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Computational Modelling of the Mechanical Behavior of Nanocrystalline Metals Based on the Deformation Mechanisms and Their Transitions

A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy in Structural Engineering by

Baozhi Zhu

Committee in charge:

Professor Petr Krysl, Chair
Professor Robert J. Asaro, Co-chair
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Professor David Benson
Professor Michael Holst

2006
The dissertation of Baozhi Zhu is approved, and it is acceptable in quality and form for publication on microfilm:

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University of California, San Diego

2006
To my dear parents

Yuchun Zhu, Xiuyan Chen
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ABSTRACT OF THE DISSERTATION

Computational Modelling of the Mechanical Behavior of Nanocrystalline Metals Based on the Deformation Mechanisms and Their Transitions

by

Baozhi Zhu

Doctor of Philosophy in Structural Engineering

University of California San Diego, 2006

Professor Petr Krysl, Chair

Professor Robert J. Asaro, Co-Chair

There has been a growing research interest in understanding the mechanical behaviors and the deformation mechanisms of nanocrystalline metals and alloys in the past a few decades, due to their extraordinary mechanical prosperities, such as high strength, hardness, and wear resistance, which have great potentials in engineering applications.

As grain sizes in crystalline metals and alloys transit down to the lower end of the nanometer range, the plastic deformations are no longer dominated by the intragrain dislocation activities. Instead deformations assisted by grain boundary start to play a more important role in deciding the mechanical response of the bulk materials, as the interfacial volume fraction increases with the reduction of grain sizes. A polycrystalline constitutive theory is developed in the form of the extend aggregate Taylor model of Asaro and Needleman for the nanocrystalline metals. The plastic deformation description is based on the Asaro, Krysl and Kad (AKK) model, which considers deformation mechanisms such as the emission of perfect, partial dislocations and deformation twins from grain boundary and grain boundary sliding when the grain size is sufficiently small.
in the nanometer regime (less than 100nm), and their transitions are governed by the factors such as grain size, stacking fault energy, temperature, and strain rate, etc. Therefore the effect of grain size distributions in addition to the mean grain size is considered important on the mechanical response in this constitutive theory. The grain size distributions can be simulated with the experimentally determined lognormal distributions for the electro-deposited nanocrystalline metals for example.

Numerical simulations are carried out for nanocrystalline Ni, Cu, Al and Pd, and the simulated phenomena include the mechanical response of these materials when subjected to uniaxial tension and compression under different deformation rates, texture development under high pressure torsion (HPT), and the grain growth effect during nanoindentation, etc, where the contribution of each deformation mechanism is carefully studied. The obtained numerical results are in reasonably good agreement with the experiments. Due to the fact that the deformation mechanisms in nanostructured materials are not yet fully understood, this constitutive theory will need to be further improved with the future findings of deformation mechanisms, which this theory has the flexibility to easily incorporate.
Chapter 1

Introduction

1.1 Overview

Nanocrystalline metals and alloys are a unique class of materials with grain sizes typically smaller than 100 nanometers, which is two to three orders of magnitude smaller than the coarse-grained metals. The reduction of grain sizes not only alters the microstructures, but also improve the properties of the materials significantly. Some examples of the appealing properties are high strength, hardness, wear resistance, electrical conductivity, corrosion resistance, thermal stability and improved magnetic performance, and these properties make them very desirable for many engineering applications. Since the early 1980’s when they were first synthesized by compaction of nanopowders produced by Inert Gas Condensation (IGC) and their extraordinary properties were suggested by Gleiter, [1], nanocrystalline metals and alloys has been attracting more and more research interest during the past a few decades, due to the scientific curiosity and their engineering potentials. Efforts have been paid to several aspects of this group of materials, for example synthesis procedures, microstructure optimization, experimental studies, computer simulations, deformation mechanisms characterization and the establishment of connections between the extraordinary properties and engineering applications, etc [2, 3]

Although challenged by the difficulties usually presented in the new research
topics, the study of nanocrystalline metals and alloys has been significantly advanced in the areas from processing procedures to technological applications with the aids of the synergy between experimental study and theoretical modelling. “A full understanding of the material is not yet available, and a few concerns and issues need to solved” To date nanocrystalline metals and alloys are commercially available in power, foil and bulk forms, and can be produced with several synthesis approaches. They have been successfully used in a wide range of applications such as medical implantations, coatings and automotive and aerospace industry, etc.

One of the interests to the research effort is to understand the deformation mechanisms behind the superior mechanical properties of nanocrystalline materials, such as extraordinarily high strength, hardness, wear-resistance, and inverse Hall-Petch relation between grain size and strength. As the grain size is reduced into the nanometer range, the plastic deformation mechanism of coarse grained metals, intragrain dislocation slip, is evidently shut off [4, 3]. The experimental studies and molecular dynamics simulations show the grain boundary assisted deformation mechanisms, grain boundary sliding, perfect/partial dislocation emission and deformation twinning from the grain boundary start to dominate the plastic deformation of nanocrystalline metals when the grain size is smaller than, say, 50 nm, which depends on the material parameters, such as stacking fault energy, and loading conditions, such as temperature and loading rates. Exploring the deformation of the nanocrystalline metals is the goal of this dissertation.

1.2 Objective and Outline

The main objectives of our research is to study the deformation mechanisms and the mechanical behavior of mainly nanocrystalline FCC metals and alloys. A constitutive model is proposed to predict the mechanical response of the NC FCC metals with 3d equi-axed grains whose size is smaller than 100 nm. The theoretical basis of this model is the Asaro-Krysal-Kad (AKK) model, which describes the most likely plastic deformation processes based on the recent experimental studies and the molecular dynamics
simulations, e.g., grain boundary emission of perfect dislocation and partial dislocation and grain boundary sliding, along with deformation twinning. The AKK model also discussed how these mechanisms set the limit of the material strength and as well as the transitions between these deformation mechanisms. Therefore this constitutive model accounts for the simultaneous contributions of these deformation mechanisms, as well as the transition between the relative dominance of each. Another model that this research is based on is the polycrystalline plasticity of extended Taylor model by Asaro and Needleman [5]. According to the recently recognized issues associated with the nanocrystalline metals and alloys, such as, grain size distribution, grain growth, are discussed. This research explores the effect of grain size distribution, material parameters, such as stacking fault energy, temperature, and strain rate on the overall mechanical behavior of the nanocrystalline metals and alloys. One of the specific concerns mentioned above is the effect of grain size distribution as well as the mean grain size on overall nanocrystalline aggregate response. Grain size distributions are simulated with log-normal distributions and incorporated into the AN aggregate model in the form of distributions of the volume fraction of grains with various sizes. The effect of grain growth during deformation is also quantitatively assessed via simulation of recently obtained data on indentation tests in which dynamic grain growth was documented through the measurement of changes in grain size distribution and concomitant changes in hardness. The simulations provide a plausible description of the observed phenomenology and further underscore the unstable nature of nanocrystalline grain size distributions. The possibility of incorporating additional potential deformation mechanisms such as Coble creep, as has been proposed in other models, is discussed and shown to be straightforward addition to the model. Recently obtained data on texture development is analyzed via texture predictions for aggregates subject to finite deformations via high pressure torsion (HPT). The phenomenology is assessed specifically with regard to the potential use of texture measurements for confirming the importance of crystallographic mechanisms vs. those such as grain boundary sliding.

This thesis is organized as the follows. Chapter 2 briefly reviews the most
commonly used processing methods of nanocrystalline metals in its first section, and the mechanical properties that have been observed in the experiments and molecular dynamics simulations are discussed next, finally the last section of Chapter 2 reviews the recent discoveries with regards to the deformation mechanisms of the nanocrystalline metals, and the details can be found in the reference given in the chapter. Chapter 3 reviews one of the two theoretical basis of our constitutive theory, Asaro-Krysl-Kad model [4], and the extended Taylor model of Asaro and Needleman [5] is included in the discussion of the constitutive model formulation in Chapter 4. The detailed calculation procedures are explained in Chapter 5. Chapter 6 represents the numerical simulations of a range of FCC nanocrystalline metals with different stacking fault energy and with different grain size distribution under different loading rates, loading condition, temperature etc. The simulation cases also explore the grain growth and texture evolution issue during deformation. The comparisons of the numerical simulation results with the experimental results are also provided. Conclusions follow in Chapter 7, and discuss the effect of grain size distribution, material parameters and loading parameters on the mechanical behavior of nanocrystalline FCC metals, and whether or how texture evolution can be used as a diagnostic tool to reveal the dominant deformation mechanisms under given conditions. At the very end of the dissertation, crystal plasticity and the component form are appended.
Chapter 2

Literature Review

2.1 Processing Methods

Fabrication is the foundation of the study of noncrystalline metals and alloys. It is the starting point of this research area, and it also has direct impact on the understanding of material properties and future engineering applications. Therefore it is one of the most decisive factors that effect the progress of the nanoscience and technology. Synthesis methods currently applied to produce noncrystalline metals and alloys are numerous, and currently several methods are available commercially to produce large-scale noncrystalline metals and alloys, while many others are still used for laboratory investigations. Most of the approaches can be grouped into the following two complimentary categories, “bottom-up” and “top down”. Each of those methods has its own advantages and disadvantages against the others, and synthesis approaches that are cost-affordable, reproducible and able to provide sizeable products are highly desirable.

2.1.1 “Bottom-up” Approaches

“Bottom-up” method can be defined as those that produce noncrystalline metals and alloys by the assembly of atoms or particles using chemical reaction in solid, liquid or gaseous state. Two types of procedures can be employed to fabricate bulk
nanostructured materials by “bottom-up” methods. The first type is to divide the fabrication processes into two steps, nanopowder synthesis and consolidation, and one typical example is gas condensation and consolidation, while the second type is to combine the nanopowder synthesis and consolidation into one single operation, for example electrodeposition and spray forming routes. There are several techniques that are widely used to generate nanometer-sized clusters (particles or powders). For example inert gas condensation used by Gleiter H. in 1981 [1] is the first technique used to produce noncrystalline particles, and other examples are sol-gel processing, chemical vapor deposition (CVD), aerosol method, mechanical attrition, etc. The processes of assembling nanopowders into bulk materials can be realized by consolidation.

**Inert Gas Condensation and Consolidation**

Inert gas condensation (IGC) and consolidation is one of the long-established fabrication method of bulk nanostructured materials. IGC was used to synthesize noncrystalline powders with grain sizes from a few nanometers to 50nm as early as in 1950s by Kimoto [6], and it is also one of the methods that produces nanopowders for commercial use. It was the group of Birringer and Gleiter [1] that developed the first system that combines IGC with subsequent consolidation to produce bulk nanostructured materials. Fig 2.1 illustrates the two steps involved in this process.

The source materials are first vaporized into pressurized ultra pure inert gas in a pre-vacuumed synthesis chamber, where the evaporated atoms condense in the form of crystallized nanoparticles after transferring their thermal energy to the inert gas. For example 99.9996% purity He at a low pressure of 2kPa was used to synthesize noncrystalline iron crystals of 6nm [7, 8], and 99.9999% purity He at a pressure of 600Pa was used to synthesize Cu and Pd nanopowders [6]. The synthesized particles will then be collected on a rotating liquid nitrogen cooled cylinder, i.e. the cold finger collector, and removed from the collector constantly by the scrapers. Higher pressure or the molecular weight of the inert gas will increase the nanoparticle sizes. Versatility is one of the advantages of IGC, wherein composite powders can be produced by feeding
Figure 2.1: Illustration of using inert gas condensation method and *in situ* consolidation to produce nanostructured materials [6].
two sources of materials simultaneously, or replacing inert gas with reactive gas, and particle sizes can be controlled by the evaporation rate and the condensation gas pressure. Large quantities of nanopowders can be synthesized by IGC. In the second step the collected particles are transferred to a attached compaction chamber, where they are consolidated into bulk materials under a high pressure of a few GPa at room temperature or elevated temperature for several minutes. Using the procedures described above, bulk nanostructured materials in the form of disks with diameter of a few micrometers and thickness of a few hundred microns can be obtained.

IGC and consolidation can produce noncrystalline metals and alloys of grain sizes within the range of a few nanometers. However it must overcome several challenges before successful commercialization. First, IGC is susceptible to the contamination caused by air, which leads to the presence of hydrogen and oxygen in the final products. The impurities not only impair the material properties, but also weaken the nanoparticle bonding in the consolidation process. Second, the process of consolidation of nanopowder has not been very successful at producing fully dense materials of large scale. The result densities are often lower than 99% of the theoretical density. Hence the bulk nanostructured materials produced by this approach usually have the processing defects such as high porosity and impurity, which reduce the ductility and also affect other properties. A improved system was designed by Sanders et. al. at Argonne National Laboratory [6]. The new system provides cleaner IGC process, more efficient nanopowder transfer and a consolidation unit that is able to conduct cold or warm compaction, which enhances diffusional bonding and therefore reduces the porosity. The nanostructured materials produced by the new system showed improved material properties, such as ductility, and microstructures. One issue associated with the new system is grain growth. Because of the unstable nature of nanostructured materials, the grain boundary surface area tends to shrink as a result of the overall free energy reduction. The impurity existing in the grain boundary provides obstacle to grain coarsening, so it is difficult for the nanomaterials with reduced impurity to maintain extremely fine grains. While the grain sizes of nanostructured materials with higher impurity can stay in the
range of 7-9nm, the grains can grow to 25-30nm within a few weeks for those with high purity after the synthesis. The advantages associated with this synthesis approach are the capabilities to produce nanostructured materials with very fine equi-axed grains that are texture-free.

**Electrodeposition**

Different from IGC and consolidation, electrodeposition is a synthesis technique that is able to produce bulk nanostructured materials in one single step, and doesn’t require precursor powders. Electrodeposition is one of the successful approaches to routine production of large scale noncrystalline metals and alloys with high purity and density in the forms of coating, ultrathin film, sheet, plate, wire and even more complex shapes. Therefore it has been applied commercially to produce nanostructured materials such as pure metals, binary, ternary alloys, as well as ceramics and ceramic nanocomposites, etc with grain sizes smaller than 100nm [9].

Electrochemical deposition of metals and alloys has been in practice since the beginning of the last century. The basic principle is to reduce metal ions from electrolytes by providing external power supply, i.e.,

\[
M^{z+}_{\text{solution}} + ze^{-} \rightarrow M_{\text{lattice}}
\]  

(2.1)

where M is the metal element and M\(^{z+}\) is its ions. Fig 2.2 schematically illustrate the electrodeposition cell. The crystallization is affected by the substrate microstructure and electrodeposition parameters, such as bath composition, pH value, operating temperature, bath additives and overpotential, which is defined as the difference between the potential of the electrode with external current running through and its equilibrium potential without external current. During the process, electrocrystallization occurs in the form of either the growth of the existing crystals or the nucleation of new ones. Hence the idea of synthesizing nanostructures is massive nucleation of new crystals and inhibition of grain growth. Grain growth is more favored at low overpotential and high surface
diffusion rates. Therefore electrocrystallization can result in nanostructured materials production by increasing the overpotential and adding grain refiners, which are able to reduce the surface diffusion rate. Examples of grain refiners are saccharin, coumarin, thiorea and HCOOH [9]. Early reports on producing ultrafine-structured materials by electrodeposition can be found in [11] by Brenner et al., 1963. For example, noncrystalline Ni with the grain sizes in the range from 10-40nm can be produced by using Watts-type baths containing nickel sulfate, nickel chloride and boric acid with properly chosen electrodeposition parameters [12], where saccharin is added as grain refiner and the overpotential is increased by supplying square-wave cathodic pulses.

The microstructures of electrodeposited noncrystalline metals and alloys may vary from batch to batch [13], but they share the characteristics of full density and narrow grain size distribution. For example the maximum grain size will not exceed 80nm for the materials with grain size of 20-30nm [13]. The deposits usually show preferred orientations. The final products may contain light impurities of sulfur, carbon
and hydrogen which is usually in the form of nanobubbles.

Compared to other synthesis techniques of bulk nanostructured materials, electrodeposition has several advantages, such as low cost and the ability to produce fully dense large scale products. Consequently electrodeposition has been winning more attention than techniques such as IGC, and it has also been widely applied in several industrial applications, such as coating and ElectrosleeveTM [9].

2.1.2 “Top-down” Approaches

As opposed to the “bottom-up” method, the basic concept of “top-down” approaches to nanostructured material fabrication is to start with bulk solids and decompose coarse microstructures into nanostructures by forming a large volume fraction of non-equilibrium grain boundary within the parent materials, which can be done by supplying mechanical and other forms of energy and storing high energy in the parent materials. Compared to bottom-up methods, top-down methods are more traditional and lack precise control of atoms arrangement. But they are more straightforward, cost-efficient and capable of producing large scale bulk nanostructured materials, including various metals, alloys and metallic composites. The typical examples of “top-down” approaches include ball milling, equal channel angular processing (ECAP) and high pressure torsion (HPT). Among all the variants of the top-down processes, only ball milling, HPT and accumulative roll bonding can regularly produce noncrystalline materials with grain size smaller than 100nm [14], other processes such as ECAP usually result in microstructures in the range of a few hundred nanometers.

Ball Milling of Powder Particles

Ball milling, or mechanical attrition, of powders is a powerful processing technique that has been used to produce a wide range of metastable structures including nanostructured materials [15, 16, 17].

There are several types of ball milling instruments, such as vibratory mills, tumbler mills, attrition mills, shaker mills and planetary mills, etc [18]. But the essential
process of all types of ball milling is the same, that is, to shake hardened steel balls or tungsten carbide balls (WC) and material powders together in a sealed milling chamber violently. The collision between balls and powders during the milling processes provides large plastic deformation to the powder particles at high strain rates. The mechanism of particle refinement for ball milling is to introduce large number of defects--dislocation cells networks, subgrains and high angle grain boundaries--by subjecting powders to severe plastic deformation. The three steps proposed by Fecht and co-workers [19] are:

(1) Deformation localized in shear bands with high dislocation densities.

(2) When the strain is sufficiently high, the dislocations annihilate and recombine to small angle grain boundaries, and subgrains of 20-30nm are formed. Further milling extends small grains throughout the volume.

(3) Grain boundary sliding and other superplastic deformation leads to grain rotation, and random orientation of grains are formed.

The final structures are effected by several milling parameters, such as operating temperature, atmosphere, frequencies, weight ratio between balls and powders, etc, and by properly choosing the milling parameters, very small grain sizes of \(\sim 20\)nm can be achieved for various materials. For example, impact forces imposed on powder particles during collision can be enhanced by increasing the kinetic energy of the milling balls, so heavier balls and higher velocity are desired, and higher velocities can be obtained by using high frequencies and small amplitudes of vibrations [20]. Ball milling decomposes microstructures by fracture and cold-welding in addition to heavy plastic deformation, hence it is a process more suitable for hard and brittle materials. FCC structured metals are known to be too ductile and soft for effective energy storage, and the “sticking to milling tools” phenomenon often occur during milling processes, but by choosing Hydrogen atmosphere, FCC metals and alloys can be embrittled and therefore successfully refined by mechanical attrition down to nanoscale [21].

One of the major disadvantages associated with ball milling is contamination caused by the milling tools and the milling atmosphere, which lead to Fe, O\(_2\) and N\(_2\)
impurities. However the contamination issue can be greatly alleviated by coating the milling tools with materials corresponding to powder materials and better sealing the milling container. Reduction of milling time and using inert gas atmosphere also help the situation substantially. Fe-based wear debris can generally be reduced to less than 1-2% and O and N contamination to less than 300ppm, which is better than the nanostructured materials produced by IGC and other chemical processes [20]. Another major disadvantage of mechanical attrition is that a follow-up consolidation is necessary in order to obtain bulk nanostructured material, and it is usually hard to control the grain coarsening problem, and therefore hard to maintain nanostructures during consolidation. However mechanical attrition generally has the reputation of easy procedures, and capability of large scale production of various nanostructured materials.

Severe Plastic Deformation of Bulk Materials

Similar mechanism of structure refinement can be applied to bulk materials through severe plastic deformation, and the most commonly applied approaches are Equal Channel Angular Pressing (ECAP), High Pressure Torsion (HPT) and multiple forging [22]. Severe plastic deformation methods have the unique capability of producing porosity-free and impurity-free bulk samples, compared to synthesis techniques that require follow-up consolidation and chemical processing. However SPD methods, especially ECAP, often result in ultrafine microstructures, which are defined as those that are on the order of a few hundred nanometers in the current literature as opposed to nanostructures that are defined to be smaller than 100nm. Materials processed by ECAP are in the shape of billets and on the other hand materials processed by HPT are in the shape of small disk, hence producing massive ultrafine materials is still a challenging problem for severe plastic deformations [22].

1. Equal channel angular pressing

The typical device for ECAP is illustrated in Fig. 2.3. It is composed of two channels with the same cross section (shape and area) intersecting each other at a specific angle, usually close to 90°. The cross section can be either circular or
Figure 2.3: Equal channel angular pressing [22].

square. Specimens that can fit in the channels are pushed through both channels under sufficient amount of pressure P, and the device is conditioned in such a way that the specimen is deformed via frictionless simple shear as it goes through the corner where the two equal channels meet. Both of the angle between the axes of the two channels and the angle of the outer arc of curvature have a direct impact on the strain caused by ECAP. For instance, an equivalent strain close to one can be imposed to the specimen if the intersecting angle is $90^\circ$ [23] and the outer angle of curvature is $20^\circ$ [22]. After each pass, the cross section of the specimen remains the same, hence intense plastic deformation can be accumulated by subjecting the specimen to several passes consecutively. There are three different routes of conducting ECAP passes, route A, B, and C, as illustrated in Fig. 2.4.

**Route A:** The orientation of the specimen remain unchanged after each pass;

**Route B:** The specimen is rotated $90^\circ$ around its longitudinal axis after each
Figure 2.4: Three routes for ECAP and their shearing directions (a) route A; (b) route B; (c) route C [22].

pass; if the rotation is made in the same direction, it is called route $B_A$, or if the rotation direction is changed between counterclockwise and clockwise alternately, it is called route $B_C$;

**Route C:** The specimen is rotated $180^\circ$ around its axis after each pass.

The difference between the three routes is the shearing direction and the shear plane orientation, as illustrated in Fig. 2.4. Some of the studies show that route $B_C$ is more effective at producing equiaxed ultrafine microstructures [24, 25], but further investigation is needed to establish the relative effectiveness of the four rotation schemes. During the procedure in order to achieve a frictionless shear deformation condition, the longitudinal faces of the specimen can be polished and coated with lubricant, and the entrance channel can be often designed in such a way that its cross section is slightly larger than that of the exit channel [25]. The
first two passes or so result in subgrains separated by low angle boundaries within grains, and the following passages will produce ultra fine grains with high angle misorientations. The minimum grain size is about 200nm for ECAP methods.

