Abstract

Nanolayered composites can exhibit unprecedented combinations of material properties. In principle, they also offer a superior system to understand how internal defects—such as grain boundaries or interfaces—control strength. However, in practice, only average composite properties are measured, while the underlying strengthening phenomena occur within individual layers. To address this missing capability, two novel methods have been developed to determine the constituent strengths of nanolayered composites. The first, an indentation-based method, couples finite element simulations with experimental nanoindentation and micropillar compression. The second, a diffraction-based method, uses heated x-ray diffraction and provides useful, external verification of the first method. Both methods are applied to the Cu/Ni system, and interestingly, layer constituent strengths are in good agreement with published strengths of pure, nanocrystalline Cu and Ni. The methods serve complimentary purposes. The diffraction-based method reveals previously unreported features of work hardening, reverse plasticity, and the role interfaces play as dislocation sources, but is limited to crystalline systems on substrates. The indentation-based method provides only individual constituent strengths but allows for more rapid, widespread adoption. It also exposes potential errors in the conversion of hardness to uniaxial strength simultaneously providing new routes to optimize the hardness of nanolayered composites.
Dedication

This document is dedicated to my parents who instilled in me a love of learning and gave me the opportunity to pursue my passions.
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Vita

June 2003 .............................................Walsh Jesuit High School
June 2008 .............................................B.S. Materials Science and Engineering,
                                        The Ohio State University
August 2010 .......................................M.S. Materials Science and Engineering,
                                        The Ohio State University
2010 to present .....................................Graduate Research Associate, Department
                                        Materials Science and Engineering, The
                                        Ohio State University

Publications

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Ray Diffraction Studies of Forward and Reverse Plastic Flow in Nanoscale Layers


Fields of Study

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Chapter 1: Introduction

1.1 Motivation

Material property trade-offs are inherent to materials, that is, improving one property may have a negative impact on another, and many of the grand challenges in environmental sustainability, national security, bioengineering, and energy require combinations of such opposing properties that cannot currently be met by conventional materials [1]. One strategy to meet the desired property combinations is by the judicious combination of two or more distinct materials into a composite material [2], another is to reduce the microstructural size scale. However, many limitations persist and require novel strategies like merging these two approaches—combining two or more constituents at the nanoscale to create nanostructured composites. One example is Cu/Nb nanolayered composites which exhibit a coveted combination of material properties including: strength of 1-2 GPa while maintaining good ductility (>30% at failure in compression) [3,4], temperature stability [5], and radiation tolerance [6].

Despite being a critical property for applications and although more than 30 unique nanolayered composite systems have been fabricated, our ability to predict nanolayered composite strength is still limited. In the systems tested, there is a consensus that strength increases with decreasing layer thickness and is defined by the ability of the
interfaces to resist dislocation transmission. Moreover, strength is generally attributed to a difference or “mismatch” in bulk properties including: stress-free lattice parameter, elastic shear modulus, stacking fault energy, Burgers vector, crystal system, or to interfacial shear strength, yet isolation of these relative contributions has proven elusive.

Problems predicting nanolayered composite strength are a result of the nearly exclusive use of nanoindentation to experimentally determine it. Nanoindentation is a convenient test method, particularly for thin film nanolayered composites where only small sample volumes are available, but it suffers from two primary drawbacks: (i) indentation generates a complex, multi-axial stress state which leads to potential errors when converting to uniaxial strength, especially in heterogeneous materials; (ii) standard indentation analysis provides only average, composite properties. In contrast, individual constituent strengths are typically used to predict composite strength in bulk composite materials [2]. Access to constituent strengths in nanolayered composites could provide additional insight into their strength and deformation mechanisms.

A better way to investigate interface properties and predict nanolayered composite strength would be to compare individual constituent strengths in systems with a variety of interfaces. For example, one could determine the strength of 20 nm thick Cu layers when layered with 10 or 30 nm of Ni to explore the contribution lattice parameter mismatch (coherency). Or one could access the contribution of slip continuity by comparing the strength of 20 nm thick Cu layers when layered with Ni vs. Nb layers. The lack of
accessible methods to extract individual constituent strength limits the ability to fully evaluate nanolayered composites.

1.2 Objective

The objective of this thesis is to detail two methods for extracting constituent strengths from nanolayered composites. The first couples finite element indentation simulations with experimental nanoindentation and micropillar compression. The second uses heated x-ray diffraction and provides useful external verification of the first method. In combination these methods reveal potential errors in the conversion from hardness to uniaxial strength of nanolayered composites and provide new routes to optimize hardness. Cu-20/Ni-20 nm is used as a model system.

