]]]];

If[l == 1, n = l, 
If[l == 2 \&\& l == 3, n = 4, 
If[l == 1 \&\& l == 3, n = 5, 
If[l == 1 \&\& l == 2, n = 6, 
If[l == 3 \&\& l == 2, n = 4, 
If[l == 3 \&\& l == 1, n = 5, 
If[l == 2 \&\& l == 1, n = 6]])]]]]];

aInverse2[[m, n]] = aInverseLarge2[[i, j, k, l]]];

MatrixForm[aInverse2]
(Transforming \( \mathbf{cijP} \) to \( \mathbf{cijP2} \) using \( 2^\pi \) a matrix,
where \( \mathbf{cijP2} \) is the second new stiffness matrix for a basis that is \( \theta \) degrees away
from a given axis *)

\[
\mathbf{cijP2} = \mathbf{a2.cijP.Transpose[a2]};
\]

For \[i = 1, \ i < 6, \ i++, \ \text{For} \[j = 1, \ j < 6, \ j++,
\]

\[
\text{If}[\text{Abs}[\mathbf{cijP2}[i, j]] < 1 \times 10^{-30}, \ \mathbf{cijP2}[i, j] = 0]]]]\] (*eliminating rounding errors*)

\[
\text{MatrixForm}[\mathbf{cijP2}] \] (*second rotated stiffness matrix -
\( \theta \) degrees from a given axis in \( \{\text{New1, New2, New3}\} \)*
Roi Arie Meirom was born in Haifa, Israel on April 7th, 1983, the son of Ronit Ana Blum and Doron Meirom. After immigrating to the United States in 1996, he attended Tenafly High School, from which he graduated in 2001. From 2001-2005, he attended The Johns Hopkins University where he earned his Bachelors of Science in Biomedical Engineering, with concentrations in computer engineering and materials science. After graduation, he arrived at the Pennsylvania State University where his research, under the advisory of Dr. Christopher Muhlstein, focused on the mechanical properties of nanograined materials. He earned his Masters of Science in 2008, and his Doctorate of Philosophy in 2011. When not occupied with school, Roi indulges in microhobbies and hopes his upcoming move to Portland, OR will allow him to explore new avenues.