2. High pressure torsion (HPT)

HPT introduces severe plastic deformation within the materials through torsion under high pressure. The device of conducting HPT is shown in Fig. 2.5, and the procedure is to place a sample, in the shape of disks with dimensions of \( \sim 20\text{mm} \) in diameter and \( \sim 0.2\text{mm} \) in thickness, between the two anvils, and press it with a pressure of a few GPa and rotate the bottom anvil at the same time, and therefore the friction between the sample and the anvil caused by the pressure \( P \) brings the sample to shear. Because of the large friction between the anvils and the sample and as well as the confinement of the device, the stress state experience by the sample can be considered to be quasihydrostatic, and the shape of the disk is maintained, hence HPT is capable of processing hard and brittle material as well. However in the case of hard or brittle samples, care needs to be taken when the HPT device is designed in order to reduce the sliding between anvils and the sample, for example, strong materials may be desirable for anvils.

After deformation by the first 1/2 revolution, a refinement of microstructure can be observed, but it is usually necessary to conduct several revolutions to achieve the homogenous ultrafine microstructures [26, 27]. Although the relations between the final microstructure and the strain experienced by the sample is not clearly established as in the case of ECAP yet, but the experimental studies show that it is actually more reasonable to consider the number of rotations and not the strain values calculated by the analytical equations. The texture of the final ultrafine materials processed by HPT is usually close to those in the case of simple shear.

Compared to the other often used severe plastic deformation approach, HPT is able to produce microstructures finer than 100nm. The lower end of the reported grain size range is 106–170nm for HPT processed coarse-grained Ni [28], and HPT
Figure 2.5: High pressure torsion [22].
is considered as more effective at refining microstructures than ECAP [29]. To date
grain size as small as 20nm has been reached by HPT. And one more advantage of
HPT is its capability of processing brittle materials as mentioned above. However
one major disadvantage of HPT is that the final sample size is small. Samples
processed by HPT usually has the maximum diameter of ∼20mm and the maximum
thickness of ∼1mm. In addition to refine material microstructures by severe plastic
deformation, HPT sometimes can also be used as a tool for the consolidation of
powders.

2.2 Microstructure

As material properties depend on their building blocks and the atomic struc-
tures, the refinement of grain size changes the material microstructures in such a way
that the material properties become much superior than those of the same matter at
the bulk scale. The microstructure of NC metals and alloys have been investigated with
tools, such as molecular dynamic simulations, X-ray diffraction (XRD), and transmission
electron microscopy (TEM) imaging, etc. X-ray diffraction to gain insight of the grain
size, microstrain, and texture, and TEM can be used to count the grain size distribution
and to study the grain boundary structures, but grain boundary relaxation may cause
difficulties in interpreting the observations.

One of the typical microstructure of NC metals is the significantly increased
volume fraction of the misfit region (grain boundary) between crystallites and the triple
junctions with the grain size refinement, for example for an average grain size of 10nm,
atoms residing in the grain boundaries can take up from ∼14% to 27% of the volume, and
these grain boundaries play as the role of sources and sinks for dislocations, and provide
stress relief mechanisms, such as grain boundary diffusion and grain boundary sliding,
and TEM images of grain boundaries finds that the crystallinity is usually maintained
up to the grain boundary, in stead of the amorphous region with in the grain bound-
daries [3]. Molecular dynamic simulations of noncrystalline metals simulated by Voronoi
construction by Van Swygenhoven et al. found the grain boundaries fundamental same to their coarse grained counterparts [30]. The NC Pd interface studies by Rodriguez et al. using high resolution TEM (HRTEM) found (i) boundaries with large amounts of disorder up to 2 nm are present; (ii) low angle boundaries with straight edges and twins are found to coexist; (iii) triple junctions with amorphous packets and disorder are seen; (iv) no evidence for “as-like” disorder have been noticed [31].

Huang et al. studied the microstructure of nanostructured Cu with grain size between less than 100nm and a few hundred nanometers processed by repetitive corrugation and straightening (RCS), using TEM and HRTEM, and they found that most of the grains are heavily strained and separated by high angle grain boundaries, high density of dislocations, dislocation cell structures, subgrains formed by dislocation arrays, and low-angle grain boundary of 5° misorientation were observed in the grains. Part of the HRTEM images that they obtained are illustrated in Fig. 2.6 and Fig. 2.7, the latter of which shows the low angle grain boundary configuration that they observed. Fig. 2.7(d), the structural model corresponding to Fig. 2.7(c), shows dislocations of two types that are both necessary to accommodate the grain boundary geometrical misorientation, and they are called geometrically necessary dislocations, but in Fig. 2.7(c) there are more dislocations of the second type, and they are extrinsic, i.e., non-geometrically necessary. This suggests that this section of the grain boundaries is in a high energy configuration, and is non-equilibrium grain boundaries, which is characterized by high density of extrinsic dislocations and lattice distortion near the grain boundaries. Non-equilibrium subgrain boundaries are also seen [32].

Among many other researchers, Dalla Torre and the co-workers used X-ray diffraction and TEM, and studied the microstructure of commercially available electrode-deposited noncrystalline Ni of two different batches manufactured by Goodfellow Metals, and they found that their microstructure is inhomogeneous and batch dependent, see the TEM bright field images shown in Fig. 2.8. Both of the samples have a preferential orientation along \( \{200\} \) family planes, but batch B has a stronger texture than batch A. The grain size distributions are shown in Fig 2.9, which shows that the grain size
Figure 2.6: (a) A TEM micrograph showing fine deformation structures in a grain. The numbers 1–3 denote three subgrains; the two arrowheads point out an array of dislocations; the four stars mark a low-angle GB; the white circle marks the dislocation tangle zone (DTZ); the white square marks a transition from DTZ to dislocation cell. Grain size in mc, ufc and nc metals and alloys [32].
Figure 2.7: (a) A TEM micrograph of a low-angle grain boundary. (b) An EDP corresponding to (a), and the grain boundary misorientation measured from EDP is $9^\circ$. (c) and (d) A Fourier filtered HRTEM image and a structural model of the upper-left or the low-angle GB shown in (a). (e) A Fourier filtered HRTEM image from the low-right part of the low-angle GB shown in (a) [32].
distribution is relatively narrow for these electrodeposited noncrystalline Ni, and the mean grain size is roughly 20nm for both batches. No clear evidence of dislocations was found in the high resolution TEM images, and groups of grains of small misorientation were observed.

Impurities, such as Cobalt, iron, sulfur, oxygen, hydrogen and nitrogen, caused by the processing routes are found to present in the samples, but the amount of each of the impurities are different for each batch. Usually artifacts, such as porosity and impurity, exist in the NC metals and alloys. Materials produced by compactions of nanopowders often have large amount of porosity in the grain boundary, and they are not fully condensed, while preparation method, like electrodeposition and inert gas condensation always result in impurity, for example the NC Ni used in the mechanical testing of Dalla Torre et al. are found to have impurities of Al, Ca, Co, Cu, Fe and Pd etc, which is listed in Table 2.1.

It is important to know that the microstructure of ultrafine/nano crystalline metals and alloys are usually depends on the manufacturing methods and the processing parameters, and it is also generally batch-dependent [33]. On the other hand, due to the metastable nature of the grain boundaries, the microstructure usually evolve...
Figure 2.9: Grain size distributions of the samples used by Dalla Torre et al. [33]

Table 2.1: Chemical impurity of Batch A and B of the specimens used by Dalla Torre et al. [33]

<table>
<thead>
<tr>
<th>Element</th>
<th>Batch A (ppm)</th>
<th>Batch B (ppm)</th>
<th>Detection limit (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>6.5</td>
<td>45.9</td>
<td>1</td>
</tr>
<tr>
<td>Ca</td>
<td>8.75</td>
<td>2.56</td>
<td>0.02</td>
</tr>
<tr>
<td>Co</td>
<td>881</td>
<td>104</td>
<td>0.5</td>
</tr>
<tr>
<td>Cu</td>
<td>155</td>
<td>473</td>
<td>0.1</td>
</tr>
<tr>
<td>Fe</td>
<td>127</td>
<td>135</td>
<td>0.1</td>
</tr>
<tr>
<td>Pb</td>
<td>19</td>
<td>&lt;</td>
<td>10</td>
</tr>
<tr>
<td>S</td>
<td>883</td>
<td>476</td>
<td>5</td>
</tr>
<tr>
<td>W</td>
<td>&lt;</td>
<td>263</td>
<td>10</td>
</tr>
</tbody>
</table>
and experiences grain growth during deformation, especially under large stresses [34]. Therefore it is extremely important to record the microstructure of each sample before and after the experiment, so that logical comparisons can be made between different experimental results and obtain further insight into the mechanisms of ufc/nc metals and alloys.

2.3 Mechanical properties

Reducing the grain sizes not only has a big impact on the micro-structures of the noncrystalline materials, but also alters their mechanical properties significantly. The most important mechanical properties of noncrystalline metals and alloys include significantly increased strength, hardness, strain rate sensitivity and wear resistance, etc. with respect to the decreasing grain sizes, which make them very desirable engineering applications. It is important to realize that the mechanical properties of NC metals and alloys don’t only depend on the average grain size, but more importantly the grain size distribution and the microstructure, such as grain boundary structures, have critical effect on their mechanical properties. However there are still unresolved concerns with regards to the noncrystalline metals, such as the inverse Hall-Petch relations, low ductility, which usually comes with the high strength, and the grain growth phenomena observed when the materials are subject to extremely high stresses and substantial deformation strains, for example, the high pressure torsion [28] and nano-indentation tests [34].

2.3.1 Strength and hardness

The effect of grain sizes on the mechanical strength have been studied mainly via the approaches of uniaxial tension/compression experiments, and due to the fact that noncrystalline materials sample is usually very small, micro/nanoindentations are also extensively used by many researchers, for details please see the publication of Kumar in 2003 [3] and the reference wherein. The yield strength can usually be approximated
Figure 2.10: Schematic representation of the variation of yield stress as a function of grain size in mc, ufc and nc metals and alloys [3].

as 1/3 of the hardness measurement. Typically the experimental results show that the yield strength of polycrystalline metals and alloys increases with decreasing grain sizes down to ∼100nm, following the classical Hall-Petch law,

\[
\sigma_y = \sigma_0 + k_y d^{-1/2},
\]  

where \( \sigma_y \) is the yield strength, \( \sigma_0 \) is the fraction stress that dislocations start to move, \( k_y \) is the material constant, and \( d \) is the average grain diameter. Most of the experiments show that after the grain size is smaller than ∼100nm, the increase of strength vs. grain sizes start to slow down and deviate from the Hall-Petch relation, which can be interpreted as the index of Eq. (2.2) become smaller than 1/2 and close to zero [35], and when the grain size is in the very fine regime, say smaller than 10nm, the yield strength even starts to decrease with the further decreasing grain sizes [36]. See Fig. 2.10. The grain softening effect is often explained with creep deformation mechanism [37, 38] and grain boundary sliding [39].

Although it has been accepted as one of the mechanical properties of the nano-
crystalline metals and alloys, caution should be raised with regards to the understanding of the so-called “inverse Hall-Petch relations”, because the currently available process methods usually result in nanocrystalline materials of high porosity and impurity when the grain size comes down to below 15nm or so, for example IGC and the electrode-position techniques, as reviewed in the previous sections, and the mechanical behavior of nanocrystalline metals and alloys may actually present more of the defects than the material itself [40, 41, 42]. On the other hand, the reliability of the experimental results are usually questionable due to the small sample size and the experiment equipment, especially for those of uniaxial tension/compression tests. One more thing to note about the mentioned strength analysis is that the microstructure of the materials is represented by the mean grain size, but the reality is that a wide range of grain sizes may exist in the material, and the grains of size larger than the mean grain size may take up most of the material volume and therefore decide the material strength. The effect of grain size distributions on the mechanical behavior has been emphasized in the late studies [35, 38, 42, 43, 44].

2.3.2 Ductility

Low ductility is usually associated with the high mechanical strength, especially under tension. On the other hand, the prediction of increasing ductility with decreasing grain size for conventional coarse-grained metals ceases to apply to NC metals according to the experiment results, for example, strain to failure of less than a few percent has been reported for NC metals with mean grain size of less than 50nm under tension, and the material fails with very little cross section area reduction [6, 45, 46, 47] It has been explained with plastic instability [48, 49], internal flaws and impurity such as Hydrogen [33], lack of strength hardening and the small specimen size, etc. Youssef et.al. synthesized bulk NC copper with mean grain size of 23nm, but with no porosity and other processing defects, and this NC Cu exhibited high yield strength about 11 times higher than the coarse grained copper and a strain to failure of as high as 14% [50]. Lu et. al. found high tensile ductility with strain-to-failure of 30% for a fully dense
nanocrystalline copper with average grain size of 27nm prepared by electrodeposition [51], which again suggests how significantly the mechanical behavior of NC metals and alloys can be affected by the internal artifacts. Higher elongation to fracture can also be obtained with higher loading rate [52].

Low ductility has been considered as one of the major concerns with respect to the applicability of the nanocrystalline metals. Solutions have been proposed with regards to this issue [53, 54]. The problem of low ductility of NC metals is often considered to be caused by the lack of the strain hardening sources, so one of the possible strategies to improve the ductility is to introduce some mild structural modification so that a small amount of larger grains is included, to provide strain hardening sources at the expense of slightly lower material strength, assuming the crystalllographic slip is the only source of plastic deformation, and another solution may be to produce the bimodal grain size distribution on the nano-mircro scale and therefore introduce a certain volume fraction of grains containing higher dislocation density [53]. Ma reviewed eight routes that utilize the stability mechanisms to overcome the instabilities, which usually lead to lower tensile elongation of NC metals and alloys, and these approaches to the enhanced ductility can be generally grouped into two categories: strain hardening and strain rate hardening [54].

Strain hardening

(1) The bimodal grain size distributions on the nano-micro-scale can be usually achieved through recrystallization or consolidating a mixture of grains of different sizes;

(2) Multiphase alloys can be used instead of simple element metals to obtain high strength with high ductility;

(3) Use nanoscale growth twins to strengthening, because coherent internal interfaces are good sources of blocking dislocations;

(4) Disperse nano-precipitates and nanoparticles, which has been used as strengthening methods for alloys;
Use transformation-induced plasticity and twin-induced plasticity;

Encourage the strain hardening mechanisms by lowering of dynamic recovery at low temperature (cryogenic temperatures) and/or dynamic strain rates, which has been usually used for coarse grained metals and alloys.

Strain rate hardening

Higher strain rate sensitivity;

Flawless materials.

2.3.3 Strain rate sensitivity

Extensive research has been done on the strain rate sensitivity of NC metals with the purpose of understanding their deformation mechanisms. Fcc NC metals has been shown to be more sensitive to the loading rate than their coarse-grained counterparts [55, 56, 57, 58, 52, 59]. The parameter used to describe the strain rate sensitivity, \( m \), can be determined with the following equation,

\[
m = \frac{\partial \log(\sigma)}{\partial \log(\dot{\epsilon})}.
\]  

(2.3)

The higher \( m \) means higher strain rate sensitivity, and \( m \) is often seen in a general power-law type rate-dependent constitutive relation,

\[
\dot{\epsilon} = \dot{\epsilon}_0 \left( \frac{\sigma}{\sigma_0} \right)^m,
\]  

(2.4)

where \( \dot{\epsilon}_0 \) and \( \sigma_0 \) are the reference strain rate and the effective von Misses stress at the reference strain rate, and \( \dot{\epsilon}, \sigma \) are the plastic strain rate and corresponding effective stress respectively.

Wang et.al. used strain rate change test (jump test) to determine the strain rate sensitivity index \( m \) to be 0.01 for the ECAP Cu that they used when strain rate \( \dot{\epsilon} \) of \( 1 \times 10^{-4} \) is used under room temperature, while \( m \) is a few times smaller for coarse-grained
Figure 2.11: Comparison of experimental and computational results for tensile tests of ultrafine and nc Ni. The 1% offset yield stress and strain at tensile strength are shown versus strain rate Schwaiger et.al. 2003. [56]

Cu [57]. Schwaiger et.al. conducted series of systematic tests using two experimental techniques of depth-sensing indentation and tensile testing on coarse-grained (> 1µm) and electro-deposited ultrafine (200nm average grain size) and nanocrystalline (20nm) Ni respectively [56]. They found when the average grain size is above 100nm, the materials undergo rate-independent plastic flow over the loading strain range $3 \times 10^{-4}$ to $3 \times 10^{-1}$s$^{-1}$, but when the average grain size is on the order of ∼40nm, NC Ni exhibits very high rate sensitivity. Fig. 2.11 illustrates that the NC Ni is much more sensitive to the loading rates. The grain size dependence of the strain rate sensitivity for fcc micro, ultrafine nanocrystalline metals is compiled in Fig. 2.12. The loading rate dependence of strain rate sensitivity, illustrated in Fig. 2.13, was reported by Wang et.al. for ECAP ultrafine Cu, and it is shown that not only the ultrafine Cu is more sensitive to the strain rate than the coarse grained Cu, but also its strain rate sensitivity is more strain rate dependent than the coarse-grained Cu.
Figure 2.12: Strain rate sensitivity exponent vs. grain size for FCC metals such as Cu, Ni at room temperature, and the open diamonds represents the data obtained with materials with average grain size of roughly 500nm and ∼50nm nanoscale twins. [52]

Figure 2.13: Strain rate sensitivity exponent vs. strain rates for ECAP Cu using strain-rate change tensile tests at room temperature, compared with coarse-grained Cu [57].
Recent studies also show that the activation volume, which is defined as

\[ v = \sqrt{3}kT \left( \frac{\partial \ln \dot{\varepsilon}}{\partial \sigma} \right), \]  

(2.5)
decreases with the grain size refinement, shown in Fig. 2.14, and the lower activation volume usually is associated with the high strain rate sensitivity of NC metals [52]. Wang et al. expanded the temperature under which the stress relaxation studies are carried out to a range from low to elevated temperatures, and showed that strain rate sensitivity of electro-deposited NC Ni also depends on the temperature, see Fig. 2.15 [58].

Different from the coarse grained materials, the strain rate has effects on both of the yield strength [57] and the ductility of the nanocrystalline metals [52, 57]. The higher strain rate is, the higher yield strength and ductility may be obtained. Schwaiger et al. and Kumar suggested that no clear trends should be concluded on the effect of strain rate on the tensile strain to failure. It has been found that the ultrafine or nanocrystalline bcc metals exhibit much lower strain rate sensitivity than their coarse
Figure 2.15: (a). Strain rate sensitivity vs. temperature for conventional coarse-grained Ni and NC Ni annealed at 373K for 1 hour, and the data shown is obtained from the first cycle of stress relaxation curve for each temperature. (b). Normalized apparent activation volume vs. temperature for NC Ni, and the inset is the corresponding for coarse-grained Ni using stress relaxation method [58].
grained counterparts [60].

2.4 Issues

Although NC metals and alloys have many very excellent mechanical properties, they have only been applied to a few industrial applications, especially the bulk NC metals with mean grain size smaller than 100nm, in that there are still several challenges existing in the study and applications of this group of materials.

The first challenge is within the processing techniques of the NC metals and alloys. The most common preparing approaches to nanostructured metals, such as inert gas condensation followed by compaction, electrodeposition, and severe plastic deformation usually experience difficulties in producing artifact and impurity free NC/ultrafine grained metals and alloys, as discussed in Section 2.1, and high volume fraction of the internal flaws, such as pores, and impurity usually lead to the lower density, ductility, strength, and even the Young’s modulus for NC metals and alloys. Some of the experimental results represent the flaws more than their mechanical response [42]. Furthermore, some processing techniques, such as, electrodeposition, can’t repeatedly produce bulk NC metals and alloys of consistent microstructures for laboratory investigations, which presents one of the major difficulties in comprehending the deformation mechanisms of NC metals and alloys. For example, electrodeposition can produce NC metals that are only several hundred microns thick, although the in-plane dimensions can be 100×100mm, and the experiment samples made from these materials tend to buckle when subjected to compression. It is also hard to control the deformation without imposing out-of-plane bending and buckling, and the range of loads, stress level, stress intensity factors that can be applied to them are very limited [3].

In addition to the low ductility of, the stability of the internal structures of the nanocrystalline metals has been a long time concern of NC metals with regards to their engineering applicability, due to the large energy associated with the grain boundaries. Zhang et al. observed rapid stress-driven grain growth for NC Cu under microhardness
indentation at cryogenic temperature, and suggested that grain coarsening will affect or even invalidate the hardness/strength measurements of NC metals, especially when the applied stress is high and the sample is pure [34]. The starting material that they have studied is 99.999% pure nanocrystalline Cu with a mean grain size of 20nm, which is made by IGC and compaction. They put the samples under microhardness indentation with the dwell time of 10 seconds, 1 minute, 5 minutes, and half an hour respectively under room temperature and -190°C, and they found that the samples undergo grain growth at both of the temperatures, and the samples indented at -190°C experiences faster grain growth, see Fig. 2.16. The faster grain growth at lower temperature suggests that it is driven by stress instead of grain boundary diffusion. The hardness measurements were found to decrease as the dwell time increases as a linear function of the logarithm of
the dwelling time, which is consistent with the indentation creep test of high purity NC Cu carried out by Zhang et al. [61], see Fig. 2.17. Zhang et al. also suggested microstructure examination at the end of each mechanical testing, and the grain growth rate tends to decrease with increasing impurity.

There is a growing body of experimental studies and theoretical predictions of the mechanical response and deformation mechanisms, but it is still difficult to have a clear understanding of the mechanical properties and deformation mechanisms of the NC metals and alloys, because there are also many controversial results within these studies. The reason is that the experimental results under comparison are obtained by materials processed by different methods, so the interior structures, such as grain size distribution, may be different and contribute to different mechanical response. The second reason is that the experimental methods, such as loading methods, used to explore the mechanical response are often different, and thirdly the sample size also has an important effect on the overall experimental results.

Therefore it is desirable to have the material engineering techniques that is able to repetitively produce large quantities of NC metals and alloys, that have optimal mechanical properties, as the limited amount of materials present challenges to perform mechanical testings, especially for the materials produced by IGC and compaction. At the same time, systematic experimental routes are also very important for the studies of NC metals and alloys.

2.5 Applications

The excellent mechanical properties of NC metals and alloys have made them very desirable for many industrial applications. Efforts from the industry and universities have been paid to the possibilities of the applications. The Nano-App Summit was held in last year, and the meeting was focused on the real products of nano technologies, including nanocrystalline metals, alloys, and composites.