1.3 Thesis Organization

Chapter 2 follows the general organization of most studies on the topic of nanolayered composite mechanical behavior. The goal of Chapter 2 is to guide readers new to the field of nanolayered composites through common analysis procedures and identify areas for improvement, particularly in mechanical testing. Discussion begins with descriptions of the common fabrication methods followed by the resulting structure and how it is characterized. Next, techniques to determine mechanical behavior are summarized and discussed in terms of deformation mechanism proposed in the literature.
In Chapter 3, a series of finite element indentation simulations are used to examine how individual constituent properties affect the conversion from hardness to uniaxial strength. The significance of in-plane residual stress, constituent strength mismatch, and elastic properties is assessed. Additional information is provided to help identify when residual contact area may need to be directly measured. The key result are plots of the Tabor factor (hardness normalized by uniaxial strength) that allow for the extraction of constituent strengths provided that, in-plane residual stress, uniaxial strength, elastic modulus, and hardness are measured experimentally.

The indentation-based method for extracting constituent strengths is presented in Chapter 4. Here, in-plane residual stress, uniaxial strength, elastic modulus, and hardness are experimentally determined for a Cu-20/Ni-20 nm system and are then compared with the finite element simulations performed in Chapter 3. Results suggest that 20 nm Ni layers are 3 times as strong as 20 nm Cu layers, and illustrate that accurate calculation of the Tabor factor requires uniaxial and hardness testing at comparable strain rates.

The diffraction-based method for extracting constituent strengths is presented in Chapter 5. X-ray diffraction is used to calculate in-plane stress in situ during a heating and cooling cycle. Since films are deposited on a Si substrate with a much lower thermal expansion coefficient, the film is compressed during heating and stretched during cooling. Again Cu-20/Ni-20 nm is used as a model material, although Cu-10/Ni-10 nm is
also included for comparison. This chapter follows the recently published work Ref. [7], but has been edited slightly for consistency.

In **Chapter 6**, Cu and Ni constituent strengths extracted from Cu-20/Ni-20 nm using the indentation and the diffraction-based methods are compared to each other as well as to the strength of thin film, nanocrystalline, and single crystal nanowire Cu and Ni.

**Chapter 7** summarizes the conclusions from each chapter and provides key outcomes and potential future directions for this work. Routes to improve the indentation and diffraction-based methods are emphasized.
Chapter 2: Structure-Property Relationships

2.1 Fabrication

Nanolayered composites, also referred to as nanolaminates, multilayers, superlattices, or synthetically modulated structures are constructed of nanometer-scale layers of two distinct materials. Of primary concern to mechanical behavior is control over layer thickness, interfacial morphology, and chemically purity of the interfaces. Three common synthesis techniques will be discussed in the following sections: (i) physical vapor deposition including evaporation and sputtering, (ii) electrodeposition, and (iii) severe plastic deformation. Advantages and limitations of each method are discussed.

2.1.1 Physical Vapor Deposition

Physical Vapor Deposition (PVD) is a process in which removal of a source material, facilitated by thermal (evaporation) or kinetic energy (sputtering), is followed by deposition of the source material onto a substrate [8]. Deposition is done under high vacuum to allow efficient transport of the target material to the substrate. PVD is an attractive method to fabricate nanolayered composites because there are essentially no limitations on source material; for example, in addition to metal/metal systems, both Al/TiN [9] and Cu/amorphous PdSi [10] films have been deposited using sputtering.
Moreover, PVD maintains good control of layer uniformity and reproducibility over layer thicknesses from tens of nanometers to tens of micrometers [8]. PVD, however, suffers from inflexibility of substrate shape, slow deposition speed (10-100 Å/s, [11]), and limited scalability compared to electrodeposition and severe plastic deformation-based fabrication methods. Two types of PVD used to fabricate nanolayered composites, evaporation and sputtering, will be discussed in more detail in this section.

Evaporation techniques use thermal energy to vaporize the source material. The vaporized material travels through a vacuum where it is deposited onto a substrate. The quality of the evaporation process is highly dependent on the method used to vaporize the source material, and fabrication of metallic nanolayered composites is typically performed using an electron beam [12,13]. Although resistive heating is less expensive, it suffers from contamination issues (from the crucible and resistance wire) and difficulties depositing materials with high melting temperatures [8]. Pulsed Laser Deposition (PLD) has also been attempted but shows evidence of problems achieving a uniform layered structure [14].