NC metals and alloys/composites are great for wear-resistant coating, due to
Figure 2.17: Influence of sample purity on grain coarsening. (a) Plots of hardness versus logarithm of indenter dwell time for a 99.6% pure IGC Cu sample, 10 nm average grain size and two 99.999% pure IGC Cu samples of 20 and 45 nm average grain size. (b) Number fraction and (c) volume fraction size distributions for the 99.6% pure IGC Cu sample in the initial condition and after 30 minutes indenter dwell time. Indentation made at room temperature Zhang et al. 2005 [34].
their extraordinary hardness and wear resistance. Nanostructured wear-resistant coatings for cutting tools and wear-resistant components have been in use for several years. For example, Timken has utilized the wear bearing ability of nanocomposites under high temperature and long time operation, and applied them to tribological coating applications. NanoMetal of Integran, such as nanocrystalline Co-P alloy, has been intended in the landing gear, industrial hydraulic cylinders, engine application, Nanocoated ABS and nanometal composite armor in the aerospace applications. Nano composite coatings with dispersed hard nanophase crystalline in the elastic matrix have the capabilities of wear resistance and friction reduction, and their friction coefficient if much lower than steel. They can be harder and more elastic than steel. Therefore they are also applied to automobile industry The ultra high strength and hardness of NC metals and alloys can serve in advanced structural applications, such as stronger automobile frames and spacecraft shielding, etc.

Electrodeposited NC metals have been applied to the Electrosleeve™ insitu repair of nuclear steam generator tubing, due to their superior mechanical properties. In this application, nanocrystalline Ni is electrodeposited onto the interior surface of the tube on the spots where the tube is broken due to cracking or corrosion. This process has been successfully applied in the US and Canada [9, 62].

Ultrafine/nanocrystalline metals and alloys are also very useful in manufacturing the micro-electronic devices, where very small components are required and uniform microstructure is desired, and ufc/nc metals are able to provide a large amount of grains in the cross section of an extremely small components to approximate the uniform structure.

There are few applications of bulk nanocrystalline metals and alloys, especially for those with the average grain size of 100nm or less, because there are some issues associated with these materials, such as low ductility, unstable nano structures, preparing materials of large quantities, manufacturing, cost, etc.
2.6 Deformation Mechanisms

While the grain sizes of polycrystalline metals are reduced into the nanometer scale, not only the microstructure and the mechanical properties change significantly as discussed in the previous sections, but also the materials undergo different deformation mechanisms than the coarse-grained metals, as a consequence of the distinct nanostructure. There have been both experimental evidence and theoretical prediction with regards to the transitions of the plastic deformation mechanisms. As the grain size decreases, the volume fraction of the grain boundaries increases, and therefore grain boundary assisted deformation mechanisms are expected to play more important roles in deciding the mechanical behaviors of NC metals, compared to the coarse-grained metals.

Coarse-grained metals are known to deform plastically and strengthen through intragrain dislocation interactions, and the polycrystalline crystal plasticity based on dislocation theory can be found in many early publications such as those of Asaro, Needleman, Hirth, Hill, and Rice, etc. [63, 64, 65, 66, 67, 68]. In the traditional polycrystalline metals, stress required to move the dislocation usually increases when the dislocations meet obstacles such as grain boundaries, and before the critical stress is reached, the dislocations will be stopped at the grain boundary. As the dislocations further pile up against the grain boundaries, the grain boundaries experience stronger pressure from the front of the pileup, which causes the grain boundaries to yield and the deformation progresses into the neighboring grains. The grain size dependence of the flow stresses for the coarse-grained metals flows the Hall-Petch type relation as described in Eq. 2.2. The smaller the grain is, the higher strength it gets.

However the relations between strength and grain size for nanocrystalline metals are often found to depart from the Hall-Petch relation and even decrease with the grain size refinement, see Fig. 2.10. On the other hand, according to the experimental observations and the molecular dynamic simulations [13, 69, 70, 71, 72, 73, 74, 75], the intragrain Frank-Reed dislocation sources cease to exist in the nanocrystalline metals and alloys, and by the dislocation theory, dislocation pileups are not supported in
the very fine grains [76]. Theoretically the slip of dislocations requires shear stress on the order of approximately $G b/l$, where $G$ is the shear modulus, $b$ is the magnitude of Burger’s vector’s length and $l$ is the segment length, which the simulations suggest to be smaller than a third or a quarter of the grain size [77], and this gives Ni, if $G$ is roughly 82GPa and the average grain size is on the order of 30nm, the shear strength of 3280GPa, which is much larger than what is observed in the experiments by at least a factor of three [4]. This, and together with the Hall-Petch relation deviation, suggests the deformation of nanocrystalline metals and alloys is dominated by mechanisms other than intragrain dislocations. Deformation mechanisms of nanocrystalline metals and alloys have been mostly studied via the methods of atomistic simulations and experimental observations, and there have been a good amount of published studies on this subject. According to the recent studies, nanocrystalline metals are found to accommodate the deformation and relief the stress state through grain boundary atomic shuffling and free volume migration. Mostly it has been shown that the grain boundary accommodated deformation mechanisms, such as grain boundary emission of dislocation, stacking faults (partial dislocation), and grain boundary sliding, seem to operate in nanocrystalline metals [13, 71, 72, 73, 78], which are reviewed in the following sections. This finding is not surprising, because as the grain size is on the nanometer scale, atoms residing in the grain boundary take up most of the volume. However findings of deformation mechanisms are still controversial, and it must be noted that the two currently applied methods, i.e., TEM observation and MD simulation, both have limitation with respect to accurately capturing the real deformation physics. For TEM observation, it is usually hard to identify the deformation mechanisms for bulk nanocrystalline metals, because it is usually done in a thin film/foil form [3], and when it comes to MD simulation, although the computation capability has progresses significantly nowadays, it still limits the time range that MD simulations can be performed to seconds, so in order to reach strain large enough to induce plastic deformation, unrealistic high stresses/strain rates are usually applied, which prevents the accurate reproduction of the deformation, and therefore it presents some challenge in capturing the real mechanisms. The transition/interplay be-
tween the proposed deformation mechanisms are briefly discussed in this Chapter as well.

2.6.1 Grain boundary emission of dislocations and partial dislocations

Fig. 2.7(c) by Huang et al. [32] suggests the existence of non-equilibrium grain boundaries in the nanocrystalline metals and alloys, and under sufficient stress the geometrically unnecessary dislocations that reside in the grain boundaries are able to move to the interior of the grains [4], and in nanocrystalline metals dislocations can move across the grains without impedance and be annihilated in the opposite boundary [79]. It is well accepted that grain boundaries in nanocrystalline metals act as the sources and sinks of dislocations, i.e., dislocations/partial dislocations are created in the grain boundaries and annihilated in the opposite grain boundaries, after traveling through the grains.

Grain boundary emission of partial dislocations has been observed in several molecular dynamic simulations, mainly carried out by Van Swygenhoven and the coworkers [3, 71]. Van Swygenhoven and Caro performed a series of molecular dynamic simulations on nanocrystalline Ni and Cu samples made of 15 grains with different mean grain sizes from 3.4nm to 12nm, using Voronoi construction method, and the grain boundaries in these samples are mainly high angle GB’s. Cu and Ni have substantially different stacking fault energy, since Ni is on the higher end of the reported stacking fault energy values but Cu is on the lower end. The samples were deformed by uniaxial tension with constant stress. For a strain rate of $3 \times 10^7$ with a tensile load of 1.5GPa, no dislocations and intragrain defects were found in the Ni sample with a mean grain size of roughly 5nm, but stacking faults were found in the Ni sample with a mean grain size of 12nm, which suggests a change of deformation mechanism at roughly 12nm for the NC nickel samples created in their simulations. Fig 2.18 shows the motion of a partial dislocation when it is moving across the grain, where the defect-free atoms are not shown, and the red atoms are those with the HCP crystalline structure, and they represent the stacking fault behind the traveling Shockley partial dislocation, which is shown by the blue
Figure 2.18: Two dimensional snapshots of the sample with the average grain size of 12nm at times 18, 24, and 33ps, showing the motion of the Shockley partial dislocation when it is traveling through a grain from left to right, by Van Swygenhoven and Caro [71].

Atoms above the red atoms, and the blue and green atoms are the “other 12-coordinated” and “non-12-coordinated” atoms. Similar phenomena were also observed for NC copper samples, but the change of deformation mechanisms starts at a lower grain size than Ni, mostly due to the lower stacking fault energy. Their later MD simulations of 12nm NC Ni show that some of the certain type of the grain boundary dislocations, which accommodate the misorientations between grains, can dissociate into a Shockley partial, which is caused by local atomic shuffling and stress-assisted free volume migration nearby the triple junction during the deformation, and under sufficient stress the created partial dislocation can travel through the grains. Fig. 2.20 shows the nucleation of the partial dislocation at a triple junction, and as well as the stress-assisted free volume migration, where the atoms in the perfect face centered cubic are not shown, but the black arrow points to the nucleation site of dislocations, and the thicker yellow line shows the stress-assisted free volume migration. However more partial dislocation activity is found in the simulations of NC Ni of larger grain size, but no full dislocation emission is found, and
Figure 2.19: View of one section of a grain boundary (a) before, (b) after the emission of a partial dislocation into the interior of the grain. The grain boundary planes where the grain boundary dislocations are observed are numbered. The inset in (b) shows the detail motion of the atom. [80]

Figure 2.20: The nucleation of partial dislocations, shown by the black arrow, and the stress-assisted free volume migration, shown by the thicker yellow line, nearby the triple junction. Note that only the non-fcc structured atoms are shown [81].
for 5nm NC Ni, no dislocation activity but only grain boundary sliding is found.

Grain boundary emission of full dislocation is observed by Yamakov et al. [83, 84, 85] and Wu et al. [82] using high resolution TEM in the 20–30nm grains of nanocrystalline Ni. For some FCC nanocrystalline metals like Al, after the leading partial is emitted from the grain boundary and traveling through the grain, the trailing partial usually will follows, and then complete the full dislocation emission process. In the MD simulations of NC Al approximated by a 2D columnar microstructure, Yamakov and the co-workers found that the length, $\gamma_{\text{split}}$, of the stacking fault between the leading and trailing partial dislocations that formed the extended dislocation has an important effect in deciding the dislocation emission process: if $\gamma_{\text{split}} > d$, where $d$ is the grain size of the sample, the leading partial will be nucleated in one side of the grain boundaries and absorbed in the opposite grain boundaries, and leaving stacking fault behind, but if $\gamma_{\text{split}} < d$, then the leading and trailing partial dislocations are emitted into the grains consecutively in a way that is similar to the coarse-grained Al. Van Swygenhoven and coworkers analyzed the nucleation and propagation of dislocations in the nanocrystalline FCC metals, using molecular dynamics simulations of NC Al, and they found these two processes are thermally activated, i.e., not purely mechanically driven, and the leading partial dislocation and the trailing partial dislocation can be nucleated in different sites of the grain boundaries. Different Burger’s vector and the geometry of the grain boundaries can play a role as obstacle to the propagation of leading/partial dislocations [85].

The role of stacking fault energy is discussed and reviewed by Van Swygenhoven et al [84]. They compared constant tensile stress simulations using three model potentials, shown in Fig. 2.21, and the details and the reference of the three models can be found in [84]. Fig. 2.21(a) shows that Ni with the grain size of as large as 30nm, which has the highest stacking fault energy, only extended partial dislocations are observed, because the atomic shuffling and stress-assisted free volume migration, which cause the partial dislocation emission, relax the grain boundary area, and therefore lower the stress level which is required to emit the trailing partial dislocations. Fig. 2.21(b) demonstrates
Figure 2.21: Typical deformation mechanisms observed in simulations of fully 3D samples using three model potentials. (a) Extended partial dislocations in NC Ni with a grain size of 20nm, using second moment tight binding potential of Cleri and Rosato for Ni. (b) A full dislocation in NC Al with grain size of 12nm, using the embedded atom potential of Mishin et al. for Al. (c) A partial dislocation that has nucleated at a triple junction in NC Cu using the Cleri-Rosato potential for copper. Red dots represent the stacking fault behind the traveling partials, and grey represents the atoms in the fcc structure, and green means the other 12-coordinated atoms [84].
the full dislocation emission for NC Al, which has the intermediate stacking fault energy, because the leading partial always just travels a short distance, which is beyond $\gamma_{\text{split}}$, slowly in the grain after it is emitted, and the trailing partial is usually emitted before the leading partial is annihilated in the other grain boundaries. Fig 2.21(c) shows only partial dislocations are observed for NC Cu, which possess the lowest stacking fault energy among the three, with mean grain size of 12nm. So it is clear that stacking fault energy alone is not enough to explain what observed in the simulations, but Van Swygenhoven et al. concluded that the ratio of the stable stacking fault energy to the unstable stacking fault energy is more important, as it is 0.97, 0.55 and 0.13 for Al, Ni and Cu respectively [84]. Employing the analysis of dislocation emission from the assumed grain boundary facet cracks by Rice [65], Asaro and Suresh explored the mechanisms of partial/dislocation nucleation at the grain boundary, and they again confirm the importance of both stable and unstable stacking fault energies theoretically [52]. Recently Asaro, Krysl, and Kad proposed a kinetic relation between the stain due to partial dislocation emission from the grain boundary and the effective stress, and the stacking fault energies are included [4], and the numerical results predicted from this relation seem to be reasonably consistent with what is obtained in the experiments. The theory of Asaro et al. is reviewed in Chapter 3.
2.6.2 Deformation twinning

As one of the plastic deformation processes, deformation twinning is caused by the cooperative passage of partial dislocations on successive glide planes [86], shown in Fig. 2.22, and twin boundaries are special kinds of coherent internal interfaces. Twin boundaries has been reported in many experimental studies and molecular dynamic simulations of nanocrystalline metals and alloys [13, 87, 88, 89, 90, 91].

Twinning is usually observed in FCC metals with low stacking fault energy, so copper, which has a lower stacking fault energy, is expected to develop deformation twins within their nanoscale micro-structures, and in deed, Lu et al. observed nanosized mechanical twinning in the polycrystalline copper during their study of the strain rate sensitivity [92], but twinning has also been found in NC Al and Ni. Wu et al. performed extensive tensile tests on electrodeposited NC Ni foils that have mean grain size of 25nm at low temperature, and they found before deformation there were few growth twins existing in the samples, but the TEM observations after deformation several twin boundaries were activated in a number of grains, and twinning and stacking faults also contributed to the tensile deformation [91], and their TEM observation with regards to mechanical twinning is illustrated in Fig. 2.23, in which it can be seen that lead by the Shockley partial dislocation, some of the stacking faults and twins were stopped in the interior of the grain, instead of traveling through the whole grain, and Wu et al. concluded that these twins and faults are nucleated from the grain boundaries, and grew into the grains by the emission of partial dislocation for grain boundaries. Deformation twinning is also observed by Kumar et al. in electrodeposited nc Ni during deformation [13].

Molecular dynamics simulation of NC Al by Yamakov et al. found deformation twinning as well, shown in Fig. 2.24, even though Al has a rather high stacking fault energy. Asaro et al. [52] studied the mechanisms of the emission of partial and full dislocations at grain boundaries and twin boundaries. The existence of twin boundaries are found to not only increase the material strength and hardness, but also reduce the
Figure 2.23: (a) HRTEM image of a deformation twin, pointed out by the lines, in a grain. (b) HRTEM images of a grain containing a number of microtwins and stacking faults, and arrows show the stacking faults emitting from the grain boundary [91]
Figure 2.24: Snapshot for a grain diameter of 70 nm at 10.3% plastic strain, revealing two well-known mechanisms for the formation of two distinct types of deformation twins (seen in processes 15 and 6, respectively). [88].

activation volume of the thermally activated process of partial/full dislocation emission and therefore increase the material strain rate sensitivity.

2.6.3 Grain boundary sliding

Grain boundary sliding has been considered as an important plastic deformation process during the creep or fine-structure superplasticity of polycrystalline materials. The smaller the grain size is, the more important is the influence of grain boundary sliding on the mechanical properties [86, 93, 94]. Recently it has been also observed in the simulations and experiments [95] of nanocrystalline materials, especially for those with mean grain size of a few nanometers(< 10nm), and the findings indicate that grain boundary sliding is one of the plastic deformation mechanisms contributing to the inverse Hall-Petch effect of nanocrystalline metals [39, 72, 78] as discussed in § 2.2, and as the grain size gets smaller, the grain boundary sliding becomes relatively more important.

Van Swygenhoven and co-workers carried out series of molecular dynamic simulations to study the underlying deformation mechanisms of nanocrystalline FCC metals under uniaxial tension [Van Swygenhoven 1997 ~ 2006]. They observe that depending
on the atomic configuration and thermal fluctuation, the stress build-up across the grain boundaries enables a certain amount of atoms to migrate to new locations in such a way that the local stress is relieved, and the grains sliding against each other is the result of these localized and random individual atomic jump processes and causes the macroscopic deformation. They propose a nonlinear viscous model for the macroscopic shear strain rate due to grain boundary sliding [97],

$$\dot{\gamma} = \frac{d_0}{d} \sinh \left( \frac{V \tau_e}{kT} \right) \exp \left( - \frac{\Delta F}{kT} \right),$$  \hspace{1cm} (2.6)

where $d_0$ is the characteristic elongation rate for a grain of size $d$; $\tau_e$ is the applied stress, and $V (\approx b^3)$ and $\Delta F$ are the mean values of a distribution of the activation volume and the activation energy respectively for the localized grain boundary diffusion processes. Conrad et al. [39] employed the similar assumptions and the thermal-activated shear concept to propose a phenomenological model with a further interpretation of the rate limiting factor as the follows,

$$\dot{\gamma} = N_v Ab v \exp \left( - \frac{\Delta G(\tau_e)}{kT} \right),$$  \hspace{1cm} (2.7)

where $b$ is the atomic diameter; $A=b^2$ is the area swept out per successful thermal fluctuation; $N_v = \delta/db^3$ ($\delta \approx 3b$ is the grain boundary width) is the number of places per unit volume where the thermally-activated shear can occur; $\Delta G = (\Delta F - V \tau_e)$ is the Gibbs free activation energy; $v \approx 10^{13} s^{-1}$ is the Debye frequency of vibration. Therefore it can be derived that $d_0 = 6bv$ in Eq. (2.6), i.e.,

$$\dot{\gamma} = 6bv \frac{d}{d} \sinh \left( \frac{V \tau_e}{kT} \right) \exp \left( - \frac{\Delta F}{kT} \right),$$  \hspace{1cm} (2.8)

Grain boundary sliding is a thermally activated process in super-plasticity, and what is observed in MD simulations is caused by the high stress/strain and can occur at ambient temperature [78]. Grain sliding over finite distance usually changes the grain shapes, so such deformation requires other mechanisms to accommodate the misfit and
maintain the grain boundary compatibility [79, 86]. It still needs more research to understand how important grain boundary sliding is to the nanocrystalline metals and alloys.

### 2.6.4 Grain boundary diffusion creep

Grain boundary diffusion creep is also referred as Coble creep, and it is an irreversible plastic deformation mechanism which involves with flow of vacancies along the grain boundary under applied stress in order to restore the equilibrium condition, in addition to the Nabarro-Herring diffusion, in which vacancies flow through the crystalline matrix [98]. The two creep mechanisms are illustrated in Fig. 2.25. The creep deformation usually become important when the materials are subjected to stress under long period of time and at high temperature.

Grain boundary diffusion-mediated creep (Coble creep) has been proposed in the early studies to take account of the plastic deformation of nanocrystalline metals at the room temperature [38, 58], and it has also been proposed as the accommodation mechanism to the grain boundary sliding [3, 99], which is discussed in the previous section. Yamakov and coworkers observe the diffusion creep deformation of simulated NC
palladium microstructures using molecular dynamic simulations at elevated temperature without grain growth issue [99]. In order to prevent grain growth, the samples were created in such a way that the microstructure had uniform grain size and grain shape with random orientation distribution and with only high angle grain boundaries. They commented that at room temperature Coble creep is still the possible accommodation mechanism for grain boundary sliding due to the high disordered grain boundaries. Wang et al. carried out experimental tensile and creep tests on electrodeposited NC Ni samples with a mean grain size in the range from 6–40nm at room temperature, and the creep tests were performed as the follows. For the static creep test, the samples were loaded at a certain stress level in 10 seconds and held for a given period of time, and in the dynamic creep tests the samples were loaded with different stresses and strain. They concluded from the static and dynamic creep tests that in smaller grain sizes diffusion creep mechanisms can be very important and therefore contribute to the inverse Hall-Petch relation of strength and grain size [58]. Markmann et al. carried out tensile creep tests on NC Pd with mean grain size of 10nm processed by consolidation of nanoclusters, and they found under small stress and at room temperature the samples undergoes creep rate that is compatible quantitatively with the estimated Coble creep, for example strain rate of $10^{-10}/s$ is measured when the stress is 10MPa [86, 95].

However whether the creep mechanism is a possible deformation mechanism when the grain size is in the lower end of the nano range is still controversial. Molecular dynamic simulations show that the coble creep deformation not feasible even for nanocrystalline materials at room temperature. Studies carried out by Wang and his co-worker on electrodeposited Ni concluded that the thermally-activated deformation processes, such as coble creep and grain boundary sliding may not be the dominant mechanisms for the average grain size of $\sim$30nm over a range of temperature of 77K-373K. No preferred direction has been observed in the free volume flow as what is expected from Coble creep at room temperature, and Coble creep usually occurs at high temperature where the grain boundaries become unstable, so the extrapolation of diffusion creep to the room temperature has been doubted [3]. The results/conclusion of Markmann et
was questioned by Weissmuller et al., because of the uncertainty associated with the extrapolation of grain boundary diffusion coefficients, which are measure at high temperature, to ambient temperature, and no steady state creep was reported by Markmann et al. [86]. Evidence for creep is available in the tests under extremely slow strain rate, but not in the quasistatic deformation [58], for example strain rate of $10^{-10}/s$ was established when the stress is 10MPa, and the stress for diffusive creep varies linearly with the strain rate, so it can be predicted that in order to achieve strain rates that are on the order of $10^{-1}/s$, stress on the level of $10^{10}$, which is un-physically high, must be applied [86]. The numerical simulations carried out by Ortiz and co-workers also have suggested that the coble creep deformation would require much higher stress level than what is currently observed.

### 2.6.5 Grain rotation and grain growth

Either grain boundary emission of dislocation/partial dislocation or grain boundary sliding, which are the two important deformation mechanisms proposed lately for nanocrystalline metals and alloys, can give rise to grain rotation and cause the materials’ texture to change. Shan and coworkers studied the deformation of nanocrystalline Ni with an average grain size of $\sim$10nm, which was subjected to in situ TEM tensile staining, and they found grain rotation caused the rapid formation of grain aggregates [100]. Chen et al. argued that grain rotation is due to the ambient temperature grain growth caused by the applied stress [101].