A schematic of the evaporation process for dual source electron beam evaporation appears in Figure 1(a). In this case, two source crucibles and a rotating substrate are used to achieve the layered structure. An example of a Cu/Ni nanolayered composite (layer thicknesses of 3.5 nm) produced by electron beam evaporation is shown in Figure 1(b).
Sputtering techniques use kinetic energy; high speed noble gas ions are used to dislodge the source or target material, following which, the dislodged target material condenses onto a substrate [8]. The ejected target atoms are subjected to collisions with gas molecules which results in atoms with a range of trajectories hitting the substrate. This leads to more isotropic and better step coverage than in evaporation processes [8] although the increased energy at impact could potentially lead to intermixing of layers [15]. Depending on the nature of the target material, either DC (for a conducting target) or HF/RF (for a non-conducting target) sputtering can be used. Although sputtering rates can be increased with the incorporation of an electromagnetic field, so-called magnetron sputtering [8,16], deposition rates for multilayers are remain on the order of Å/s.

A DC sputtering system is shown in Figure 2(a). Due to its superior control over layer thickness and wide spectrum of potential source materials, DC magnetron sputtering is the most common method used to fabricate nanolayered composites.
producing layers in the range of hundreds of nanometers to less than nanometer thicknesses [17]. An example of magnetron sputtered Cu/Ni multilayers with a layer thickness of 11 nm is shown in Figure 2(b) [18].

![Figure 2: Sputtering: (a) schematic of a DC sputtering system [8] and (b) a TEM image of a Cu/Ni nanolayered composite with uniform 11nm layer thickness deposited by DC magnetron sputtering on a Si substrate [18]](image)

2.1.2 Electrodeposition

Electrodeposition or electroplating is an electrochemical deposition method in which metal from an aqueous, electrolytic solution is deposited on to an electrode by passing electric current through the electrolyte. For fabrication of layered materials, a single-bath method in which constituent materials are selectively deposited onto an electrode by altering either the applied potential or the applied current is most common [19], a schematic is provided in Figure 3(a) [20].
A natural trade-off between consistent layer thickness and interface sharpness exists when depositing with electrodeposition. During potential controlled deposition, a short period of anodic current can occur when the potential is changed. The consequence is local, heterogeneous dissolution of the deposited species leading to inconsistent layer thicknesses [19]. Anodic current can be avoided using a current controlled system, but now, a change in current results in a non-instantaneous potential response and leads to diffuse interfaces [22]. However, since the deposited material is dependent on electrolyte composition, pH, temperature, and agitation in addition to potential and current density, improvements may be made with appropriate control of these variables. For example, Menezes and Anderson used current controlled deposition with the addition of an agitation modulation to produce layers as thin as 2 nm [23], and Lashmore and colleagues used a potential controlled system with the addition of a coulometer (to measure the
electrical charge) and produced Cu/Ni layers with consistent layer thicknesses of 10 nm, Figure 3(b) [21,24].

Advantages of the electrodeposition process include: low cost, scalability, the ability to tailor crystal orientation [24], low processing temperature to limit interdiffusion (e.g. 30 °C [21]), high deposition rates (µm/s, [25]), and can be used to create free-standing films or coatings.

The primary limitation however, is that not all multilayer systems can be deposited. Some systems suffer replacement reactions (Cu-Co [20]) or have difficulty nucleating uniform layers on one another. Yahalom et al. [26] used high-resolution transmission electron microscopy to show that interfaces in Cu/Ni multilayers are not atomically sharp and composition modulation leads to Cu-rich and Ni-rich layers. Compounding these problems is the lack of a more general demonstration or a theoretical treatment of multilayer electrodeposition [19].