The observation of texture elimination in the nanocrystalline metals has also lead to the discussion of grain growth and grain rotation as the possible deformation mechanisms [28, 95, 100, 101]. Markmann and coworkers studied the deformation processes of nanocrystalline Palladium produced by consolidation of nanoclusters. The samples have mean grain size on the order of 6–40nm, and they were deformed by successive cold-rolling passes at ambient temperature. The presence of random texture was found and equiaxed grains still remained in the samples even after large deformation. They suggested grain boundary sliding and grain rotation could be part of the defor-
Figure 2.26: (a) The fiber texture of the as-electrodeposited nc Ni, (b) the random texture of the electrodeposition Ni after HPT, and (c) nc Ni produced by HPT processing of CG Ni. [28]

Liao et al. carried out the high pressure torsion simulations on electrodeposited nickel, and HRTEM and X-ray diffraction were applied to analyze the microstructure of the sample. A duplex $<111>/<001>$ fiber texture was observed before the deformation, but after deformation it was found that the fiber texture was completely erased, which is illustrated in Fig. 2.26. They also found a substantial growth of the nanograins, shown in Fig. 2.27. They claimed that under stresses that are large enough, the NC materials would undergo grain growth which they considered as one of the main reasons to cause the texture elimination. In addition to grain growth, grain rotation is suspected to play a role in the situation [28]. Grain growth is also observed by Zhang and Weertman in their studies of nano indentation of nanocrystalline copper [34], and is reported by Malow et al. [96].
Figure 2.27: The histograms of the as-electrodeposited Ni (a) before (b) after deformation. The substantial grain growth is shown here [28].
Chapter 3

AKK Model of Deformation Mechanisms and Their Transitions

When the grain size of polycrystalline metals transits through the micrometer down to the nanometer there are accompanying transitions in the mechanisms of inelastic deformation as well as significant changes in constitutive properties including, \textit{inter alia}, levels of strength, strain rate sensitivity, and strain hardening. There is direct experimental evidence for these transitions (see \textit{e.g.} [102, 103, 104, 105]), theoretical evidence \textit{vis-a-vis} molecular dynamics simulations of nanocrystalline deformation [71, 72, 73], as well as suspicions that arise from what is known about the mechanisms of plastic deformation in crystalline metals. For example, in FCC metals with grain sizes in the micron, and larger, size range plastic deformation occurs \textit{via} the generation and motion of intragranular slip, \textit{i.e.} dislocation motion. This process is evidently shut off at grain sizes somewhat below a micron. The deformation mechanisms proposed to elucidate the extraordinarily high strength and high strain rate sensitivity of nanocrystalline metals and alloys include full/partial dislocation nucleation and emission from the grain boundaries, grain boundary sliding, diffusion creep, deformation twinning, \textit{etc.}, as reviewed in the

55
last chapter. There are still questions with regards to whether there is a characteristic grain size range that each of the deformation mechanisms can dominantly operate, and how the deformation mechanisms transit between each other.

Recently Asaro, Krysl, and Kad [4] developed a simple, yet compelling, mechanistic model, which is called AKK model by the authors, for the most likely scenario for the anticipated transitions in deformation mechanisms that appears to be quite consistent with experimental observations that exist to date, and which leads to a complete constitutive theory amenable to computational analysis. The model is based on the notion, which is shown to follow naturally from dislocation and partial dislocation mechanics, that at grain sizes below say 200-300nm deformation occurs via grain boundary dislocation emission; at grain sizes below, say 20 – 30nm deformation may occur instead by the emission of partial dislocations or deformation twins, and at even finer grain sizes deformation occurs by grain boundary sliding. These mechanisms, and their characteristic grain sizes, are influenced by temperature, lattice spacing, and stacking fault energy, as illustrated below. In fact stacking fault energy, *inter alia*, is revealed to be a particularly important factor in determining deformation mechanism and strength level. Moreover, it is shown that the proposed mechanisms lead to an inherent strain rate sensitivity that is associated with the various mechanisms and that is also part of deciding which mechanism is dominant at a particular imposed strain rate.

Fig. 3.1 and Fig. 3.2 explain how Asaro *et al.* interpret the emission processes of a perfect dislocation and a leading partial dislocation in the model of Asaro-Krysl-kad [4]. As a segment of the perfect dislocation is emitted from the grain boundary, it would move across the grain and create two addition dislocation segments on the grain boundaries under sufficient stress, as illustrated in Fig. 3.1. For the grain boundary emission of partial dislocation, shown in Fig. 3.2, as the segment is emitted into the grain it creates two trailing segments in the “side grain boundaries”, and in the case of a partial dislocation a stacking fault within the grain. If the Burger’s vector, $b$, of the perfect dislocation in Fig. 3.1 is taken to be $(a/2)[110]$, then the energy required to create a unit length of these segments is on the order of $1/2Gb^2$, where $b$ is the magnitude of
the Burger’s vector and $G$ is the shear modulus, for the perfect dislocation. Illustrated in Fig. 3.1, when the dislocation segment is moved into the grain with a distance $\delta x$, and if the resolved shear stress is $\tau$, then the required minimum work done by $\tau$ to do the work of creating the two residual segments in the side boundaries will be $\tau b \delta x d$, and it should be equal to the line energy of the two dislocation segments, whose length is $\delta x$, i.e.,

$$
\tau b \delta x d = 2(1/2Gb^2)\delta x
$$

$$
\tau = Gb/d,
$$

(3.1)

where $d$ is the grain size. Therefore the resolved shear stress required to move perfect dislocation into grain is on the order of $Gb/d$. The $d^{-1}$ scaling of stress level derives simply from the fact that the area over which work can be performed by the applied shear stress itself scales with $d$ for a given $\delta x$. As noted by AKK [4], this leads to forecasted
shear stresses that are too high for grain sizes less than, say 20-30nm for typical FCC metals for which data exists. Eq. (3.1) is only applicable to grain sizes that are not so small. When the grain size is small enough to approach the spacing between FCC partial dislocations, the case of partial dislocation emission should be examined.

For the case of partial dislocation emission from the grain boundary, illustrated in Fig. 3.2, as the leading partial dislocation travels through the grain, it also leaves stacking fault energy behind itself, so the energy of creating two trailing segments in the side boundaries are not the only factor that decides the material strength, but the additional requirement of creating a stacking fault is another very important factor, and as later shown by Asaro et al., stacking fault energy has significant effect on the deformation of nanocrystalline FCC metals and alloys. The energy required to generate unit length of trailing segments in the side grain boundaries is $1/6Gb^2$ due to partial dislocation emission, which can be simply explained by the fact that for a Schockley partial dislocation in a FCC crystal, the magnitude of the Burgers vector is $b_{\text{partial}} = \gamma \frac{\delta x d}{2}$.
$1/\sqrt{3b_{\text{perfect}}}$. As evident, $b \equiv b_{\text{perfect}}$ is the magnitude of the perfect Burgers vector. Similarly the contribution from the grain boundary emission of partial dislocations to the required stress is $1/3(1/2Gb^2)$, which is a reduced requirement for work associated with the residual segments in the side boundaries (owing to their lesser energy per unit length), but now the additional requirement of creating a stacking fault with an energy $\Gamma$ per unit area. The total stress required to create the two additional segments is analyzed by the extended dislocation mechanics in the AKK model for the partial dislocation emission case [4]. The geometry used in the derivation is the follows: the slip plane normal is $m = (1/3^{1/2})[111]$, and the slip direction $s = (1/2^{1/2})[10\bar{1}]$, and the third vector that is normal to $m$ and $s$ is named $z$. Assume the applied stresses on the slip plane along directions $s$ and $z$ are $\tau_{ms}$ and $\tau_{mz}$. The result of AKK model for the emission criterion is:

$$\{(\tau_{ms}/G)b_1^{(1)}/|b| + (\tau_{mz}/G)b_z^{(1)}/|b|\} = \frac{(\alpha - 1)}{\alpha}\tilde{\Gamma} + 1/3b/d \quad (3.2)$$

where $b_s, b_z$ are the Burger’s vectors, and $\delta_{eq}$ is the equilibrium spacing of the Shockley partials, and $\alpha \equiv d/\delta_{eq}$ and $\tilde{\Gamma} \equiv \Gamma/Gb$. Thus if define resultant resolved shear stress as the follows,

$$\tau^{(\alpha)} \equiv \tau_{ms}b_1^{(1)}/|b| + \tau_{mz}b_z^{(1)}/|b| \quad (3.3)$$

then one can obtain

$$\tau^{(\alpha)}/G \approx 1/3b/d + \frac{(\alpha - 1)}{\alpha}\tilde{\Gamma}, \quad (3.4)$$

which is AKK’s eq. (7) in [4]. Recall that $\delta_{eq}$ is defined as the equilibrium spacing of Shockley partial dislocations in the absence of applied stress and is given as,

$$\delta_{eq} = \frac{1}{12\pi}(Gb^2)/\Gamma. \quad (3.5)$$

The extended partial dislocations usually transverse the entire grain. Thus the spacing between the leading and trailing partial is the grain size, i.e., $\delta = d$. Eq.(3.4) is proven to predict material strength more accurately than Eq.(3.1). The numerical predictions of Eq. (3.2) and Eq. (3.5) by Asaro et al. are shown in Table 3.1,
Table 3.1: Numerical predictions of strength, equilibrium spacing, and the reduced stacking fault energy using Eq. (3.5) and Eq. (3.2) [4].

<table>
<thead>
<tr>
<th>Stress (MPa)</th>
<th>d=50nm</th>
<th>d = 30nm</th>
<th>d = 20nm</th>
<th>d = 10nm</th>
<th>$d_{eq}$(nm)</th>
<th>$\Gamma/\Gamma_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>211</td>
<td>2481</td>
<td>291</td>
<td>421</td>
<td>1.6</td>
<td>1/250</td>
</tr>
<tr>
<td>Ni</td>
<td>960</td>
<td>1027</td>
<td>1115</td>
<td>1381</td>
<td>0.5</td>
<td>1/100</td>
</tr>
<tr>
<td>Ag</td>
<td>125</td>
<td>158</td>
<td>198</td>
<td>321</td>
<td>3.4</td>
<td>1/447</td>
</tr>
<tr>
<td>Pd</td>
<td>719</td>
<td>763</td>
<td>820</td>
<td>988</td>
<td>0.54</td>
<td>1/75</td>
</tr>
</tbody>
</table>

Asaro et al. estimated the transition from perfect dislocation emission to partial dislocation emission would occur at the grain size by simply equating $(b/d)$ to Eq. (3.4) as,

$$(b/d) = \frac{1}{3}(b/d) + \tilde{\alpha} \tilde{\Gamma},$$

(3.6)

where $\tilde{\alpha} \equiv \frac{(a-1)}{a}$. For Ni, $\tilde{\alpha} \approx 1$ and the estimate is that the transition would occur at a grain size of approximately $d \approx 70b$, or $d \approx 20\text{nm}$! The implications of such transitions for polycrystalline response will be illustrated below via our simulations. Asaro et al. explored the effects of material parameters such as stacking fault energy, modulus, and lattice parameter, inter alia, and successfully explain some key trends described in the existing literature. Table 3.1 illustrates the role of stacking fault energy in deciding the strength limits of the nanocrystalline FCC metals.

An example of experimental data are is shown to illustrate the consistency of these predictions, and those to follow, and what is known experimentally. Figure 3.3 shows stress vs. strain data for tension for electrodeposited Ni with a mean grain size of approximately 20nm. In the first place, note that for this Ni the ultimate strength at the highest imposed strain rate ($\dot{\varepsilon} = 4.5 \times 10^{-3} \text{s}^{-1}$) is approximately $\sigma_{ult} \approx 1800 \text{MPa}$. If $\sigma \approx 2\tau$ is taken at yield and just after, the above with data typical of Ni (see Table 2), suggests that $\sigma_{ult} \approx 2 \times 1115 \text{MPa} = 2230 \text{MPa}$, which is of the order of the observed ultimate strength but is somewhat larger than the experimental value of 1800 MPa. This difference is reconciled by analyzing the polycrystal with a suitable grain size distribution.
Figure 3.3: Tensile behavior of nanocrystalline pure Ni with average grain size of 20nm. Electrodeposited nanocrystalline Ni was obtained in the form of 80mm × 80mm foils, 200µm thick, from Goodfellow Metals. Dog bone shaped tensile specimens were cut, via EDM, with gauge dimensions 500µm × 200µm. The gauge length was 12mm. Tests were conducted quasi-statically in an mechanically driven Instron test system at 20°C at the strain rates indicated [44].

as fitted to experimentally determined size distributions. Note the essential absence of strain hardening which may be also forecast from the AKK model as described by eq. (3.2). There is, however, much more that requires comment concerning the initiation of either perfect or partial dislocations from grain boundaries that requires comment. Such discussion is provided below.

Between the highest strain rate imposed and the lowest, viz. $\dot{\varepsilon} = 4.5 \times 10^{-5}$ s$^{-1}$, there is an approximately 200 MPa reduction in flow stress! Thus there is indeed a significant sensitivity to strain rate which, if analyzed via a power law as given above, would be estimated in the range $1/m \approx 25$. This order of magnitude will be used later vis-à-vis a phenomenological power law kinetic expression for the shear rate. A value of $1/m \approx 25$ is also consistent with the trends shown for the data of Fig. 2.12, as noted in
Asaro and Suresh [52] have recently explored mechanisms involved in the nucleation of either perfect or partial dislocations as well as deformation twins from grain boundaries for the specific purpose of rationalizing the above mentioned trends of increasing strain rate sensitivity in nanocrystalline fcc metals. Their analysis reveals the influence of both the intrinsic stacking fault energy and the so-called unstable stacking energy introduced by Rice [65] in his analysis of dislocation emission from a crack tip. Asaro and Suresh [52] indeed demonstrate how at grain sizes below 20nm, or so, the activation volume for such emission processes falls to low values on the order of $10^{-20} \text{b}^3$ and, accordingly, the strain rate sensitivity exponent, $1/m$, becomes on order of $20 - 30$ or less. Strain sensitivity parameters that are consistent with the results of Asaro and Suresh are suggested to be used. It is evident, therefore, that there is a very strong sensitivity of mechanisms and overall response to grain size and this will influence the response of nanostructured polycrystals.

When the grain size is in the very lower end of the nanometer range, grain
boundary sliding has been proposed to accounts for the plastic deformation of NC metals by Conrad et al. \cite{conrad2000boundary}. Grain boundary sliding is a thermally activated process, which depends on the temperature, strain rate and activation energy, etc. The modal of AKK utilized the phenomenological relation between stress and strain proposed, shown in Eq. (2.8), by Conrad and coworkers. Given strain rate and material parameters, such as lattice vibrational frequency, grain size, activation energy, and activation volume for the thermally activated process, then the driving stress required to start the sliding can be solved by Eq. (2.8). Numerical predictions for Ni and Cu at grain size that covers from 10nm to 50nm are calculated by Asaro et al., and the results are shown in Fig 3.4, which also included the predictions of Eq. (3.2) for Ni and Cu at the strain rates of \(3.44 \times 10^{-4}\) and \(5.66 \times 10^{-5}\) respectively. By looking at the cross point of the predictions from Eq. (3.2) and Eq. (2.8), the transitional grain size from grain boundary emission of partial dislocation to grain boundary sliding can be approximated as 32nm for Cu at the given strain rate, for example. However the strain rate shown in Fig. 3.4 are apparently too low, so it might be necessary to better quantify the contribution by grain boundary sliding.

In conclusion, the AKK model by Asaro et al. suggests there are two possible transitions from grain boundary emission of perfect dislocation to grain boundary emission of partial dislocation, and from grain boundary emission of partial dislocation to grain boundary sliding, and the transitional grain sizes depend on the stacking fault energy, strain rate, temperature, etc, shown in Eq. (3.2) and Eq. (2.8).

### 3.1 Acknowledgement

Chapter 3 is partially a reprint of the material as it appears in Acta Materialia 2006, Baozhi Zhu; Robert J. Asaro; Petr Krysl; Kai Zhang; Julia R. Weertman, Elsevier Press 2006. The dissertation author is the principle investigator and author of this paper.
Chapter 4

A Constitutive Model

4.1 Perspective on Discreteness

To begin, it is revealing to inquire as to the actual number of dislocations or stacking faults that would need to be emitted into a typical grain whose dimensions are on the order of, say 20 or 30 nanometres. Figure 4.1 presents a simple analysis of this for perspective. The important point to be illustrated here is that to induce strains that are less than, say 10%, the number of defects involved in a given grain is itself
quite modest and typically less than 10. This, in turn, illustrates the rather discrete nature of the deformation process that occurs in grains of this size. We will, nonetheless, view the process in what follows as occurring in a continuous manner despite its obvious discrete nature. For analyzing polycrystalline regions, this is viewed as representing suitable averaging. In other words, we take the view that the discrete slip increments given grains undergo over a short time scale on the order of $10^{-6}$s can be time-stretched over much longer times, provided the average ensemble’s strain increment is the same in both cases. This means that in the analysis, and at any given moment, the number of defects emitted will be non integer, yet the average plastic strain in a representative polycrystalline aggregate will be equal to what would have been produced by discrete slip events in a discrete group of grains.

4.2 Dislocation and Partial Dislocation Slip Systems

The slip systems associated with perfect dislocations are the usual 12 (or 24) FCC systems involving the octahedral \{111\} planes, and the face diagonal <110> directions lying within those planes. The choice of 12 or 24 is simply one of allowing the slipping rate to possess algebraic sign or to be strictly positive, respectively. In the latter case, slip systems describing slip in positive and negative directions are required. Figure 4.2 illustrates the kinematics associated with partial dislocations, which are themselves associated with parent perfect dislocations. The parent, i.e. perfect, dislocation Burgers vector is denoted as $\tilde{b}$. Partial systems are associated with each parent FCC slip system, and for our purposes we may restrict attention to slipping along only a single sense along each <110> direction. This is because each perfect slip system naturally defines two partial systems, one for slip along the parent <110> direction and the second for slipping in the anti direction. Thus slip in what may be referred to as the + and − directions, in any \{111\} plane, can be described by 24 partial systems. Note that partial slip events occur in particular sequences, e.g. slipping over the perfect Burgers vector, $\tilde{b}$, occurs in the sequence, $\tilde{b}^+$ followed by $\tilde{b}^-$. Slipping in the direction $-\tilde{b}$ on the other hand
occurs in the sequence $-\tilde{b}^-$ followed by $-\tilde{b}^+$. Now we recall that slip events involving partial dislocations, *i.e.* the emission of stacking faults into the grains, involves emitting only the leading partial dislocation. Therefore from the perfect slip system, $(m, b)$ we

![Diagram of partial dislocation slip systems](image)

Figure 4.2: Partial dislocation slip systems.

obtain the two partial slip systems, $(m, b^+)$ and $(m, -b^-)$. Table 2 lists the 24 such partial slip systems, each associated with a perfect slip system.

The restriction of allowing only the “leading” partial dislocation to be emitted derives from several rationales. First, we recall from the dislocation analysis above that on energetic grounds the emission of a single partial dislocation is favored over the emission of a perfect dislocation at sufficiently small grain sizes. Secondly, and entirely consistent with this view, are the results of a series of molecular dynamics simulations performed by Van Swygenhoven and co-workers [71, 72, 73], which show the same phenomena as summarized below.

Before reviewing this, however, the complete list of partial dislocation, *i.e.* stacking fault based, slip systems is provided in Table 4.1.

These will provide the basis for developing the kinematics of slip *via* the emission of partial dislocations from grain boundaries. We will not include, in what follows,
Table 4.1: List of faulting system

<table>
<thead>
<tr>
<th>Plane</th>
<th>Vector</th>
<th>$b^+$</th>
<th>$b^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(111)</td>
<td>[101]</td>
<td>[112]</td>
<td>[211]</td>
</tr>
<tr>
<td>(111)</td>
<td>[011]</td>
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<td>[211]</td>
</tr>
</tbody>
</table>

the specific mechanism of deformation twinning as, for example, analyzed by Asaro and Suresh [52] (2004), but note that in the context of the present analysis the criteria for twin emission would be similar to that used here for partial dislocation emission.

4.3 Perspectives from Molecular Dynamics Simulations

The simulations performed by Swygenhoven and co-workers, noted above, have provided much insight into the process of stacking fault emission in sufficiently small grains. Figure 4.3 illustrates an example of stacking fault emission in Ni taken from their simulations. The stacking fault is indicated in orange and the grain boundary atoms are colored as blue. The fault is shown at a particular time as it passed through the grain as it, in fact, did in this simulation. There are several aspects to the computed phenomenology that are directly relevant to the development of a continuum theory for such deformation.

The partial dislocations observed in such simulations are generally observed to
transit entirely across individual grains, yet on occasion multiple faults in a grain will interact and appear to block each other. Such occurrences may, in fact, give rise to at least modest levels of strain hardening. When faults are preferred (over for example grain boundary sliding which is preferred at very fine grain sizes), only the leading partial dislocations are observed, as described and rationalized above. The leading edge of faults, i.e. the partial dislocations themselves, are generally not perpendicular to the “side boundaries” as is readily apparent in the figure. This suggests that there is resistance to motion of the partial dislocation within the side boundaries. This, in turn, may derive from the need to create segments of partial dislocations in the side boundaries. Imagine for example, that the partial dislocation were observed to be tangent to the side boundary. This would mean the partial dislocation would exert a line tension force on the boundary equal to its energy per unit length, which is as noted above, equal to \( \frac{1}{2} G b_{\text{partial}}^2 \). This leads to the same picture as outlined above for the required shear stress for partial motion. But this particular simulated event shows an angle much greater than 0 which, of course, indicates that less work is being performed at these side boundaries. This has direct relevance to the discussion associated with Figure 3.2 and the effect of the first term in eq. (3.4) and with a possible, albeit partial, explanation of the rate sensitivity seen in Figure 3.3.

### 4.4 A Continuum Theory for Deformation via the Emission of Stacking Faults

With the perspectives offered above, a continuum theory for deformation of nanocrystalline metals, via the emission of stacking faults, can be constructed as follows. Suppose that \( n^{(\alpha)} \) stacking faults have been emitted on the \( \alpha \) fault system within a given grain during the time period \( T \), where each contributes a strain \( \Delta \epsilon^{(i)} \), then the average
strain rate they contribute during that time interval would be,

$$\dot{\epsilon}_p = \frac{1}{T} \sum_{i=1}^{n^{(\alpha)}} \Delta \epsilon^{(i)}.$$  \hspace{1cm} (4.1)

Next realize that, as described by Table 2, there are some 24 distinct fault systems that are, in general, activated in parallel. The total strain rate is then, following the example of relation eq. (4.1),

$$\dot{\epsilon}_p = \frac{1}{T} \sum_{\alpha=1}^{n} n^{(\alpha)} \Delta \epsilon^{(\alpha)},$$  \hspace{1cm} (4.2)

where, after examining Fig. 4.1, we identify $\Delta \epsilon^{(\alpha)}$ as

$$\Delta \epsilon^{(\alpha)} = \frac{1}{d} b^{(\alpha)} m^{(\alpha)}.$$  \hspace{1cm} (4.3)
In eq. (4.3), $\mathbf{b}^{(\alpha)}$ is the Burgers’ vector of the $\alpha^{th}$ fault system, and $\mathbf{m}^{(\alpha)}$ is the normal to the plane that fault acts on. At this point the approximation is made of taking the time average over a single nano-grain, or an ensemble average over many such nano-grains, to obtain,

$$\dot{\epsilon}^P = \sum_{\alpha=1}^{n} \dot{n}_g^{(\alpha)} \frac{1}{d} \mathbf{b}^{(\alpha)} \mathbf{m}^{(\alpha)}.$$

(4.4)

The above relation is to be calibrated vis-a-vis the data shown in Figure 3.3.