2.1.3 Severe Plastic Deformation

In contrast to PVD and electrodeposition, Severe Plastic Deformation (SPD) is a top-down approach in which bulk materials are plastically strained to create a refined microstructure allowing the fabrication of bulk-size specimen. Accumulative Roll Bonding (ARB) is a sub-category of SPD processing in which ultra-fined grained bulk sheet material has been produced [27]. In this process a sheet material is cut, a surface
treatment is performed, and the sheets are then stacked and rolled as shown in Figure 4(a) [28]. The process can then be repeated with intermittent heat treatments to achieve progressively finer microstructures. However, attempts to produce layered structures of dissimilar metals typically results in fractured layers prior to reaching nanoscale dimensions [29–32]. Fragmentation of the layers occurs due to a difference in work hardening rates of the constituents [31], and it can significantly reduce strength compared to sputter deposited films. But recently, layered structures with layer thickness below 10 nm (with some variability in layer thickness) have been achieved in Cu/Nb [28], Figure 4(b). The strength of non-fragmented Cu/Nb layered composites produced by ARB is comparable to sputter fabricated composites even though the interface structure differs [33]. With successful fabrication of ARB Cu/Nb nanolayered composites, ARB appears to be a plausible process method allowing for relatively quick, low-cost manufacturing of bulk metallic nanolayered composites.
Figure 4: Accumulative roll bonding: (a) process schematic and (b) TEM micrograph of a Cu/Nb multilayer with 9 nm average layer thickness [28]

2.2 Structure

Understanding the structure of nanolayered composites is necessary to evaluate their mechanical properties and to establish dominate deformation mechanisms. Transmission Electron Microscopy (TEM) and x-ray based techniques are the primary characterization techniques are used to determine key characteristics including: layer thickness, grain size, residual stress, interface structure, interface morphology, and chemical sharpness of the interface. TEM provides local structural information. In contrast, x-ray techniques provide more global, average structural information, and require reduced sample preparation. Specific examples of TEM and x-ray techniques applied to nanolayered materials are discussed.
2.2.1 *Transmission Electron Microscopy*

In Transmission Electron Microscopy (TEM), information is obtained from the interaction of a high energy beam of electrons with a sample. Thin samples are required such that generated electrons and interaction are not entirely absorbed by the sample. Typically, samples with a thickness on the order of 100 nm are utilized. Cross-sectional TEM samples of nanolayered composites are often made using focused ion beam (FIB) techniques [34]. A number of other techniques to create thin samples for TEM analysis are summarized in Ref. [35].

Layer thickness, layer morphology, and interlayer grain size are primarily determined from bright field imaging, in which the transmitted or direct beam is used for imaging. In bright field imaging, a primary source of contrast is mass-thickness contrast. The thicker or higher mass (higher atomic number, Z for pure materials) an area of the specimen is, the greater the degree of scattering, and the darker the area will appear. Mass-thickness contrast is observable in an Al/Nb multilayer, where the higher mass Nb (Z = 41) is much darker than the lower mass Al (Z =13), **Figure 5(a)**. With the two phases identified, layer thickness, layer morphology, and interlayer grain size can be determined. Interlayer grain size is better illustrated in the Cu/Zr layers shown in **Figure 6(a)**.
Figure 5: Cross sectional TEM of an Al-5/Nb-5 nm layered composite: (a) bright field image showing mass contrast and SAD inset (b) HRTEM of an Al/Nb interface [36].

The inset in Figure 5(a) is a Selected Area Diffraction (SAD) pattern and provides crystal structure and orientation information about the sample. As its name suggests, SAD utilizes information from diffracted electrons. The pattern comes from a “selected area” of interest, the size of which can be controlled to some degree by apertures in the TEM. A spot on the diffraction pattern corresponds to a diffraction condition that is satisfied by the sample’s crystal structure. Radial distance from the direct beam (the central spot) is indicative of lattice spacing which allows indexing of planes, and strong spots indicate a preferred orientation. The SAD pattern in Figure 5(a) was used to confirm that the Al-5/Nb-5 nm has a strong Al\{111\} and Nb\{110\} texture with a Kurdjumov-Sachs (K-S) orientation relationship, such that \{111\}_Al||\{110\}_Nb and \textless 110\textgreater _Al\|\textless 111\textgreater _Nb [36].
High-Resolution TEM (HRTEM) can provide atomistic scale resolution [35], and is useful for determining intermixing and dislocation structure at interfaces. Figure 5(b) shows an image of the interface between Al and Nb in an Al-5/Nb-5 nm sample, and was used to conclude that minimal intermixing occurred at the Al/Nb interface [36]. Zhang et al. [37] illustrated HRTEM can also be used to image interfacial misfit dislocations at Cu/Zr interfaces, Figure 6(b). Similar work was performed on Cu/Ni interfaces by Misra et al. [38]. HRTEM has also been utilized to study deformation mechanisms in Cu/Nb by examining interlayer dislocation structure before and after deformation [39].

When electrons interact with a sample, they can produce x-ray radiation which, in a TEM, can be used to provide local compositional information like the degree of

Figure 6: Cross sectional TEM of an Cu-20/Nb-20 nm layered composite: (a) Layer structure and with compositional profile produced by EDS overlaid (b) HRTEM of a Cu/Zr interface used for determining interfacial dislocation structure [37].
intermixing at an interface. An example for a Cu/Zr layered composite is shown in Figure 6(a) [37]. This technique, known as Energy-Dispersive X-Ray Spectroscopy (EDX, EDS, or XEDS), is predicated on the principle that each element has a unique atomic structure allowing for a unique set of x-ray peaks in the x-ray spectrum [35]. Measured x-ray spectra can be compared to reference spectra to determine compositional variations on the nanometer scale.

2.2.2 X-Ray Scattering

TEM is centered on the interaction of electrons with the sample, while x-ray scattering is based on similar interactions of x-rays with the sample. X-ray scattering is a well-established, non-destructive characterization technique frequently used for determining the structure of materials. X-ray scattering experiments on nanolayered composites require minimal sample preparation and provide more global, film average properties compared to TEM. Relevant to nanolayered composites, x-ray scattering techniques can be separated into two regimes: reflectivity for determination of layer thickness and interface roughness, and diffraction for determining phases, crystal orientation (texture), and residual stress.

X-Ray Reflectivity (XRR), sometimes called low-angle x-ray diffraction, provides layer thickness information through the reflection of incident x-rays off interfaces between layers [40,p.171]. The geometry of an XRR experiment on a thin film is provided in Figure 7. The incident x-ray beam makes a shallow angle, $\theta = 0-3^\circ$ with
the film surface, known as a grazing incidence. The outgoing, reflected x-ray beam intensity is reduced by reflection at the interface and absorption within the film before being measured by a detector also at an angle $\theta$ with the film surface. The geometry is analogous to Bragg diffraction geometry in crystalline solids, but here the material need not be crystalline. Constructive interference occurs when:

$$2t \sin \theta = m\lambda$$

(1)

where $m$ is the integer reflection index, and $\lambda$ is the x-ray wavelength. Equation (1) is analogous to Bragg’s law if the film thickness $t$ is replaced by the interplanar lattice spacing $d$.

![Figure 7](image)

**Figure 7**: Schematic of an XRR experiment on a thin film – substrate system [40]

An example XRR pattern used to calculate layer thicknesses for a Mg-50/Ti-50 nm layered composite is shown in **Figure 8** [41]. Layer thicknesses measured using XRR are typically comparable to TEM measured layer thicknesses [41].
Intensity oscillations in the reflectivity occur due to the interference of x-rays that are reflected from interfaces. The peaks of the so-called Kiessing-fringes can be used to calculate layer thickness through **Equation (1)**. Similar XRR analysis for determination of layer thickness has been applied to: Mo/TiC [42], Ag/Cu [43], Pd/Ti [44], Mo/Ni [45], Pb/Ge [46], Pb/Cu [46], and Ti/Ni [45]. Additionally, the decay in intensity has been used to estimate an average interface roughness [44].

![XRR pattern](image)

**Figure 8:** An XRR pattern for a Mg-50/Ti-50 nm layered composite used to determine layer thicknesses of Mg and Ti [41].

At higher incident angles, X-Ray Diffraction (XRD) can be used to measure interplanar lattice spacings normal to the film surface [40,p.12]. Lattice spacings can provide information about the phase, structure, and texture of the sample. Example XRD patterns obtained in Cu/Ni films with predominately (111) and (100) planes normal to the
film surface are shown in Figure 9(a) and (b) respectively. Diffraction peaks are labeled with their corresponding phase and crystallographic \{hkl\} plane indices which are determined using Bragg’s law. In Figure 9(a) the Cu/Ni film has a (111) texture—no other Cu or Ni peaks are observed—and the (111) planes in the Cu and Ni are parallel to the (110) planes in Si, \((111)_{\text{Cu/Ni}} \parallel (110)_{\text{Si}}\). Figure 9(b) indicates that, in this case, the Cu/Ni film has a (100) texture with \((100)_{\text{Cu/Ni}} \parallel (100)_{\text{Si}}\). These differences are easiest to observe at the largest layer thickness, \(h = 100\) nm. At smaller layer thicknesses, \(h \leq 10\) nm, superlattice reflections appear and can be used to estimate layer thickness [45,47,48], and, over time, provide evidence of interdiffusion [49,50]. Note that the Si peaks at \(2\theta \approx 47^\circ\) in Figure 9(a) and \(2\theta \approx 69^\circ\) in Figure 9(b) are labeled Si (110) and Si (200); however, structure factor rules forbid diffraction of these Si planes. Instead, they should be labeled Si (220) and Si (400).
Residual stress is caused by both the mismatch in lattice spacing between the two constituents in a nanolayered composite and the presence of the substrate. Moreover, residual stress can affect measurement of mechanical properties. An excellent example is the supposed “supermodulus” effect. The effect was based on bulge testing results that suggested the elastic modulus of nanolayered composites significantly increased at small layer thicknesses [51], but subsequent measurements of residual stress and finite element modeling in similar systems indicated the increase in modulus was a consequence of neglecting residual stress [52].