To this end we recall that the data shown in Fig. 3.3 which reveals a clear rate sensitivity. We assume that this arises from the rate dependent process of producing what we have referred to as the side boundary partial dislocation segments whose energy was described as, $\frac{1}{6} G b^2$ above in addition to the nucleation of dislocations as described, for example, by Asaro and Suresh [52]. At sufficiently low rates of deformation we assume that the need for such segments is precluded. Thus we postulate a kinetic law for $\dot{n}_g^{(\alpha)}$ as

$$\dot{n}_g^{(\alpha)} = \begin{cases} \dot{n}_0 \left\{ \frac{\tau^{(\alpha)}/G - \tilde{\alpha}\tilde{\Gamma}}{g^{(\alpha)}} \right\}^{1/m} & \text{if } \tau^{(\alpha)}/G - \tilde{\alpha}\tilde{\Gamma} > 0 \\ 0 & \text{otherwise} \end{cases}$$

(4.5)

where

$$g^{(\alpha)}(n) = \frac{1}{3} b/d + f(n).$$

(4.6)

Some additional explanation is required at this stage of development. In eq. (4.5), the rate of generation of faults, $\dot{n}_g^{(\alpha)}$, represents the rate of generating faults in the entire grain; accordingly we can define the rate $\dot{n}^{(\alpha)} = \frac{1}{d} \dot{n}_g^{(\alpha)}$ as that per unit length of grain boundary. If, however, faults are preferentially generated at grain boundary triple points, there may well be a grain size dependence to this generation rate. Now, fault generation is only possible, if the driving stress is sufficient to do the work of creating the associated stacking faults and this is reflected by the fact that $\dot{n}_g^{(\alpha)}$ and $\dot{n}^{(\alpha)}$, would vanish if $\tau^{(\alpha)}/G - \tilde{\alpha}\tilde{\Gamma} \leq 0$. At sufficiently low rates of deformation, fault generation would ensue as long as, as noted $\tau^{(\alpha)}/G - \tilde{\alpha}\tilde{\Gamma} > 0$, but at high deformation rates $\tau^{(\alpha)}/G - \tilde{\alpha}\tilde{\Gamma}$ would have to be a significant fraction of $g^{(\alpha)}$; how significant would, of course, depend on the strain
rate sensitivity parameter, $1/m$. As noted below, during the discussion of calibration, the numerology associated with the data of Fig. 3.3, suggests that $1/m \sim \mathcal{O}(20)$ or $\mathcal{O}(30)$; for that matter the same data suggests that $\dot{n}_0 \sim \mathcal{O}(5 \times 10^{-2}) - \mathcal{O}(5 \times 10^{-1})$. The interchapters of emitted faults represent impediments to continued fault propagation, and this represents a form of strain hardening. To account for this, the phenomenological term $f(n)$ has been included. Here, and as an example, $n \equiv \sum_{\alpha=1}^{n} n^{(\alpha)}$ and $f(n)$ describes an increase in the resistance to generating and fully emitting faults as faults accumulate within a given grain.

Finally, let $b^{(\alpha)} = b^{(\alpha)} s^{(\alpha)}$, i.e. let $s^{(\alpha)}$ be a unit vector along $b^{(\alpha)}$ and $b^{(\alpha)}$ is the magnitude of the partial dislocation Burgers’ vectors, that we immediately note are all crystallographically equivalent in a FCC crystal. Thus, since $b^{(\alpha)} = \bar{b}$, for all systems we can write,

$$
\dot{\epsilon}^p = \sum_{\alpha=1}^{n} \dot{n}^{(\alpha)} \bar{b} s m = \sum_{\alpha=1}^{n} \dot{\gamma}^{(\alpha)} s m,
$$

where

$$
\dot{\gamma}^{(\alpha)} = \begin{cases} 
\frac{1}{d} \dot{\gamma}_0 \left\{ \frac{\tau^{(\alpha)}}{g^{(\alpha)}} \right\}^{1/m} & \text{if } \frac{\tau^{(\alpha)}}{G - \tilde{\alpha} \bar{\Gamma}} > 0 \\
0 & \text{otherwise}
\end{cases}
$$

and where we may define a reference shearing rate as $\dot{\gamma}_0 \equiv \frac{1}{d} \dot{\gamma}_0 \bar{b}$ so that eq. (4.8) becomes,

$$
\dot{\gamma}^{(\alpha)} = \begin{cases} 
\dot{\gamma}_0 \left\{ \frac{\tau^{(\alpha)}}{G - \tilde{\alpha} \bar{\Gamma}} \right\}^{1/m} & \text{if } \frac{\tau^{(\alpha)}}{G - \tilde{\alpha} \bar{\Gamma}} > 0 \\
0 & \text{otherwise}
\end{cases}
$$

### 4.5 A Composite Model for Grain Boundary Sliding

As noted above, when the grain size is sufficiently small deformation may occur via grain boundary sliding (GBS). This was described in the AKK model via the phenomenological kinetic relations proposed by Conrad and Narayan [39]. Figure 4.4 above illustrates a composite scenario for such dual deformation mechanisms. This model assumes that that as individual nanocrystalline grains deform by the emission of stacking
faults, they may also flow past each other via sliding along their mutual boundaries. The result would be the formation of shear zones, highlighted in “red” in the figure. As noted, Conrad and Narayan [39](2000) have recently provided a correlation between a simple phenomenological model of grain boundary sliding in nano-structured metals and available data - we use that model to attempt to provide a rationale for the transition between dislocation induced deformation and GBS. This will turn out, not surprisingly, to lead to a picture that is strain rate dependent. Figure 4.4 illustrates the scheme, consistent with their model. They construct what they refer to as the macroscopic shearing rate as,

\[ \dot{\gamma} = \frac{6b\nu_D}{d} \sinh(v\bar{\tau}/kT) \exp(-\Delta F/RT), \]  

where \( \nu_D \) is a typical lattice vibrational frequency (\( \approx 10^{13} \)), \( \nu \) is an atomic volume (taken as \( b^3 \) by them), and \( \Delta F \) is an activation energy for localized lattice/grain boundary diffusion. We further propose to interpret this shearing rate as an effective plastic strain.
rate within the framework of an isotropic flow theory, in particular $J_2$-flow theory. In eq. (4.10), $\bar{\tau}$ is an effective shear stress defined as $\bar{\tau} = \sqrt{\frac{1}{2} \sigma'_ij \sigma'_ij}$, so that $\bar{\tau} \dot{\gamma}$ represents the rate of working per unit volume of material. $J_2$-flow theory assumes that the plastic part of the rate of deformation, $D^{ps}$, is directed so that $D^{ps} \parallel \sigma'$, or given the definition of $\bar{\tau}$ that
\[ D^{ps} \parallel \partial \bar{\tau} / \partial \sigma. \] (4.11)

The flow law for this part of the deformation rate then becomes,
\[ D^{ps} = \dot{\gamma} \frac{1}{2} \sigma' / \bar{\tau}. \] (4.12)

At this point we assume that the total plastic rate of deformation is given as the sum of what is contributed by SF emission and by GBS, i.e. we take for the the rate of deformation due to SF emission $\dot{\epsilon}^p \Rightarrow D^{psf}$. Thus the total plastic part of the rate of deformation is given as,
\[ D^p = D^{psf} + D^{ps}. \] (4.13)

These specifications for the plastic parts of the deformation rate will now be inserted into a finite deformation kinematic and full constitutive framework. Associative multiplicative elasto-plasticity have been discussed by Belytschko, Moran, Miehe, etc [107, 108, 109].

### 4.6 Constitutive Framework

The material is assumed to flow through the partial dislocation slip systems and via GBS, whereas elastic deformation occurs via deformation of the lattice itself (with material embedded on it. Rigid body rotations are included in this lattice part. Hence as in Lee [106] or in the context of crystalline slip, in Asaro and Rice [68], the
deformation gradient is decomposed as,

$$ F = F^* \cdot F^p, \quad (4.14) $$

where $F^*$ and $F^p$ are the lattice and plastic parts of $F$, respectively. Note that the crystallographic vectors introduced earlier, i.e. $s$ and $m$ convect with the lattice so that in the deformed state they become,

$$ s^* = F^* \cdot s \quad m^* = m \cdot F^{*-1}. \quad (4.15) $$

Note that as $s$ and $m$ are originally orthogonal, so are $s^*$ and $m^*$. Using eq. (4.14) to form the velocity gradient we uncover its lattice and plastic parts, which can be expressed in

$$ \dot{F} : F^{-1} - \dot{F}^* : F^{*-1} = D^p + \Omega^p = \sum_{\alpha=1}^{n} \dot{\gamma}^{(\alpha)} s^* m^* + \frac{1}{2} \dot{\gamma} \frac{\sigma'}{\bar{\tau}}, \quad (4.16) $$

where all terms have meanings as described above. Now define

$$ P^{(\alpha)} = \frac{1}{2} \{ s^* m^* + m^* s^* \} \quad \text{and} \quad W^{(\alpha)} = \frac{1}{2} \{ s^* m^* - m^* s^* \}. \quad (4.17) $$

Then

$$ D^p = \sum_{\alpha=1}^{n} \dot{\gamma}^{(\alpha)} P^{(\alpha)} + \dot{\gamma} \frac{1}{2} \sigma'/\bar{\tau} \quad \text{and} \quad \Omega^p = \sum_{\alpha=1}^{n} \dot{\gamma}^{(\alpha)} W^{(\alpha)}, \quad (4.18) $$

where we have explicitly made the assumption that GBS, expressed within a $J_2$-flow theory framework contributes nothing to the plastic spin! The, as shown in Asaro and Needleman [5], the resulting constitutive relation for a crystal is given as

$$ \nabla \tau = \mathbf{L} : \mathbf{D} - \sum_{\alpha=1}^{n} R^{(\alpha)} \dot{\gamma}^{(\alpha)} \mathbf{L} : \left\{ \frac{1}{2} \dot{\gamma} \sigma' / \bar{\tau} \right\}, \quad (4.19) $$
where

\[ \mathbf{R}^{(\alpha)} = \mathbf{L} : \mathbf{P}^{(\alpha)} + \beta^{(\alpha)} \]
\[ \beta^{(\alpha)} = \mathbf{W}^{(\alpha)} \cdot \mathbf{\tau} - \mathbf{\tau} \cdot \mathbf{W}^{(\alpha)} . \]

\[ \nabla \mathbf{\tau^*} = \dot{\mathbf{\tau}} - \Omega^* \cdot \mathbf{\tau} + \mathbf{\tau} \cdot \Omega^* = \]
\[ \mathbf{L} : \mathbf{D}^* + \mathbf{D}^* \cdot \mathbf{\tau} + \mathbf{\tau} \cdot \mathbf{D}^*. \]

In eqs. (4.19) and (4.20) the two Jaumann stress rates are

\[ \nabla \mathbf{\tau^*} = \frac{\nabla}{\tau} + \sum_{\alpha=1}^{n} \beta^{(\alpha)} \dot{\mathbf{\gamma}}^{(\alpha)} , \]

where

\[ \beta^{(\alpha)} = \mathbf{W}^{(\alpha)} \cdot \mathbf{\tau} - \mathbf{\tau} \cdot \mathbf{W}^{(\alpha)} , \]

4.7 An Aggregate Model

We follow here the construction of Asaro and Needleman [5] and imagine a collection of grains all of which are characterized by a constitutive law such as given in eq. (4.19). The aggregate occupies a volume \( V \) bounded by a surface \( S_{\text{ext}} \). The region is subjected to all around displacement conditions that are taken to be such as to cause homogeneous deformations in what is assumed to be an initially homogeneous sample. Averaging theorems that rely on strict equilibrium and compatibility are available, but here we will have to relax the requirement of point-wise equilibrium as follows.

Introduce the nominal (1st Piola-Kirchhoff stress) as

\[ \mathbf{n} = \mathbf{F}^{-1} \cdot \mathbf{\tau} . \]

Note that \( \mathbf{n} \) is related to the force, \( d\mathbf{P} \), transmitted through a surface element \( \mathbf{\nu} dS \) in
the reference state via \( d\mathbf{P} = \nu \cdot d\mathbf{S} \). Now let \( \mathbf{F} \) be a deformation gradient that satisfies compatibility in each grain. Then using the divergence theorem,

\[
\int_V \mathbf{n} : \mathbf{F} dV = \sum_g \int_{V_g} \mathbf{n} : \mathbf{F} dV = \int_{S_{int}} \mathbf{\Delta T} \cdot \mathbf{u} dS + \oint \mathbf{T} \cdot \mathbf{u} dS.
\]

(4.25)

In eq. (4.25), \( V_g \) represents the volume of a grain, \( S_{int} \) represents the internal interfaces between grains (i.e. grain boundaries), and \( \mathbf{\Delta T} \) is the traction difference between the grain boundaries. Note that if point wise equilibrium held, \( \mathbf{\Delta T} = 0 \). Note also that an identity of the form eq. (4.25) holds with \( \mathbf{F} \) or \( \mathbf{n} \), or both replaced by their corresponding rates since the equilibrium equations expressed in terms of \( \mathbf{n} \) are, \( n_{ij,j} = 0 \) and in rate form \( \dot{n}_{ij,j} = 0 \) in the absence of body forces. Here, as typical, commas denote differentiation and the summation convention is used.

The homogeneous displacement boundary conditions to be imposed take the form \( \mathbf{u} = \tilde{\mathbf{F}} \cdot \mathbf{x} \) on \( S_{ext} \). Substituting this into the last integral, and rearranging terms, in eq. (4.25) gives

\[
\sum_g \int_{V_g} \mathbf{n} : \mathbf{F} dV - \int_{S_{int}} \mathbf{\Delta T} \cdot \mathbf{u} dS = \left\{ \oint_{S_{ext}} \mathbf{x} \mathbf{T} dS \right\} : \tilde{\mathbf{F}}.
\]

(4.26)

The basic assumption underlying Asaro and Needleman’s [5] averaging model is that the contributions arising from any lack of equilibrium across the grain boundaries will be small compared to the integral taken over the external surface, an approximation difficult to precisely measure in general. Invoking this assumption, however, yields

\[
\sum_g \int_{V_g} \mathbf{n} : \mathbf{F} dV = \left\{ \oint_{S_{ext}} \mathbf{x} \mathbf{T} dS \right\} : \tilde{\mathbf{F}}.
\]

(4.27)

In particular, if we specify \( \mathbf{F} \) to have the uniform \( \tilde{\mathbf{F}} \) in each grain

\[
\sum_g \int_{V_g} \mathbf{n} : \mathbf{F} dV = V \tilde{\mathbf{n}} : \tilde{\mathbf{F}},
\]

(4.28)
where
\[ \bar{n} = \frac{1}{V} \sum_g \int_{V_g} \mathbf{n} dV \quad V = \sum_g V_g. \] (4.29)

Since \( \bar{\mathbf{F}} \) is trivially the average of \( \mathbf{F} \) in the aggregate, the average Kirchhoff stress is
\[ \bar{\tau} = \bar{\mathbf{F}} \cdot \bar{n}. \] (4.30)

To put the constitutive description in terms of the nominal stress and rate of change of the deformation gradient we need only recall from eq. (4.24) that
\[ \dot{n} = F^{-1} \cdot \dot{\tau} + F^{-1} \cdot \tau, \] (4.31)

and from the definition of the Jaumann rate of Kirchhoff stress that,
\[ \dot{\tau} = \nabla \tau + \Omega \cdot \tau - \tau \cdot \Omega. \] (4.32)

These two expressions allow the constitutive relation, eq. (4.19), to be rephrased as
\[ \dot{n} = K : \dot{\mathbf{F}} - \dot{\mathbf{B}}, \] (4.33)

and if we designate individual grains with the superscript \( \eta \), the constitutive relation for the grain \( \eta \) becomes,
\[ \dot{n}^{(\eta)} = K^{(\eta)} : \dot{\mathbf{F}}^{(\eta)} - \dot{\mathbf{B}}^{(\eta)}. \] (4.34)

We recognize that when any such relation is constructed for an individual grain that it is most naturally done with respect to a set of axes that are native to the crystalline grain in question, \textit{i.e.} on crystal axes belonging to that grain itself.

### 4.8 Grain Distributions

Experimental techniques available for the full characterization of structure at the nanoscale have been primarily based on TEM and X-ray diffraction, from which the
average grain size and grain size distributions can be estimated, subject to statistical uncertainty that we specifically address here. For grain size distributions, the numbers of grains of various diameters in nanocrystalline materials can usually be well represented by a log-normal distribution function,

\[
P(D) = \frac{1}{(2\pi)^{1/2} D\sigma} \exp \left[ -\frac{1}{2} \left( \frac{\ln(D/D_0)}{\sigma} \right)^2 \right]
\]

where the symbol $D$ is used for the grain diameter and $D_0$ and $\sigma$ are constant parameters describing the median and shape parameters (i.e. the standard deviation of $\ln D$) of the distribution respectively and $\int_0^\infty P(D)dD = 1$. The arithmetic mean size $\bar{D}$ can be calculated \[110\] as

\[
\bar{D} = D_0 \exp\left(\frac{1}{2}\sigma^2\right).
\]

$\tilde{\sigma}$, the variance of $D$, is the average value of the quantity $(D - \bar{D})^2$, and is calculated from

\[
\tilde{\sigma} = D_0^2 \exp(\sigma^2)(\exp(\sigma^2) - 1).
\]

Commonly, the arithmetic mean grain size is often given by material suppliers or can be obtained from the experimental measurement; if we assume the variance $\tilde{\sigma}$ is known, then the parameters, $D_0$ and $\sigma$ which describe the lognormal distribution can be obtained by inverting eqs. (4.36) and (4.37), which yields

\[
D_0 = \sqrt[4]{\frac{\bar{D}^4}{\tilde{\sigma} + \bar{D}^2}}
\]

\[
\sigma = \exp \left( \sqrt{\ln \left( \frac{\tilde{\sigma}}{\bar{D}^2} + 1 \right)} \right).
\]

Most of the relevant available literature considers that the mean grain size, internal strains and texture obtained from TEM and XRD well describe the structure of the sample material (e.g. Dalla Torre [33]). However, there is usually considerable uncertainty associated with both of these methods (see e.g. the discussion in [111]).
For example, the question of whether a true characteristic region(s) of the sample was investigated for TEM can be routinely raised. Therefore, an uncertainty analysis on the grain size distribution is necessary, in order to provide a more accurate description of the actual behavior of the material, especially with respect to interpreting experimental specimen to specimen scatter.

We assume that the arithmetic mean grain size is given, and what is uncertain is the variance of the grain size distribution. According to eqs. (4.38) and (4.39), we obtain the parameters (the median and variance) of the lognormal distributions for a certain arithmetic mean grain size, using reasonable standard deviations. An example is shown in the left side figure of Fig. 4.5. In this the the mean grain size is taken to be 20nm, and the variance varies from 50 to 200. As noted below, this mean grain size is consistent with that measured for electrodeposited Ni as tested by Dalla Torre et al. [33] and ourselves.

However as mentioned earlier, for the current analysis of dislocation emission and grain boundary sliding, the volume-weighted grain distribution is considered to be more directly relevant than the number-weighted grain distribution as described by eq. (4.35). If one assumes each grain in the sample has the same shape, a sphere for example, then the total volume of the sample is

\[
V = \int_0^\infty kD^3 P(D) dD, \tag{4.40}
\]

where \(k\) is a constant describing the shape of the grains (e.g. \(k = \frac{4}{3} \pi \frac{1}{2^3}\) for a sphere), and the volume weighted grain size distribution is then simply

\[
P_v = \frac{kD^3 P(D)}{V}. \tag{4.41}
\]

We can then convert the lognormal distribution to a volume fraction weighted distribution according to eq. (4.41). The right side figure in Fig. 4.5 shows the volume weighted grain distributions for the above example, whereas the left side figure illustrates the frequency distribution. These distributions are illustrated via different forms below and in
specific connection to the simulated experimental results.

Figure 4.5: Grain size distributions based on an assumed mean grain size of 20nm with to different variances.
The resulting volume weighted grain distributions are then used in the aggregate model of Asaro and Needleman [5]. For efficiency, the volume weighted distributions are grouped into histograms with suitable subintervals, and the grains inside the aggregate are assigned the different grain sizes according to the relative proportions described by the histograms.

### 4.9 Acknowledgement

Chapter 4 is partially a reprint of the material as it appears in Acta Materialia 2006, Baozhi Zhu; Robert J. Asaro; Petr Krysl; Kai Zhang; Julia R. Weertman, Elsevier Press 2006. The dissertation author is the principle investigator and author of this paper.
Chapter 5

Calculation Procedure

5.1 Rotational Change of Basis

Two Cartesian coordinate systems are involved during the calculation of the mechanical response of polycrystalline metals and alloys. One is the global, or laboratory basis \( e_i \) and the other is the crystal lattice basis \( a_i^{(k)} \), where the superscript \( (k) \) indicates the \( k \)th grain. The relation between the two bases is rotation, which can be described by an orthogonal rotation matrix \( \Phi^{(k)} \), i.e.,

\[
e_i = \Phi^{(k)} a_i^{(k)}, \quad \text{or} \quad a_i^{(k)} = \Phi^{(k)} e_i, \tag{5.1}
\]

where \( \Phi^{(k)} = \Psi^{(k)T} \), \( \Phi^{(k)} \Phi^{(k)T} = I \), and \( \det \Phi^{(k)} = \det \Psi^{(k)} = 1 \).

Tensors are independent of coordinate systems, and their components in each of the coordinate systems are related as the follows, if one ignores the difference between covariant and contravariant components at the moment.