With reference to a stress-free lattice spacing $d_0$, lattice spacings measured by XRD, $d$ can be used to calculate residual strain:
\[ \varepsilon = \frac{d - d_o}{d_o} \] (2)

**Equation (2)** provides the strain in \{hkl\} planes parallel to the scattering vector, which in standard diffraction geometry is normal to the surface of the film. If instead we wish to determine the strain in another direction we must tilt and/or rotate the sample as shown in **Figure 10**.

![Figure 10: Sample and laboratory reference frame for 4-circle XRD geometry][1]

**Figure 10** illustrates the sample reference frame \((X_1, X_2, \text{ and } X_3)\) and the four-circle diffraction geometry with the four corresponding angles [53]:

- \(\psi\), is the angle between the scattering plane and the sample normal, \(X_3\)
• \( \phi \), the rotation angle in the plane of the sample
• \( \omega \), the angle between the incident beam and the surface of the sample
• \( 2\theta \), the angle between the incident beam and the scattered beam

The measured strain at angles \( \psi \) and \( \phi \)—parallel to a set of \{hkl\} planes—can be written in terms of strains in the specimen coordinate system using tensor transformation rules [40,54]:

\[
\varepsilon_{\psi \phi} = \frac{d_{\psi \phi} - d_0}{d_0}
\]

\[
\varepsilon_{\psi \phi} = \varepsilon_{11} \cos^2 \phi \sin^2 \psi + \varepsilon_{22} \sin^2 \phi \sin^2 \psi + \varepsilon_{33} \cos^2 \psi + 
\varepsilon_{12} \sin 2\phi \sin^2 \psi + \varepsilon_{13} \cos \phi \sin 2\psi + \varepsilon_{23} \sin \phi \sin 2\psi
\]

Following Equation (3), the full strain tensor can be determined if strain is measured in six independent directions, less if assumptions about the stress/strain state are made. Independent knowledge of the materials elastic constants allows one to calculate stress through Hooke’s law, defined in the sample coordinate system:

\[
\sigma_{ij} = C_{ijkl} \varepsilon_{kl} \quad \text{or} \quad \varepsilon_{ij} = S_{ijkl} \sigma_{kl}
\]

Thin films are often assumed to have a biaxial stress state defined as [40]:
\[
\sigma_{ij} = \begin{pmatrix}
\sigma_{ip} & 0 & 0 \\
0 & \sigma_{ip} & 0 \\
0 & 0 & 0
\end{pmatrix}
\] (5)

Assumption of a biaxial stress state and either a (100)-oriented single crystal or a sample with a (100) fiber texture reduces Equation (3) to [53]:

\[
\varepsilon_{\psi\psi} = [2S_{12} + (S_{11} - S_{12}) \sin^2 \psi] \sigma_{ip}
\]
\[
d_{\psi\psi} = [2S_{12} + (S_{11} - S_{12}) \sin^2 \psi] \sigma_{ip} d_0 + d_0
\] (6)

Or equivalently for a (111) single crystal/fiber texture [53]:

\[
\varepsilon_{\psi\psi} = \left( 2S_{12} + \frac{S_{44}}{2} \sin^2 \psi + \frac{2}{3} S_0 \right) \sigma_{ip}
\]
\[
d_{\psi\psi} = \left( 2S_{12} + \frac{S_{44}}{2} \sin^2 \psi + \frac{2}{3} S_0 \right) \sigma_{ip} d_0 + d_0
\] (7)

with \( S_0 = S_{11} - S_{12} - S_{44} / 2 \)