1. Vectors, such as slip directions and normals to the slip planes,

\[
r = r_i e_i = r_i^{(k)} a_i^{(k)} \tag{5.2}
\]

\[
r_i = \Phi_{ji}^{(k)} r_j^{(k)} \tag{5.3}
\]
2. Second order tensors, such as stress, strain tensors and deformation gradient,

\[ \mathbf{\sigma} = \sigma_{ij} \mathbf{e}_i \otimes \mathbf{e}_j = \sigma^{(k)}_{ij} a_i^{(k)} \otimes a_j^{(k)} \]  

(5.4)

\[ \sigma_{ij} = \Phi^{(k)}_{mi} \sigma^{(k)}_{mn} \Phi^{(k)}_{nj}, \]  

(5.5)

3. Fourth order tensors, such as elasticity moduli and tangent moduli,

\[ \mathbf{C} = C_{ijmn} \mathbf{e}_i \otimes \mathbf{e}_j \otimes \mathbf{e}_m \otimes \mathbf{e}_n = C^{(k)}_{ijmn} a_i^{(k)} \otimes a_j^{(k)} \otimes a_m^{(k)} \otimes a_n^{(k)} \]  

(5.6)

\[ C^{(k)}_{ijmn} = \Phi^{(k)}_{pi} \Phi^{(k)}_{qj} C^{(k)}_{pqrs} \Phi^{(k)}_{rm} \Phi^{(k)}_{sn}, \]  

(5.7)

The overall calculation is based on the laboratory coordinate system, so the components of quantities like slip directions, normals to the slip plane and elasticity matrix that are directly known in the crystal lattice coordinate system \( \mathbf{a}_i \) can be transformed into the laboratory basis \( \mathbf{e}_i \) through the rotational operations as in Eqns (5.3), (5.5) and (5.7).

### 5.2 Texture and Anisotropy

Crystalline metals and alloys are isotropic if the grains are randomly oriented within the materials, but on the other hand, if the grains are distributed with a preferred direction, then they are considered as anisotropic, or they have a crystallographic texture. Crystalline materials can be initially anisotropic, but crystallographic textures can also be introduced by recrystallization or plastic deformation, the latter of which occurs through irreversible slips on some crystallographic plans along certain slip directions. Anisotropy has direct effects on several aspects of materials, and it can be helpful for some applications but it can also be undesirable for the other applications. Therefore it is necessary to conduct texture analysis of this type of materials.

Spherical and stereographic projections represent visually the angular relations between crystalline directions and planes. A spherical projection of a direction is ob-
tained by placing a crystal cube in the center of an imaginary sphere and letting a line parallel to the desired direction go through the center of the sphere and intersect the surface of the sphere at a point which is called the spherical projection of the direction. The angular relation between two directions are preserved by the angular distance between their spherical projection points. A stereographic projection is to project the sphere in spherical projection onto the “equatorial plane”. For cube crystals if the projection plane is one of the crystalline planes of low indices and the projections include all the importance planes of crystal lattice, such stereographical projection is called standard stereographical projection. Due to the cubic symmetry, projections of all possible crystal directions will fall within a basic stereographic triangle for cubic crystals, \textit{i.e.} standard triangle, and its boundaries.

Pole figures are sets of points in the stereographical projection of the chosen crystal direction of all grains in the polycrystalline aggregate to the projection plane, \textit{i.e.}, the equatorial plane used in the spherical projection, of the laboratory coordinate system. If one of the crystallographic planes is taken as the projection plane, in another word if the equatorial plane is in the lattice coordinate system, then the sets of points are called the inverse pole figure. In either of the case, the points illustrate graphically the angular distribution function of a chosen crystal direction. Direct and inverse pole figures are considered to be the fundamental approaches to the documentation of texture and its evolution.

In this study, attention is paid to the formation and evolution of deformation textures due to plastic deformation especially induced by high pressure torsion and axisymmetric compression, and the inverse pole figures are employed with regards to this purpose.

5.3 Grain Orientation Distribution

Details of constructing the initial grain orientation distribution can be found in Asaro 1985. The basic procedure is the follows.
Figure 5.1: Standard triangle (Asaro and Needleman, 1985)

If a cubic crystal lattice is taken as reference and due to the cubic symmetry the laboratory $\mathbf{e}_2$ axis goes through the [100], [110], [111] standard triangle at a specific angle with respect to each individual grain orientation, as shown in Fig 5.1. The initial grain orientation distribution is created in such a way that the $\mathbf{e}_2$ axis falls uniformly within the standard triangle. An example is shown in Fig. 5.2. To approximate a uniform distribution of grain orientations, there is one point that represents the grain of the [100] orientation, i.e. the $\mathbf{e}_2$ axis shares the same orientation with $\mathbf{a}_1$ axis of the unit cube of the reference crystal lattice, and each of the rest of the points in Fig. 5.2 corresponds to three grain orientations that are $120^\circ$ apart around the $\mathbf{e}_2$ axis from each other. For example in Fig. 5.2 there are total 66 points in the standard triangle, but they correspond to a total of 196 ($1 + 65 \times 3$) grains.

For each orientation the second axis, $\mathbf{e}_1$ or $\mathbf{e}_3$, is generated with random numbers, and the third axis can be obtained through the cross product of the first two axes, for instance, $\mathbf{e}_3 = \mathbf{e}_1 \times \mathbf{e}_2$, and the rotation matrix $\Phi^{(k)} = \{\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3\}^{(k)}$. 
5.4 Deformation Texture

The procedure of plotting the inverse pole figures of a chosen direction, $\mathbf{e}$, in the standard triangle shown in Fig. 5.2 is the follows. First to express the direction vector in the lattice coordinate system as,

$$\mathbf{e} = h\mathbf{a}_1 + k\mathbf{a}_2 + l\mathbf{a}_3,$$

(5.8)

Next to scale the absolute indices with the maximum of $|h|, |k|$, and $|l|$, and plot the medium and the minimum of the scaled values in the standard triangle in such a way that the medium value is plotted horizontally and the minimum value is plotted vertically.

With such approach, the inverse pole figure of laboratory $\mathbf{e}_2$ axis for the initial texture is illustrated in Fig. 5.2. As the specimen deforms, the elastic part of the deformation gradient rotates each of the grains such that,

$$\mathbf{a}_i^* = \mathbf{F}^e \mathbf{a}_i,$$

(5.9)

so it is necessary to find out the indices of $\mathbf{e}_2$ axis in the rotated lattice coordinate system.
Due to the rotational relation between $a_i$ and $e_i$,

$$a_i = \Phi^T e_i,$$  \hspace{1cm} (5.10)

one can get,

$$a_i^* = F^e \Phi e_i.$$  \hspace{1cm} (5.11)

So the indices of $e_2$ axis in the rotated lattice coordinate system are the values in the second row of the matrix $F^e \Phi^T$. The inverse pole figures then can be easily plotted with the procedures described above.
Chapter 6

Numerical simulations

6.1 Material Data

The applications below are carried out for the case of nanocrystalline Ni, Cu, Pd and Al, whose properties are listed in Table 2 along with the grain size distributions described in the previous section. The phenomenological hardening term, \( f(n) \), in eq. (4.6) is neglected in the simulated cases presented below.

Table 6.1: Material data used in the simulations.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( G ) (GPa)</td>
<td>80</td>
</tr>
<tr>
<td>( b ) (nm)</td>
<td>0.249</td>
</tr>
<tr>
<td>( \bar{b} ) (nm)</td>
<td>0.144</td>
</tr>
<tr>
<td>( \Gamma/Gb )</td>
<td>1/100</td>
</tr>
<tr>
<td>( \delta_{eq} )</td>
<td>0.5</td>
</tr>
<tr>
<td>( \Delta F ) (kJ/mole)</td>
<td>97.5</td>
</tr>
<tr>
<td>( v ) ( (m^3) )</td>
<td>( 1.54 \times 10^{-29} )</td>
</tr>
<tr>
<td>( m )</td>
<td>0.037</td>
</tr>
<tr>
<td>( \dot{\gamma}_0 )</td>
<td>( 10^{-3} )</td>
</tr>
</tbody>
</table>
6.1.1 Grain Distributions for Nanocrystalline Ni

The grain size distributions represented in Fig. 4.5 are shown again in different form in Fig. 6.1 as functions of the variance of the distribution. In Fig. 6.2 are shown the two distributions as measured and reported by Dalla Torre et al. [33] for electrodeposited Ni and our theoretical fit using the lognormal distribution give by eq. (4.35) above. In the simulations described below, we use these distributions to describe the grain size along with the material data listed in the next section.

6.2 Tensile and compressive deformation simulations

6.2.1 Boundary Conditions

Denote the axes of a fixed Cartesian “laboratory” frame by \( e_i \) and the cube axes in the grain \( \eta \) by \( a_i \); for example, if a tensile test were being set up the tensile axis could be the \( e_2 \) axis. For a FCC crystal the \( e_2 \) axis would fall somewhere within the standard triangle whose vertexes are the [100], [110], [111] crystal directions. The initial orientation of the “laboratory” axes on with respect to the cube axes of a the typical grain \( \eta \) are described via the transformation,

\[
e_i = \Phi^{(\eta)} \cdot a_i^{(\eta)}.
\]

Note that this involves describing the orientation of each grain in a polycrystalline aggregate by the specification of its transformation tensor, \( \Phi^{(\eta)} \). Methods for constructing such distributions are discussed in detail by Asaro and Needleman [5]. For the calculations presented herein, we have taken the polycrystal as being isotropic and thus initially composed on a uniformly random distribution of grain orientations. Suppose that there are \( N \) such grains, and further suppose that each has the same initial volume, i.e. each occupies the same initial volume fraction of the aggregate. Then when averages are taken as specified in eq. (4.29) for example the aggregate’s constitutive response is described
Figure 6.1: (a) Comparison of the distributions with different variance and (b) Histogram of the distribution with mean = 20nm and variance = 100
Figure 6.2: (a), (b) Number weighted grain size distributions according to Dalla Torre et al. (2002); (c) a simulated fit to the histogram of (b) (Dalla Torre et al.’s (2000) Batch B).
by,

\[ \dot{n} = \bar{K} : \dot{F} - \dot{B}, \]  

(6.2)

where

\[ \dot{n} = \frac{1}{N} \sum_{\eta=1}^{N} \dot{n}^{(\eta)}, \]

(6.3)

\[ \bar{K} = \frac{1}{N} \sum_{\eta=1}^{N} K^{(\eta)}, \quad \dot{B} = \frac{1}{N} \sum_{\eta=1}^{N} B^{(\eta)}. \]

To use the tensile test as an example, we let the tensile axis be the \( e_2 \) “laboratory” axis; thus the line of material particles initially along the \( e_2 \) axis remaind so aligned so that,

\[ \bar{F} \cdot e_2 = \bar{F}_{22} e_2, \]

(6.4)

and

\[ \bar{F}_{12} = \bar{F}_{32} = 0, \]

(6.5)

so that that tensile fiber remains along the \( e_2 \) axis.

The remaining boundary conditions for axisymmetric loading are:

\[ \bar{T}_1 = \bar{n}_{11} = 0 \Rightarrow \dot{\bar{n}}_{11} = 0 \text{ on } x_1 = \text{ constant} \]
\[ \bar{T}_1 = \bar{n}_{31} = 0 \Rightarrow \dot{\bar{n}}_{31} = 0 \text{ on } x_3 = \text{ constant} \]
\[ \bar{T}_3 = \bar{n}_{33} = 0 \Rightarrow \dot{\bar{n}}_{33} = 0 \text{ on } x_3 = \text{ constant} \]
\[ \bar{T}_2 = \bar{n}_{12} = 0 \Rightarrow \dot{\bar{n}}_{12} = 0 \text{ on } x_1 = \text{ constant} \]
\[ \bar{T}_2 = \bar{n}_{32} = 0 \Rightarrow \dot{\bar{n}}_{32} = 0 \text{ on } x_3 = \text{ constant} \]
\[ \bar{F}_{21} = 0 \Rightarrow \dot{\bar{F}}_{21} = 0 \]

(6.6)

Note that eqs. (6.4) and (6.5) also require that

\[ \dot{\bar{F}}_{12} = \dot{\bar{F}}_{32} = 0, \]

(6.7)
and that $\hat{F}_{22}$ be specified, that is

$$\hat{F}_{22} = \text{specified stretching rate.} \quad (6.8)$$

For plane strain loading the $3^{rd}$ of eqs. (6.6) is replaced by

$$\bar{F}_{33} = 0 \Rightarrow \hat{F}_{33} = 0. \quad (6.9)$$

Other types of boundary conditions are easily specified by following the example of tensile loading described above.

### 6.2.2 Results

Figure 6.3 shows the simulated results using the grain size distributions described above for uniaxial tension at the three different strain rates we performed our uniaxial quasi-static tension tests for electrodeposited nanocrystalline Ni. The experimental uniaxial stress vs. strain curves from Fig. 3.3 have been superposed for comparison. Note that as described above, the mean grain size here was taken from the best fit to the data of Dalla Torre et al. [33] (i.e. their batch B) with a mean grain size of 20nm and our fitted variance of 100. The simulated curves are clearly below the experimental curves. The right side figure in Fig. 6.3 shows the contributions from the three deformation modes, viz. perfect and partial dislocation emission, and grain boundary sliding, to the overall tensile deformation. With this distribution, the deformation is forecast to primarily involve the emission of perfect dislocations.

The left side figure in Fig. 6.4 shows another simulated stress vs. strain curve, but with an assumed mean grain size of 23nm and variance of 70. Note that now the agreement with experiment is much better except for an apparent larger ultimate tensile stress as simulated than what the experimental curves appear to display. This apparent discrepancy is discussed in the next chapter, but here we claim the agreement is in fact quite good using a grain size distribution that nearly equally fits the Dalla Torre et
al. [33] data then does that used to obtain the results shown in Fig. 6.3. Note also that the predicted trend in strain rate sensitivity is in good accord with experiment. This agreement has been accomplished using a value of $1/m$ in complete accord with the data of Fig. 2.12, viz. $1/m \approx 27$.

The right side figure in Fig. 6.4 shows the computed contributions to the overall
tensile plastic strain for a simulated uniaxial tension test for a nanocrystal with a mean grain size of 10nm and a variance of 50. Note that with this smaller grain size there is noticeably more contribution from deformation modes including partial dislocations (i.e. stacking fault emission) and grain boundary sliding. Of course, as the temperature is increased we expect contributions from modes such as grain boundary sliding to increase further [39, 112]. It should be recalled from eq. (3.6) that, given the material properties of Ni, the grain size where we expect a transition from perfect to partial dislocation emission is approximately 20nm - this is what these simulations show, at least at ambient temperatures like 20°C.

In the next section we explore, in far more detail, the influence of grain size distribution, material properties, temperature, and strain rate on material response. This is also analyzed vis-à-vis stress and strain state via example simulations of plane strain vs. uniaxial tension and compression deformation.

6.3 Parameter Variations for Electrodeposited Ni

To understand the effect of grain size distribution, uniaxial tension simulations for nanocrystalline Ni are studied with different mean grain sizes and variances under different strain rates and temperature. It is suggested that a careful documentation of grain size distributions is crucial for studying nanocrystalline metals and alloys, our simulations show that there can be a few hundred MPa drop in the ultimate tensile stresses with the increasing of the variance, even though the mean grain size remains the same. This is simply due to the fact that more percentage of the aggregate will be constituted by large grains of lower strength, and as a result the overall strength will be reduced, when the variance increases. Figure 6.5 illustrates this relation between mechanical responses and variances for Ni with mean grain size of 10 and 20nm from left to right respectively at room temperature under quasi-static uniaxial tension.

The deformation mechanisms and their transitions in nanocrystalline metals and alloys are temperature and strain rate dependent as discussed previously. Figure 6.6
Figure 6.4: Computed stress vs. strain response (left side figure) for nanocrystalline Ni with average grain size of 23nm and variance of 60 as in eq. (4.37). Contribution to the overall plastic strain arising from the three deformation mechanisms considered but for a simulated nanocrystal with a mean grain size of 10nm and a variance of 50. All simulations are carried out at 20°C.

explains the effect of temperature and strain rate sensitivity on the mechanical responses of nanocrystalline Ni with mean grain size of 20nm and variance of 100 under uniaxial tension. The left figure shows that the ultimate tensile stresses decrease with the increasing of the temperature under quasi-static loading rate, and especially when the temperature is near 50°C the decreasing of the ultimate stresses becomes much faster;
Figure 6.5: Effect of grain size distribution on the uniaxial tensile response at room temperature with strain rate of $10^{-3}$.

while the right figure illustrates at room temperature the strain rate sensitivity of these group of materials are so strong that there can be nearly 700MPa drop in the ultimate stresses when the loading rate is decreasing from $10^{-2}$ to $10^{-5}$. Figure 6.7 shows the effect of strain rate sensitivity on mechanical responses when the material is subjected
to uniaxial con... 6.8 sum-

Figure 6.6: Simulated effect of temperature and strain rate

marizes the dependence of ultimate tensile strength on temperature for nanocrystalline Ni with different mean grain sizes and variances. It is evident that the ultimate tensile stress slightly decreases with increasing temperature up to 20°C; however, sharp drops of the ultimate tensile stresses occur when the temperature increases to 50°C and above.
Figure 6.7: Response of Ni with mean grain size of 20nm and variance of 100 at room temperature.

This observation can be justified with the understanding of the contributions of the deformation mechanisms to the total deformation, which are shown in the right figures of Figure 6.10 and Figure 6.12. These two figures share the pattern that the contributions from grain boundary sliding is trivial, and the deformation is dominated by dislocation
and partial dislocation emission, when the temperature is below 50°C; at higher temperatures the contribution from grain boundary sliding grows significantly at the early stage of the deformation, accompanied by the decreasing contributions from dislocation and partial dislocation emission, which causes the ultimate stresses to rapidly decrease.

Figure 6.8: Effect of temperature on response of nanocrystalline Ni.
In addition to Figure 6.5 and 6.6, which summarize additional data of the simulated ultimate tensile stress for nanocrystalline Ni with a mean grain size of 20nm, Figure 6.9 and the left figure of Figure 6.10 explore phenomenology expected under different tensile strain rates, temperatures, and grain size variances. These figures again show the clear trend that the ultimate tensile stress decreases with respect to increasing both the variance and temperature, as well as decreasing the loading rate. The right figure of Figure 6.10 shows the contributions of various deformation mechanisms to the total deformation vs. the total effective plastic strain. The simulation results for Ni with mean grain size of 20nm is illustrated in Figure 6.11 and 6.12. These effects are briefly discussed in the figure captions.

Similar simulations are also carried out for nanocrystalline Al and Pd at room temperature, and compared with those for nanocrystalline Ni as shown in Figure 6.13, where the ultimate stresses are normalized with respect to the shear modulus of these three types of materials to show the effect of intrinsic stacking fault energy. The ranking of the data lines in Figure 6.13 corresponds to the normalized stacking fault energies $\Gamma/\text{Gb}$, which are taken to be 0.01333, 0.01 and 0.01 for Pd, Ni and Al respectively in the numerical simulations.

### 6.4 Effect of Dynamic Grain Coarsening in Cu

As noted by Zhang et al. [34], the large excess energy associated with grain boundaries in nanocrystalline metals is expected to cause instability in their internal structure. Indeed recent experiments [61] on indentation creep in high purity nanocrystalline Cu have shown that the hardness drops rapidly as the dwell time of the indenter in the sample increases. Grain growth is observed in these cases and undoubtedly is a primary cause of the decrease in hardness. Figure 6.17 shows such results obtained by Zhang et al. [34] on Cu processed via Inert gas Condensation (IGC). Zhang et al. [34] also measured the grain size distributions after varying hold times and these are shown for one set of specimens in Fig. 6.17. Note that the material had, before indentation, an
Figure 6.9: Ultimate tensile stresses for Ni with mean grain size of 10nm. The marked effect of decreased strength with increased variance is clearly indicated.

average grain size in the 20nm size range. We note for later reference, that the grain size distributions grows over time and, after 1800s still continue to grow. Our objective is to simulate the time evolution of hardness using their measured grain size distributions.
Figure 6.10: Effect of strain rate and variance, and the contribution from each deformation mechanism.
Figure 6.11: Ultimate tensile stresses for Ni with mean grain size of 20nm

6.4.1 Indentation Simulation Details

The hardness is determined by the response of the zone of high stress or the plastic zone beneath the indenter. It is assumed that with increasing dwell time, the grain growth zone spreads and eventually occupies the entire plastic zone. Estimates
(a) Ultimate tensile stresses for Ni with mean grain size of 20nm at temperature 50°C.

(b) The contribution of the various mechanisms to the total deformation vs. the total strain. Note that at temperatures below even 20°C the relative contribution of grain boundary sliding is vanishingly small.

Figure 6.12: Effect of strain rate and variance, and the contribution of each deformation mechanism.

indicate that the time it takes for this is well over the 1800s that was the largest time followed by Zhang et al. [34]. For simplicity then, we initially assume that the volume
fraction of the grain growth zone, with respect to the plastic zone, increases linearly from 0% to 100% in a time $t_f$. We further take the properties of the material to be a simple average of those of the original distribution and those associated with the grown grain size distribution, i.e. if $R$ is the volume fraction of the grain growth zone, with respect to plastic zone, then the properties are computed as $R \times P_{\text{grown}} + (1 - R) \times P_{\text{original}}$ where $P_{\text{grown}}$ and $P_{\text{original}}$ figuratively represent the constitutive properties of material with the respective coarsened and original grain size distributions. Hardness is estimated by first simulating the ultimate strength in uniaxial tension and assuming the hardness to be equal to $3\sigma_{\text{ultimate}}$.

### 6.4.2 Grain Coarsening Simulation Results

As discussed above, the hardness is estimated as being equal to three times the ultimate tensile strength. For this purpose the ultimate stresses for each grain size distribution in Figure 6.17 are calculated under quasi-static uniaxial tension at room temperature. Results are shown in Figure 6.19 assuming for the moment $t_f = 1800$ s. Now simply using the ultimate strength as shown in Figure 6.19 to estimate hardness is
Figure 6.14: Contribution from each deformation mechanism to the overall strain under different strain rate.

Figure 6.15: Contribution from each deformation mechanism to the overall strain at different temperature.
Figure 6.16: Contribution from each deformation mechanisms to the overall strain with different variance.

tantamount to assuming $t_f \approx 1800s$ (i.e. 30min), and there are two reasons for not doing so. For one, the estimated hardness would be too low. The second, more compelling reason, is that Zhang et al.’s data indicate that grain growth, as witnessed by continued decreasing hardness, continues beyond $t = 1800s$. To better predict the overall response of the material by the simple averaging as suggested above, one needs to more accurately estimate the volume fraction of the grown grains, which may be determined by studying the TEM image of the cross chapter of the indent. Since the structure of the plastic zone is not yet known, then according to the observations of Zhang et al. [34] that the hardness decreases linearly with the logarithm of the indenter dwell time, the volume fraction of the grown grains is assumed to increase linearly with the logarithm of this time. The right hand side of Figure 6.20 shows the assumed relation between volume fraction of coarsened grains and the dwell time for $t_f = 1.5 \times 10^6s$, which leads to the almost exact match between the numerical simulations and the hardness measurements, shown on the left.
Figure 6.17: (a) Number fraction and (b), volume fraction grain size distributions in the initial condition and after various indenter dwell times of a 99.999% pure nanocrystalline IGC Cu sample with average grain size of 20 nm. (Zhang et al. [34]).
Figure 6.18: Schematic illustration of spreading grain growth zone within the zone of high stress, or possibly the plastic zone, beneath the indenter. As the dwell time increases, the grain growth zone occupies an increasing volume fraction of the zone of high stress, or plastic zone, that determines the hardness.

Figure 6.19: Simulated ultimate tensile stresses vs. the indenter dwell time with grain size distribution shown in Figure 6.17.
Note that the time evolution of the volume fractions in reality may differ from the linear relations, in particular at longer times. Thus further justification of, as well as a better understanding of how to extrapolate the data in Figure 6.20 is needed from future experiment. To explore the sensitivity to this optimal value of $t_f$, however, we have performed a series of simulations wherein $t_f$ was varied in the range $2 \times 10^3 \, s \leq t_f \leq 10^8 \, s$; the results are shown in Figure 6.21. Only when $t_f$ falls below $t_f < 10^5 \, s$ do the estimates of hardness fall to values that are clearly inconsistent with Zhang et al. [34]. Thus the results of our analysis are plausible vis-à-vis the experiments, but more detailed experimental estimates of the grain growth zone are required to make them more definitive.

### 6.5 Crystallographic Texture Development

Deformation *via* crystallographic mechanisms, whether by perfect or partial dislocation slip, produces deformation textures as is well documented in the literature. For reference, we note the work of Harren *et al.* [113] which deals with shear (*i.e.* torsion) textures in detail in fcc metals. Deformation by grain boundary sliding, in particular as describe herein *via* an isotropic $J_2$-flow theory, will not produce crystallographic textures. Documenting texture development, then, provides useful evidence for establishing the dominance of deformation mechanisms that involve dislocation (or twin) activity *versus* mechanisms like grain boundary sliding. Although this is the case in principle, we note from the above simulations that the application of combinations of high stress and finite plastic strains causes grain growth and expectedly a concomitant effect on texture. High pressure torsion (HPT), unlike tension or compression, conducted under large compressive loads provides a way of imposing plastic strains large enough to induce textures. Figures 6.22 and 6.23 show pole figures for electrodeposited Ni before and after the application of HPT as obtained by Valiev *et al.* [114]. From figures like those in Fig. 6.23, it has been suggested that the original texture has been largely eliminated and this may be evidence for grain boundary sliding. This possibility is examined below,
Figure 6.20: (a) Simulated hardness vs. time with experimental measurements by Zhang et al. [34] superimposed for comparison; (b) Assumed time evolution of volume fractions of grown grains.
but for now we recall the previous discussion regarding grain growth and reserve for the Discussion comment on how grain growth may affect the end process texture. We also explore the effects of varying material properties and demonstrate what is perhaps a little known effect of strain rate sensitivity on texture development.
Figure 6.22: Pole figure of electrodeposited nanocrystalline Ni before HPT, Valiev et al. [114]. Note the slight pre-texture is the “as processed” Ni foils as supplied by Goodfellow, Inc.

Figure 6.23: Pole figure of electrodeposited nanocrystalline Ni after HPT. HPT was conducted under a compressive stress of approximately 3GPa, Valiev et al. [114].

6.5.1 Torsion Boundary Conditions

Torsion simulations were carried out using the geometry shown in Fig. 6.24. Torsion is simulated by applying a fixed rate of $\dot{F}_{12}$. It was reported that during torsion the specimens spread laterally and thus were not totally so constrained. Now, the precise degree of lateral constraint was not known and thus we simulate the torsion process using two types of boundary conditions. These are referred to as the constrained and unconstrained sets, respectively. The constrained set involves setting $F_{11} = F_{33} = 0$ along with their rates, i.e. $\dot{F}_{11} = \dot{F}_{33} = 0$. This precludes lateral expansion during torsion and will result in stress states with high hydrostatic compression. The unconstrained set sets $n_{11} = n_{33} = 0$ along with their rates. This allows for free lateral expansion. In addition, simulations were carried out with and without the application of a fixed compressive stress of $n_{22} = 3$GPa. For each of the simulation cases, the plane of shearing is the
Figure 6.24: Geometry for the simulation of torsion.

\[ x_1 - x_2 \text{ plane, and the material fibers along } x_1 \text{ direction (the torsion direction) remain in that direction, so that} \]

\[ \mathbf{F} \cdot \mathbf{e}_1 = \bar{F}_{11} \mathbf{e}_1 \]  

\[ \text{and} \]

\[ \bar{F}_{21} = \bar{F}_{31} = 0 \Rightarrow \dot{\bar{F}}_{21} = \dot{\bar{F}}_{31} = 0. \]  

\[ \text{In addition, the material lines along } x_2 \text{ direction remain in } x_1 - x_2 \text{ plane, } i.e., \text{ they remain perpendicular to } x_3 \text{ axis, so that} \]

\[ \bar{F}_{32} = 0 \Rightarrow \dot{\bar{F}}_{32} = 0. \]  

\[ \text{The rest of the common boundary conditions for each case are} \]

\[ \dot{n}_{31} = \dot{n}_{32} = 0 \text{ on } x_3 = \text{ constant, and} \]

\[ \dot{\bar{F}}_{12} = \dot{\gamma}, \]  

\[ \text{where } \dot{\gamma} \text{ is the prescribed strain rate. For the constrained torsion problem, the remaining boundary conditions are} \]

\[ \bar{F}_{11} = \bar{F}_{33} = 0 \Rightarrow \dot{\bar{F}}_{11} = \dot{\bar{F}}_{33} = 0, \]  

\[ n_{22} = 3\text{GPa} \Rightarrow \dot{n}_{22} = 0; \]
for the corresponding case without applying the fixed compressive stress \( n_{22} \)

\[
\bar{F}_{11} = \bar{F}_{33} = 0 \Rightarrow \dot{\bar{F}}_{11} = \dot{\bar{F}}_{33} = 0, \tag{6.15}
\]

\[
n_{22} = 0 \Rightarrow \dot{n}_{22} = 0;
\]

for the unconstrained torsion problem, the rest of the conditions are

\[
\bar{n}_{11} = \bar{n}_{33} = 0 \Rightarrow \dot{\bar{n}}_{11} = \dot{\bar{n}}_{33} = 0, \tag{6.16}
\]

\[
n_{22} = 3\text{GPa} \Rightarrow \dot{n}_{22} = 0.
\]

The results for two values of the strain rate sensitivity exponent, \( \nu \), that corresponding to what has been experimentally documented for nanocrystalline fcc metals with average grain sizes in the 20nm size range, \( 1/m \approx 20 \), and an extreme value of \( 1/m = 1 \). The latter value, representing a very high rate sensitivity, is meant to reveal the above mentioned little known effect of rate dependence on texture evolution as originally noted by Harren et al. [113].

### 6.5.2 Torsion Simulation Results

As noted above, lateral expansion of the HPT specimen was experimentally observed but its precise extent was not determined. Therefore, we explore here the effect of such constraint by first assuming free lateral expansion and then fully constrained expansion. The former is accomplished by setting \( n_{11} = n_{33} = 0 \), the latter by setting and maintaining \( F_{11} = F_{33} = 0 \) as noted above. The results for both cases are shown via inverse pole figures in Figs. 6.25a,b respectively. In both cases a strain rate sensitivity exponent of \( 1/m = 20 \) was used as has been noted is consistent with measured values for fcc metals with grain sizes in the 20nm range. A normal sustained compressive stress \( n_{22} = 3\text{GPa} \) was imposed as was done in the HPT experiments of Valiev et al. [114]. For the freely expanding case, the textures that are shown in Fig. 6.25a resemble those obtained by Asaro and Needleman [5] for plane strain compression of simple fcc metals. There are important differences in detail due to the fact that the present case involves
Figure 6.25: Inverse pole figures for the cases of HPT under conditions of free lateral expansion, (a), and fully constrained lateral expansion, (b). In both cases \(1/m = 20\), the average grain size is 20nm, variance = 100, and \(n_{22} = 3\)GPa. The pole figures shown are for a value of of shear strain corresponding to \(F_{12} = 1.25\).
imposed shear as well. For the case of fully constrained shear, i.e. Fig. 6.25b, the textures are consistent with those found by Asaro and Needleman [5] who imposed a similar state of shear strain; Asaro and Needleman [5], however, used values of $1/m = 50$ and larger consistent with fcc metals with average grain sizes well above 100nm. Thus, on the one hand, the effect of constraint is indeed significant with respect to the types of textures found. The other important finding here is that with values of material parameters consistent with those measured in these materials, textures do form in ways consistent with fcc metals. On this basis, it may be judged that texture development provides evidence for crystallographic processes such as dislocation emission. It is necessary, however, to recall that other events such as dynamic grain coarsening may intervene and cause gross alterations in texture patterns.

As noted above, crystallographic mechanisms of deformation induce textures, whether the process is via full or partial dislocation emission. As texture development via partial dislocation slip has yet to be explored, we confirm this by showing the results in Figs. 6.26a,b. When Fig. 6.25a is compared with its counterpart in Fig. 6.26b, the obviously close correspondence confirms the comments made at the outset. There are differences in detail, but the general patterns are quite similar both qualitatively and in quantitative extent. The texture shown in Fig. 6.26a is, however, far more diffuse that that shown in Fig. 6.25a.

Documenting texture development in nanostructured metals is important since, as has been noted, they show relatively strong sensitivity to strain rate. As it happens, rate sensitivity has a (perhaps unexpected) role in determining the types and extent of texture development. As an example, Figs. 6.27a,b show inverse pole figures for cases where an extremely high rate sensitivity corresponding to $1/m = 1$ was assumed. In both cases, fully constrained boundary conditions were used, but in one case the compressive stress of 3GPa was imposed, while in the second not. Fig. 6.27a, shows the resulting inverse pole figures obtained without the application of compressive stress, i.e. with $n_{22} = 0$; Fig. 6.27b shows the corresponding results for the HPT case of $n_{22} = 3$GPa. Two effects are obvious. On the one hand, with or without the application
of a high compressive stress no texturing is observed as these pole figures are effectively identical with the originally assumed uniform distribution of grain orientations. This is an observation originally due to Asaro and Needleman [5]. If, however, Figs. 6.25b and 6.27b are compared it is noted that the textures that develop are still influenced by material rate sensitivity - as the rate sensitivity increases, the textures become less strong. We note that so long as $1/m > 5$, noticeable textures develop, but if $1/m < 10$ they may well be too weak to experimentally confirm!

### 6.6 Acknowledgement

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Figure 6.26: Inverse pole figures for the cases of HPT under conditions of free lateral expansion, (a), and fully constrained lateral expansion, (b) for an idealized nano-polycrystal with a uniform grain size of 10nm. In this case, deformation is nearly entirely via partial dislocation emission. In both cases $1/m = 20$, the average grain size is 20nm, variance = 100, and $n_{22} = 3\text{GPa}$. The pole figures shown are for a value of of shear strain corresponding to $F_{12} = 1.25$. 
Figure 6.27: Inverse pole figures for the cases of HPT under conditions of fully constrained lateral expansion. In both cases $1/m = 1$, the average grain size is 20nm, variance = 100. In (a) $n_{22} = 0$ and in (b) $n_{22} = 3$GPa. The pole figures shown are for a value of shear strain corresponding to $F_{12} = 1.25$. 
Chapter 7

Discussion & Conclusions

The influence of grain size distribution on the response of nanoaggregates has been considered in several models and some of these are briefly discussed in context. Masumura et al. [38], for example, attempted to explain experimental reports (summarized by them) of reductions in yield strength as the grain size fell below a critically small range. This they did by invoking the idea that within grains of a certain small size, $d^*$, and smaller, the deformation mechanism switches from traditional intragrain dislocation processes, for which a Hall-Petch relation would hold, to Coble creep. No account for temperature or strain rate was given in the form of a constitutive law, but temperature and rate dependent Coble parameters were noted. No full constitutive framework was attempted in this model other than to simulate 1-dimensional rate independent response. The “rate independent strength” associated with Coble creep was given by a relation of the form

$$\tau_c = \frac{A}{d} + Bd^3. \quad (7.1)$$

Once the grain size fell below $d^*$ the Coble mechanism, operating only, and exclusive of all other mechanisms, in those grains where $d < d^*$ would then contribute to a decrease in strength as grain size decreased further. Masumura et al. [38] also used a lognormal grain size distribution to account for the effect of nonuniform grain size. We point out that, should the contribution of Coble creep be verified experimentally and the
relevant parameters documented (as functions of temperature and rate), Coble creep is straightforwardly included in the Zhu et al. [44] model. Specifically, classical descriptions for the tensile strain rate accompanying Coble creep are of the form (see e.g. [115])

\[
\dot{\varepsilon} = A_c \frac{D_{GB}\delta'}{d^3} \frac{\sigma \Omega}{kT},
\]

where the parameters have well known descriptions. As the Coble creep mechanism would be judged to be essentially isotropic, and describable within the framework of a \(J_2\)-flow theory, one would identify our shearing rate, \(\dot{\gamma}\) as in eq. (4.10), for grain boundary sliding with the now combined effective plastic shearing rate for grain boundary sliding and Coble creep

\[
\dot{\gamma} \leftarrow \dot{\gamma} + A_c \frac{D_{GB}\delta'}{d^3} \frac{\sigma \Omega}{kT}.
\]

Model simulations would be straightforward, and would undoubtedly show that flow stress, at various temperatures and strain rates, would decrease as \(d\) decreased sufficiently, etc. However, further experimental data are needed to assess the implications of what now would be a fully strain rate and temperature dependent model. A question that needs be asked, \textit{inter alia}, is how would one decouple the contributions of grain boundary sliding from those of Coble creep? That is, what are the critical experiments that would allow for a definitive decoupling of two such rate and temperature dependent isotropic, non-texturing producing mechanisms? Of course, mechanisms such as grain boundary sliding and/or Coble creep, if operative at significant rates, would raise questions regarding the stability of ultrafine grain sizes, especially in light of the observations of Zhang et al. [61, 34].

Other such models that have explicitly identified grain size distribution as being of first order importance are those of Morita et al. [43]. These have also described grain size distributions within the framework of lognormal distributions and revealed the importance of rigorously accounting for it. In particular, Morita et al. [43] note that in typical grain size distributions the smallest grains are likely to contribute little to the overall aggregate response, an observation reconfirmed by our analysis herein. The data
of Embrahimi et al. [116], especially as they interpreted it based on an assessment of non-deforming versus deforming grains, also demonstrates the importance of size distribution even at fixed average grain size.

From the simulations herein several interesting trends associated with the effects of material properties can be seen from the examples shown in Figs. 6.5 to 6.13. For example, Figs. 6.10 and 6.12 show the effect of varying temperature on the relative contribution of the various mechanisms considered so far in our model. A noteworthy feature here is that for grain sizes in the range $10\text{nm} < d < 20\text{nm}$ there is little contribution from grain boundary sliding; at temperatures near $50^\circ\text{C}$, however, there appears a significant contribution from grain boundary sliding and a concomitant decrease in the relative contributions from both perfect or partial dislocation emission. This helps explain the sudden drop in ultimate strength shown in Fig. 6.8 for $d = 10\text{nm}$ and the more gradual drop also shown for $d = 20\text{nm}$. There has been, to date, little systematic study of the effect of varying temperature in true nanocrystalline metals and the present analysis should be of considerable help in interpreting any such future results.

As shown in [44], the effect of grain size distribution is again seen to be of first order importance in determining response, especially with regards to strength. Figures 6.8 to 6.12 make this point by showing the effect of the variance, at fixed average grain size, in the grain size on ultimate strength. This again underscores the difficulty in attempts to extract information regarding the relative importance of various mechanisms in experimental studies. We are not aware of any studies on materials other than those that are characterized by grain size distributions as shown and mathematically characterized herein. Modest changes in variance can lead to 2 fold changes in ultimate strength and this can in turn lead to serious ambiguity in interpreting experimental results, especially when making comparisons among samples of different origin or even from samples taken from different locations of one larger sample. Thus, for example, bulk specimens must be extremely homogeneous if straightforward comparisons are to be made among a group of smaller specimens fabricated from a larger piece. Attempts to produce specimens with more uniform grain sizes would be of obvious value. In fact, until such specimens are
available definitive correlations between conditions and mechanisms is likely to remain ambiguous.

The effect of texture and the experimental documentation of texture has been shown to be a potentially useful tool in confirming the predominance of certain mechanisms such as perfect of partial dislocation slip. It is forecast, however, that quite similar textures develop for both perfect or partial dislocation dominated deformation. Thus unravelling the relative contributions of perfect vs. partial dislocation activity would be experimentally untenable using texture measurements. Moreover, to develop textures finite deformations are required, via say HPT methods. But recall that experimental studies have shown that nanocrystalline metals inevitably undergo dynamic grain growth which will alter texture development in ways unknown at present. Dynamic grain growth may indeed eliminate textures. Thus much more study is required of the phenomena involved during finite deformations to be clear as to how to interpret texture measurements. We have also shown that other mechanisms such as Coble creep are naturally included in the framework, but its effect on texture development is again likely to be small, thus further complicating the interpretation of the dominant mechanisms especially vis-à-vis non-texture forming mechanisms such as grain boundary sliding.

Figure 6.13 illustrates the effect of stacking fault energy on ultimate strength. As expected, when the strength is normalized by the shear modulus the ranking in terms of the magnitude of the ultimate strength reflects the magnitude of the intrinsic stacking fault energy.

The various examples presented herein provide additional insight into the trends as affected by strain rate, temperature, grain size, and material properties. However, the examples show that to rationally interpret the response of nanocrystalline metals it is vital that very careful attention be paid to documenting grain size distributions as well as potential alterations in grain size distribution. Thus experimental studies need to include detailed documentation of grain size before and after (and during) deformation. The great benefit of preparing samples with far more uniform size distribution has already been underscored. The need for experimental studies on well characterized samples with
varying strain rate, including load relaxation and creep testing, and temperature is clear. The present modelling framework provides a platform for interpreting the results.

Finally a word concerning the viability of realizing the enhanced properties of strength of nanocrystalline metals is warranted. When it is realized, first, that the strength of such ultra-fine grained metals is so sensitive to grain size distribution and secondly, that nanocrystalline metals undergo dynamic grain growth concomitant with inelastic deformation, it must be anticipated that the enhanced mechanical properties may also be unstable. Clearly focused study must be undertaken to document such trends and to mitigate them.

The examples presented above have illustrated the main focus of this discussion, \textit{viz.} the vital influence of grain size distribution on the response of nanocrystalline metals. As example, we have shown that for electrodeposited Ni with a mean grain size in the range of 20nm (typical for materials that have been reported on recently) the response is sensitive to grain size distribution yet not simply to the mean grain size, but also to the spread about the mean grain size as measured by the variance about the mean, as defined in eq. (4.37). This illustrates, \textit{inter alia}, that future experiment needs to be diligent with respect to documenting grain size distribution, but also needs to develop methodology for preparing nanocrystalline metals with better controlled grain sizes that allow for more definitive discrimination amongst the various potential mechanisms.

The comparison between the simulated tensile stress \textit{vs.} strain curves is seen to be quite good except that the experimental curves display limited ductility and terminate after quite modest plastic strains. This is clear in the curves shown in Fig. 3.3 which are repeated on the left side of Figs. 6.3 and 6.4. The experimentally observed failure mode involved abrupt necking and was ductile in that the fracture surface was dimpled. These results will be described in further detail in [117]. Similar curves in the literature likewise often display limited elongation to failure owing to the very high strength and low levels of strain hardening. In fact, it is most probable that most recorded stress \textit{vs.} strain response is terminated prematurely due to the onset of fracture brought on by the presence of small defects in the specimens.
Finally we note that a comparison of the right side figures in Figs. 6.3 and 6.4 show that when the grain size is at the transitional grain size range of 20nm and just below, as estimated for nanocrystalline Ni, the expected deformation modes indeed begin to change. What this means, however, is that at a grain size of 20nm, and with a grain size distribution typical of electrodeposited Ni, observation of faults or twins would be anticipated to be relatively rare events. In fact, as the variance of the grain size distribution increases beyond say 100, as we have defined this parameter, it is unlikely that any deformation twinning or fault emission would be observed at all. At mean grain sizes below 15nm such modes become prevalent enough to be anticipated via TEM observation but only in the smallest of the grains in the distribution. Again this shows the the need for materials synthesized with more uniform grain sizes than are currently available. With grain sizes below 15nm, grain boundary sliding is also seen to contribute to the overall deformation as seen by the right side of Fig. 6.4.

Zhu et al. [117] also explore the effect of grain size distribution, strain rate, and temperature in far more detail and use additional data for nanostructured Ni and Pd, along with the more limited data available for Cu and Al.

7.1 Acknowledgement

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Appendix A

Crystal Plasticity

The theory of crystal plasticity was pioneered by Taylor and his co-workers [118, 119] in the beginning of last century, and it was further developed by Hill [66, 120, 121], Rice [64], Havner [67, 122, 123], Asaro [5, 63, 68], et. al. In this chapter the fundamental mathematical formulation of crystal plasticity is reviewed. Further description of the theory can be found in the relative reference.

A.1 Kinematics relations

The elastic-plastic deformation of crystals is assumed to occur through two steps. First the material deforms plastically via crystal lattice slip from the reference configuration \((e_0 i)\) to the intermediate configuration \((e^* i)\). The second steps involves the elastic distortion (rigid rotation and stretch) of crystal lattices, which further takes the material from the intermediate configuration to the deformed configuration \((e_i)\). It is also assumed that the elastic properties are not effected by the plastic slip. Hence the deformation gradient can be multiplicatively decomposed as

\[ F = F^* \cdot F^p, \]  \hspace{1cm} (A.1)
where $F^p$ and $F^\star$ correspond to the plastic deformation and the elastic distortion respectively. Since the plastic deformation is induced by the simple shear on each active slip system, $F^p$ contains only the rotations of principle axes of crystal lattice, and it is reasonable to assume the plastic incompressibility, \textit{i.e.}

\begin{align}
\det F^p &= 1 \\
\det F^\star &= \det F.
\end{align}

If define the slip direction and the normal to the slip plane of slip system $\alpha$ where the simple shear occurs as $s_0^\alpha$ and $m_0^\alpha$ on the reference configuration. It can be shown that $F^p$ doesn’t change their orientations, \textit{i.e.}, the slip direction and normal are the same on the intermediate configuration as on the reference configuration, and

\begin{align}
 s^\alpha &= F^\star \cdot s_0^\alpha \\
 m^\alpha &= m_0^\alpha \cdot F^\star - 1
\end{align}

on the deformed configuration. $F^\star$ in Eq. A.1 is used for pull-backs to the intermediate configurations [107].