Using a plot of \( \sin^2 \psi \) vs. \( d_{\psi\psi} \), both the stress-free lattice spacing \( d_0 \) and the average in-plane stress \( \sigma_{ip} \) can be determined. An example is provided for Fe/Pt nanolayered composites in Figure 11 [15]. The stress-free direction \( \psi_0 \) can be determined by first setting \( d_{\psi\psi} = d_0 \) and solving for a stress-free direction, \( \psi_0 \). The stress-free lattice spacing is the intersection of the stress-free direction and the \( \sin^2 \psi \) vs. \( d_{\psi\psi} \) curve as shown in Figure 11. Daniels et al. [15] used the change in stress-free lattice spacing to estimate the degree of intermixing in Fe/Pt films.
Figure 11: Lattice spacing vs. $\sin^2 \psi$ for Fe/Pt nanolayered composites of various thicknesses with a (100) texture: (a) Fe (211) planes and (b) Pt (420) planes [15]

The average in-plane stress $\sigma_{ip}$ can be calculated either using the slope or the intercept of the $\sin^2 \psi$ vs. $d_{\phi \psi}$ curve. Alternatively it can be measured directly setting $\psi \approx 90^\circ$ as shown for Pt in Figure 11 and for Cu/Ni in Ref. [55], however, this “direct method” requires estimation of the stress-free lattice parameter. XRD-based residual stress measurement has been carried-out in nanolayered composites including: Ag/Ni
[56,57], Ag/Cu [58], Al/SiC [59] Au/Ni [53], Cu/Nb [60], Cu/Ni [7,55], Cu/W [61], Fe/Pt [15], and Ni/Mo [62]. For more discussion on the $\sin^2 \psi$-method and the measurement of residual stress see Ref. [40] and [54].

Substrate curvature measurements are not used in the present study, but it is appropriate to note that substrate curvature has been used frequently to determine residual stress in nanolayered composites including: Ag/Cu [63], Al/TiN [64], Cu/330 Stainless Steel [65], Cu/Cr [66], Cu/Nb [67], Cu/Pd [68], Cu/Pt [68], and Pd/Pt [68]. Substrate curvature is a useful complementary technique since it is not limited to crystalline systems [69]; however it does not provide phase specific residual stress.

2.3 Mechanical Behavior

Evaluation of deformation mechanisms in nanolayered composites is reliant on accurate test methods. Since the majority of nanolayered composites are fabricated in small quantities as thin films using PVD fabrication methods, traditional bulk mechanical testing techniques are not possible. With a focus on determining strength, the following section covers the three primary methods for mechanically testing thin films: nanoindentation, tensile testing, and micropillar compression. Challenges specific to testing nanolayered composites are addressed for each method. Examples of results in the literature are given where available. Other testing methods including: substrate curvature [70], rolling [71], and biaxial bulge testing [72] have been used but are not discussed in detail.
2.3.1 Nanoindentation

At present, the primary metric for evaluating the mechanical behavior of nanolayered composites is hardness as determined by nanoindentation. Brief descriptions of nanoindentation testing and the Oliver-Pharr method for calculating hardness are provided here. In order to extract deformation behavior, hardness is measured over a range of layer thicknesses and compared, however a number of potential errors exist when doing so and require discussion. Additionally, hardness is often converted into a uniaxial strength, which can also be problematic. These problems have not been addressed in the literature to this point and are a central theme of this thesis. They will be addressed in Chapter 3.

Nanoindentation is the most common method of mechanical testing for nanolayered composites—and thin films in general—due to its ease of use, small interaction volume, and minimal sample preparation. Nanoindentation, or more broadly, instrumented indentation, involves pressing an indenter of known elastic properties and geometry into the surface of a material by applying small force increments and measuring the corresponding displacement response in a sample material. Refinement in the resolution of both force and displacement measurements led to the ability to test materials using indentation depths in the nanometer range thereby earning the name nanoindentation. A schematic of the Nano Indenter G200 manufactured by Agilent
Technologies and a representative load-displacement \((P-h)\) curve produced during indentation [73] appear in Figure 12(a) and (b) respectively.