If substitute Eq. A.1 into the definition of velocity gradient,

\begin{align}
 L &= \dot{F} \cdot F^{-1} \\
 &= \{F^\star \cdot F^p\} \cdot \{F^\star \cdot F^p\}^{-1} \\
 &= \dot{F}^\star \cdot F^{\star-1} + F^\star \cdot \dot{F}^p \cdot F^{p-1} \cdot F^{\star-1}
\end{align}

and define

\begin{align}
 L^\star &= \dot{F}^\star \cdot F^{\star-1} = D^\star + W^\star \\
 L^p &= \dot{F}^p \cdot F^{p-1} = D^p + W^p \\
 l^p &= F^\star \cdot L^p \cdot F^{\star-1} = d^p + w^p
\end{align}
where $D$, $d$ and $W$, $w$ are the rate of deformation and the rate of spin respectively, then $L$ can be written as

$$\begin{align*}
L &= L^* + F^* \cdot L^p \cdot F^*^{-1} \\
&= L^* + I^p,
\end{align*}$$

(A.9)

and similarly

$$\begin{align*}
D &= D^* + d^p \\
W &= W^* + w^p
\end{align*}$$

(A.10, A.11)

The mathematical description of the incremental crystal plastic deformation is the follows,

$$L^p = \dot{\gamma}(\alpha)s^\alpha_0 m^\alpha_0,$$

(A.12)

where $L^p$ is the plastic velocity gradient, $\dot{\gamma}(\alpha)$ is the slip rate of slip system $\alpha$, and $s^\alpha_0$, $m^\alpha_0$ are the slip direction and the normal to the slip plane where the simple shear occurs. Note that the parenthesis in Eq. (A.12) indicates the subscript within it is not involved in the summation. For example, for face centered cubic structures, there are twelve slip system components on four \{111\} plane families and three slip directions on each plane family. Taking derivatives of Eq. (A.4) and (A.5) with respect to time leads to

$$\begin{align*}
\dot{s}^\alpha &= \dot{F}^* \cdot s^\alpha_0 = \dot{F}^* \cdot F^*^{-1} \cdot s^\alpha = L^* \cdot s^\alpha \\
\dot{m}^\alpha &= m^\alpha_0 \cdot \dot{F}^*^{-1} = m^\alpha \cdot F^* \cdot \dot{F}^*^{-1} = m^\alpha \cdot L^*^{-1},
\end{align*}$$

(A.13, A.14)
and due to

\[ \mathbf{F}^* \cdot \mathbf{F}^{*-1} = 1, \]
\[ \{\mathbf{F}^* \cdot \mathbf{F}^{*-1}\} = 0, \]
\[ \dot{\mathbf{F}}^* \cdot \mathbf{F}^{*-1} + \mathbf{F}^* \cdot \dot{\mathbf{F}}^{*-1} = 0, \]
\[ \mathbf{L}^* + \mathbf{L}^{*-1} = 0, \]

so Eq. (A.14) can be also written as,

\[ \dot{\mathbf{m}}^\alpha = -\mathbf{m}^\alpha \cdot \mathbf{L}^*. \] (A.15)

If substitute Eq. (A.12) into Eq. (A.8), and consider Eq. (A.4) and (A.5),

\[ \mathbf{p}^p = \dot{\gamma}(\alpha) \mathbf{F}^* \cdot \mathbf{s}^\alpha \mathbf{m}^\alpha \cdot \mathbf{F}^{*-1} \]
\[ = \dot{\gamma}(\alpha) \mathbf{s}^\alpha \mathbf{m}^\alpha \] (A.16)

The above equation can be further decomposed into its symmetric and antisymmetric parts as in Eq. (A.8),

\[ \mathbf{p}^p = \dot{\gamma}_{\alpha}(\mathbf{P}_\alpha + \mathbf{W}_\alpha), \] (A.17)

where

\[ \mathbf{P}_\alpha = \text{sym}\{\mathbf{s}^\alpha \mathbf{m}^{(\alpha)}\} \] (A.18)
\[ \mathbf{W}_\alpha = \text{skew}\{\mathbf{s}^\alpha \mathbf{m}^{(\alpha)}\}, \] (A.19)

and the following can be defined

\[ d^p = \dot{\gamma}_\alpha \mathbf{P}_\alpha \] (A.20)
\[ w^p = \dot{\gamma}_\alpha \mathbf{W}_\alpha. \] (A.21)
The mathematical formulation of the evolution of plastic slip $\gamma_\alpha$ can be described through rate dependent plasticity formulation where a constitutive relation is proposed for $\gamma_\alpha$ (see Eq. (A.51)), and rate independent plasticity where $\gamma_\alpha$ is determined by solving an equation system and the solutions are not always unique. The details will be reviewed later in this chapter.

A.2 Kinetic relations

A.2.1 Constitutive relation

It is assumed the elasticity is hyperelasticity, i.e.,

$$S^{ij*} = \frac{\partial W}{\partial E^{*}_{ij}},$$

$$\dot{S}^{ij*} = \frac{\partial^2 W}{\partial E^{*}_{ij} \partial E^{*}_{kl}} \dot{E}^{*}_{kl},$$

where

$S^*$: the second Piola-Kirchhoff stress convected with the elastic distortion;

$E^*$: the elastic Lagrangian strain tensor, $\dot{E}^* = F^{*T} \cdot D^* \cdot F^*$;

$W$: the elastic work done with the stress $S^*$ and strain $E^*$, $W = S^* : E^*$.

Introduce the fourth order elastic modulus tensor $C^*$ on the intermediate configuration,

$$C^* = \frac{\partial^2 W}{\partial E^{*}_{ij} \partial E^{*}_{kl}} e^*_i e^*_j e^*_k e^*_l,$$

and Eq. (A.23) can be written as

$$\dot{S}^* = C^* : \dot{E}^*.$$
The second Piola-Kirchhoff stress \( S^* \) can be related to the Kirchhoff stress \( \tau \) through the following equation,

\[
S^* = F^{*^{-1}} \cdot \tau \cdot F^{*-T}.
\] (A.26)

Take the time derivative of the both sides of Eq. (A.26),

\[
\dot{S}^* = F^{*^{-1}} \cdot \tau \cdot F^{*-T} + F^{*^{-1}} \cdot \dot{\tau} \cdot F^{*-T} + F^{*^{-1}} \cdot \tau \cdot F^{*-T},
\] (A.27)

and if multiply the both sides of the above equation with \( F^* \) and \( F^*T \) on the left and right respectively, then we have

\[
F^* \cdot \dot{S}^* \cdot F^{*T} = F^* \cdot F^{*^{-1}} \cdot \tau + \dot{\tau} + \tau \cdot F^{*^{-T}}F^{*T}.
\] (A.28)

Remember Eq. (A.6) and plug it into the above equation,

\[
F^* \cdot \dot{S}^* \cdot F^{*T} = -L^* \cdot \tau + \dot{\tau} - \tau \cdot L^{*T}
= -(D^* + W^*) \cdot \tau + \dot{\tau} - \tau \cdot (W^{*T} + W^{*T}).
\]

Further organization of the above equation gives us

\[
\dot{\tau} - \tau \cdot W^{*T} - W^* \cdot \tau = F^* \cdot \dot{S}^* \cdot F^{*T} + \tau \cdot D^{*T} + D^* \cdot \tau.
\] (A.29)

Realize the left hand side is the Jaumann rate of Kirchhoff stress based on lattice vorticity \( \tau^{\nabla*} \),

\[
\tau^{\nabla*} = \dot{\tau} - W^* \cdot \tau - \tau \cdot W^{*T},
\] (A.30)

and substitute Eq. (A.25) into the above equation, we have

\[
\tau^{\nabla*} = F^* \cdot \{ C^* : \dot{E}^* \} \cdot F^{*T} + \tau \cdot D^{*T} + D^* \cdot \tau
= F^* \cdot \{ C^* : (F^{*T} \cdot D^* \cdot F^*) \} \cdot F^{*T} + \tau \cdot D^{*T} + D^* \cdot \tau,
\]
and it can be proven that the first term on the right hand side of the above equation is actually \( C : D^* \), where \( C \) is the elastic modulus tensor on the deformed configuration,

\[
C = \frac{\partial^2 W}{\partial E^*_{ij} \partial E^*_{kl}} e_i e_j e_k e_l
\]  

(A.31)

so the exact hyperelastic rate constitutive relation is

\[
\tau^\nabla = C : D^* + \tau \cdot D^{*T} + D^* \cdot \tau,
\]  

(A.32)

and often the elastic modulus are much bigger quantities than the second Piola-Kirchhoff stress, so Eq. (A.32) can be approximated as

\[
\tau^\nabla = C : D^*.
\]  

(A.33)

Consider another Jaumann rate of the Kirchhoff stress \( \tau \),

\[
\tau^\nabla = \dot{\tau} - W \cdot \tau - \tau \cdot W^T,
\]  

(A.34)

and if we subtract Eq. (A.34) from Eq. (A.30), then

\[
\tau^\nabla - \tau^\nabla = (W - W^*) \cdot \tau + \tau \cdot (W - W^*)^T
\]

\[
= \mathbf{w}^p \cdot \tau - \tau \cdot \mathbf{w}^p
\]

\[
= \dot{\gamma}_\alpha \{ W_\alpha \cdot \tau - \tau \cdot W_\alpha \}
\]

\[
= \dot{\gamma}_\alpha \beta_\alpha,
\]  

(A.35)

where \( \beta_\alpha \) is defined as

\[
\beta_\alpha = W_\alpha \cdot \tau - \tau \cdot W_\alpha.
\]  

(A.36)
Substitute Eq. (A.33) into the above equation, then we have,

\[
\tau^\nabla = C : D^* - \dot{\gamma}_\alpha \beta_\alpha = C : (D - d^p) - \dot{\gamma}_\alpha \beta_\alpha = C : (D - \dot{\gamma}_\alpha P_{\alpha}) - \dot{\gamma}_\alpha \beta_\alpha = C : D - \dot{\gamma}_\alpha (C : P_{\alpha} + \beta_\alpha). \tag{A.37}
\]

**A.2.2 Resolved shear stress**

The resolved shear stress (Schmid stress) \(\tau^\alpha\) on slip system \(\alpha\) is defined in such a way that it is work conjugate to the slip strain rate \(\dot{\gamma}^\alpha\), i.e.,

\[
\sum_{\alpha=1}^{n} \tau^\alpha \dot{\gamma}^\alpha = \tau : D^p = \tau : \sum_{\alpha=1}^{n} P^\alpha \dot{\gamma}^\alpha \tag{A.38}
\]

where \(\tau\) is the Kirchhoff stress or the weighted Cauchy stress, and it is related to the Cauchy stress through

\[
\tau = J\sigma. \tag{A.39}
\]

The resolved shear stress can be written as the follows,

\[
\tau_{\alpha} = \tau : P_{\alpha} \tag{A.40}
\]

\[
= s_{\alpha} \cdot \tau \cdot m_{(\alpha)} \tag{A.41}
\]

\[
= \{m_{(\alpha)}\}_i \{s_{\alpha}\}_j b^i \cdot \tau \cdot b_j \]

\[
= \{m_{(\alpha)}\}_i \{s_{\alpha}\}_j \tau^{i}_j, \tag{A.42}
\]

The resolved shear stress simply means the shear stress acting along the slip direction in the slip plane.
A.3 Rate independent plasticity

In the assumption of rate independent plasticity, the plastic flow starts when the resolved shear stress reaches the yield stress on the slip system. As discussed earlier that for rate independent plasticity, the plastic slip strain is solved through an inverse problem, and in this section the derivation of the inverse problem is presented. It needs to be noted that sometimes the inverse problem can be ill-posed, i.e., a unique solution may not exist. This problem can usually be overcome by using rate dependent formulation. However some solutions are also offered by the inversion techniques, or by Gambin and co-workers [124] and many other researchers while the rate independent formulation is still in use.

Suppose the hardening relation is,

\[ \dot{\tau}_\alpha = h_{\alpha\beta} \dot{\gamma}_\beta \]  

(A.43)

where \( h_{\alpha\beta} \) is the hardening modulus and \( \tau_\alpha \) is the resolved shear stress on slip system \( \alpha \). Recall Eq. (A.40), and take time derivative of its both sides, we have,

\[ \dot{\tau}_\alpha = m_\alpha \cdot \{ \dot{\tau} - L^* \cdot \tau + \tau \cdot L^* \} \cdot s_\alpha \]

\[ = m_\alpha \cdot \{ \nabla^* \tau^* - D^* \cdot \tau + \tau \cdot D^* \} \cdot s_\alpha \]

If we plug in Eq. (A.33), then it can be further simplified as,

\[ \dot{\tau}_\alpha = m_\alpha \cdot \{ C : D^* \} \cdot s_\alpha + m_\alpha \cdot \{ \tau \cdot D^* - D^* \cdot \tau \} \cdot s_\alpha \]  

(A.44)

If the symmetry of \( C \) is assumed, then the first term at the right hand side of Eq. (A.44)
can be written as
\[ m_\alpha \cdot \{ C : D^* \} \cdot s_\alpha = m_\alpha s_\alpha : C : D^* \]
\[ = \text{sym}\{ m_\alpha s_\alpha \} : C : D^* \]
\[ = P_\alpha : C : D^*. \]

It can also be proven that the second term can be simplified as
\[ m_\alpha \cdot \{ \tau : D^* - D^* \cdot \tau \} \cdot s_\alpha = \beta_\alpha : D^*, \]
with Eq. (A.36) and Eq. (A.19),
\[ \beta_\alpha : D^* = \frac{1}{2} \{ s_\alpha m_\alpha \cdot \tau \} : D^* - \frac{1}{2} \{ m_\alpha s_\alpha \cdot \tau \} : D^* \]
\[ - \frac{1}{2} \{ \tau \cdot s_\alpha m_\alpha \} : D^* + \frac{1}{2} \{ \tau \cdot m_\alpha s_\alpha \} : D^*. \]

Recall \( A : B = A^T : B \), if \( B \) is a symmetric tensor and \( A \) is an arbitrary tensor. Note \( D^* \) and \( \tau \) are symmetric, so
\[ \beta_\alpha : D^* = \frac{1}{2} \{ s_\alpha m_\alpha \cdot \tau \} : D^* - \frac{1}{2} \{ m_\alpha s_\alpha \cdot \tau \} : D^* \]
\[ - \frac{1}{2} \{ m_\alpha s_\alpha \cdot \tau \} : D^* + \frac{1}{2} \{ s_\alpha m_\alpha \cdot \tau \} : D^*, \]
\[ = \{ s_\alpha m_\alpha \cdot \tau \} : D^* - \{ m_\alpha s_\alpha \cdot \tau \} : D^* \]
\[ = \{ \tau \cdot m_\alpha s_\alpha \} : D^* - \{ m_\alpha s_\alpha \cdot \tau \} : D^* \]
\[ = m_\alpha \cdot \{ \tau : D^* - D^* \cdot \tau \} \cdot s_\alpha \]
(45)

Therefore Eq. (A.44) can be simplified as,
\[ \dot{\tau}_\alpha = P_\alpha : C : D^* + \beta_\alpha : D^* \]
\[ = \{ P_\alpha : C + \beta_\alpha \} : D^*. \]
Substitute in

\[ D^* = D - d^p \]
\[ d^p = \dot{\gamma}_\alpha P_\alpha, \]

we have,

\[
\dot{\tau}_\alpha = \{P_\alpha : C + \beta_\alpha\} : D - \{P_\alpha : C + \beta_\alpha\} : \dot{\gamma}_\delta P_\delta \\
= \{P_\alpha : C + \beta_\alpha\} : D - \dot{\gamma}_\delta \{P_\alpha : C : P_\delta + \beta_\alpha : P_\delta\}
\] (A.47)

Relate the above equation with the hardening law Eq. (A.43) and simplify,

\[
N_{\alpha\delta} \dot{\gamma}_\delta = \{P_\alpha : C + \beta_\alpha\} : D,
\] (A.48)

where \( N_{\alpha\delta} = h_{\alpha\delta} + P_\alpha : C : P_\delta + \beta_\alpha : P_\delta \). As mention at the beginning of this section, the inversion of \( N_{\alpha\delta} \) may not always exist. However if the inverse matrix is named \( M_{\alpha\delta} \), then

\[
\dot{\gamma}_\alpha = M_{\alpha\delta} \{P_\delta : C + \beta_\delta\} : D
\] (A.49)

If substitute the above equation into Eq. (A.37), the rate constitutive law for rate independent crystal plasticity is the follows,

\[
\boldsymbol{\tau}^V = C^{\text{ep}} : D,
\] (A.50)

where \( C^{\text{ep}} = C - \{P_\alpha : C + \beta_\alpha\} M_{\alpha\delta} \{P_\delta : C + \beta_\delta\} \).
A.4 Rate dependent plasticity

For rate dependent plasticity, the slip rate $\dot{\gamma}_\alpha$ in Eq. (A.12) can be described by a visco-plasticity formulation by Hutchinson’s power law,

$$
\dot{\gamma}_\alpha = \dot{a}_\alpha \left\{ \frac{\tau(\alpha)}{g(\alpha)} \right\} \frac{1}{|\tau(\alpha)/g(\alpha)|}^{\frac{1}{m} - 1},
$$

(A.51)

where $\dot{a}_\alpha$ is the reference slip rate on slip system $\alpha$ and its value is the same for every slip system; $\tau(\alpha)$, $g(\alpha)$ are the resolved shear stress and slip strength of system $\alpha$ respectively, the latter of which is a function of the accumulative slip $\gamma$ and represents the hardening, i.e.,

$$
g_\alpha = g_\alpha(\gamma), \gamma = \sum |\gamma_\alpha|.
$$

(A.52)

$m$ is the rate sensitivity parameter, and as it approaches to zero, the material becomes rate independent, which means very small $\tau_\alpha$ can lead to some slip. However the reality is when the resolved shear stress is smaller than a critical value, say $g_0$, the slip caused by it should be negligible.
Appendix B

Component Form of The Constitutive Relation

The formulation of the constitutive relation can involve several different types of coordinate basis, for example the reference laboratory basis \((e_{0i})\), the reference crystal lattice basis \((a_{0i})\), the intermediate basis \((e^*_i, a^*_i)\), induced by the plastic slip and the deformed basis \((e_i, a_i)\), and their reciprocal counterparts, contravariant base vectors, \((e^i_0, a^i_0, e^{*i}, e^i, a^i)\)[125]. The crystal lattice base vectors and the laboratory base vectors are related through the orthonormal rotation matrix \(\phi\), and the base vectors of the three configurations are related through the following relations,

\[
\begin{align*}
    e^*_i &= F^p \cdot e_{0i} \\
    e_i &= F^* \cdot e^*_i \\
    e_i &= F \cdot e_{0i} \\
    e^{*i} &= F^{p-T} \cdot e^i_0 = e^i_0 \cdot F^{p-1} \\
    e^i &= F^{*T} \cdot e^{*i} = e^{*i} \cdot F^{*-1} \\
    e^i &= F^{-T} \cdot e^i_0 = e^i_0 \cdot F^{-1}
\end{align*}
\]

An arbitrary tensor can be expressed in covariant, contravariant or the mixed-
variant components form, for example a second order tensor can be written as,

\[ T = T_{ij} e^i \otimes e^j = T^j_i e_i \otimes e^j = T^{ij} e_i \otimes e_j \]  \hspace{1cm} (B.7)

Contravariant components and covariant components can be related through the contravariant and covariant metric tensors, for example,

\[ T_{kl} = e_k \cdot T \cdot e_l = e_k \cdot (T^{ij} e_i e_j) \cdot e_l = T^{ij} (e_k \cdot e_i) (e_l \cdot e_j) = a_{ki} T^{ij} a_{lj} \]

where \( a_{ki} \) and \( a_{lj} \) are defined as the covariant metric tensor, \( i.e., \)

\[ a_{ij} = < e_i, e_j > . \]  \hspace{1cm} (B.8)

Similarly the contravariant metric tensor is defined as

\[ a^{ij} = < e^i, e^j > . \]  \hspace{1cm} (B.9)

Note in the case of the Cartesian coordinate system, the metric tensors are the same as the identity matrix, but in the case of a generalized coordinate system, the metric tensors are not trivial. Suppose \( e_i \) and \( e_j \) are the covariant basis convected with deformation whose deformation gradient is \( \mathbf{F} \), and they correspond to the reference Cartesian basis
$\mathbf{e}_i^0$ and $\mathbf{e}_j^0$, i.e., $\mathbf{e}_i = \mathbf{F} \cdot \mathbf{e}_i^0$, then

$$\mathbf{e}_i \cdot \mathbf{e}_j = (\mathbf{F} \cdot \mathbf{e}_i^0) \cdot (\mathbf{F} \cdot \mathbf{e}_j^0) = (\mathbf{e}_i^0 \cdot \mathbf{F}^T) \cdot (\mathbf{F} \cdot \mathbf{e}_j^0) = \mathbf{e}_i^0 \cdot (\mathbf{F}^T \cdot \mathbf{F}) \cdot \mathbf{e}_j^0 = (\mathbf{F}^T \cdot \mathbf{F})_{ij} \quad \text{(B.10)}$$

and

$$\mathbf{e}^i \cdot \mathbf{e}^j = (\mathbf{F}^{-1} \cdot \mathbf{F}^{-T})_{ij} \quad \text{(B.11)}$$

In another word one function of contravariant metric tensor is to raise the lower indices, and covariant metric tensor can be used to lower the upper indices, for instance,

$$T_{kl} = (\mathbf{F}^T \cdot \mathbf{F})_{kl} T_{ij} (\mathbf{F}^T \cdot \mathbf{F})_{lj} \quad \text{(B.12)}$$

It is often seen that the contravariant form is used to describe stress tensors and the tangent moduli, but the covariant form is used to describe strain tensors. The two-point tensors such as deformation gradient and velocity gradient are often described by a mix-variant form.

One shall notice from Eq. (B.10) that the definition of a covariant metric tensor is the same as Green strain tensor,

$$\mathbf{C} = \mathbf{F}^T \cdot \mathbf{F} \quad \text{(B.13)}$$

or in another word that the components of the contravariant metric tensor of a deformed configuration are identical to the Green strain tensor on the reference configuration. One can also say that the Green strain tensor is the pull-back of the metric tensor.

Similarly, the Kirchhoff stress and the 2nd PK stress are related through,

$$\mathbf{\tau} = \mathbf{F} \cdot \mathbf{S} \cdot \mathbf{F}^T \quad \text{(B.14)}$$
But note that it can be proven that the components of the kirchhoff stress on the deformed lab basis are identical to the components of the second Piola-Kirchhoff stress on the reference basis, \( i.e. \)
\[
\tau_{ij} = S^{ij}, \quad \text{(B.15)}
\]

\( S \) is also called the pull-back of \( \tau \) by \( F \).

Note that in the final equation, \( \dot{N}_{ij} + \dot{B}_{ij} = K_{ijkl}\dot{F}_{lk} \), \( B_{ij} \) and \( K_{ijkl} \) are just two mathematical matrices, which do not really have specific physical meaning, but \( \dot{N}_{ij} \) and \( \dot{F}_{lk} \) are the components of the rate of the nominal stress and the deformation gradient on the reference laboratory basis respectively.
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