![Figure 12: Nanoindentation: (a) a schematic of the Nano Indenter G200 system produced by Agilent Technologies and (b) a representative load-displacement curve for an elastic-plastic material [73].](image)

Hardness is a measure of how resistant a material is to permanent shape change [74], and is defined as the peak indentation load, \(P_{\text{max}}\) divided by the projected contact area of the resulting indent, \(A\):

\[
H = \frac{P_{\text{max}}}{A}
\]  

Traditionally, \(A\) is measured directly from the residual indent impression after unloading (the Meyer hardness), however the small loads that make nanoindentation attractive for testing thin films make the indent impressions small and thus difficult to
measure [75]. Instead, following the framework provided by Oliver and Pharr [73], $A_{OP}$ represents the contact area under load and is obtained through measurement of the unloading slope, $S$ from the indentation load-displacement curve:

$$S = \frac{dP}{dh} = \beta \frac{2}{\sqrt{\pi}} E_r \sqrt{A_{OP}}$$

(9)

where $E_r$ is the reduced modulus and is used to account for the effect of a non-rigid indenter on the measured load-displacement behavior using the elastic properties of the indenter ($E_i, \nu_i$) and the sample ($E, \nu$):

$$\frac{1}{E_r} = \left( \frac{1 - \nu^2}{E} \right) + \left( \frac{1 - \nu_i^2}{E_i} \right)$$

(10)

Note that a constant $\beta$ is sometimes included in Eq. (9) to account for “any and all physical processes” that may affect $S$, specifically, to address changes in stiffness due to the lack of axial symmetry for pyramidal indenters [76]. Some debate exists over the proper value [77–79], and while $\beta = 1.034$ is commonly cited as the appropriate value [76], $\beta = 1$ is often used in practice.

The contact stiffness, $S$ is calculated by fitting the unloading load-displacement data using a power law relationship:
\[ P = \alpha (h - h_f)^m \]  \hspace{1cm} (11)

where in this case \( \alpha \), and \( m \), are fitting parameters determined by a least squares fitting procedure between the peak load and 50\% of the peak load. \( h_f \) is the final displacement depicted graphically in Figure 12(b). Stiffness is then determined by evaluating the derivative of \( P \) with respect to \( h \) evaluated at the peak load.

An important advancement is the ability to measure contact stiffness by imposing a small dynamic oscillation on the applied force signal and measuring the amplitude and phase of the corresponding displacement [76,80]. As this technique’s name suggests, the “Continuous Stiffness Measurement” (CSM) allows for measurement of stiffness continuously—as a function of indentation displacement—reducing the number of indentation tests needed, improving the ability to precisely determine the point of initial contact, and simplifying indenter calibration procedures [76]. Critical issues related to the CSM technique are discussed in more depth in Ref. [81], and Ref. [82] provides a review on the CSM technique.

Once \( S \) is determined either using unloading data or the CSM technique, hardness can be calculated using a known elastic modulus, or equivalently elastic modulus can be calculated if contact area is known. Since in many cases elastic modulus is unknown and, as pointed out previously, measurement of residual indent impressions becomes difficult at small loads, \( A_{OP} \) is estimated from an indenter area function that takes the form:
\[ A_{OP} = C_0 h_c^2 + C_1 h_c + C_2 h_c^{1/2} + C_3 h_c^{1/4} \ldots + C_n h_c^{1/2(n-1)} \] (12)

In practice, the coefficients, \( C_n \), are fit by indenting into a material of known elastic modulus, typically fused silica, over a range of indentation depths or by using the CSM technique. Details on the calibration procedure can be found in Ref. [76]. Alone, the first term describes a perfect pyramid or cone, and for a perfect Berkovich indenter, the area function reduces to \( A = 24.5 h_c^2 \). The second term describes a paraboloid of revolution or a sphere at small penetration depths, and therefore is representative of the indenter radius \( R, C_1 = 2\pi R [76,83] \).

The contact depth, \( h_c \), can be determined using available load-displacement data and the relationship [73]:

\[ h_c = h_{\text{max}} - \varepsilon \frac{P_{\text{max}}}{S} \] (13)

Initially, the geometric constant, \( \varepsilon = 0.72 \) was suggested for a Berkovich indenter [73], but \( \varepsilon \) was later changed to the geometric constant for a paraboloid, \( \varepsilon = 0.75 \), to be consistent with the indenter behavior upon unloading [76]. The unloading process is illustrated schematically in Figure 13.
Although, $h_c$ corresponds to the contact depth *under load*, Oliver and Pharr [73] showed good agreement between the contact area calculated using the load-displacement curve (Oliver-Pharr Analysis) and direct measurement of the *unloaded* or residual indent impression. An important caveat that is often neglected and bears repeating is that good agreement is intimately dependent on how contact area is measured. Specifically, in materials that experience large elastic recovery, for comparison with the contact area under load, contact area should be measured using the corners of the residual indent impression, as depicted by the larger triangle in Figure 14(b) [73]. Little elastic recovery occurs at the corners of the indent during unloading, it follows that agreement in the loaded and unloaded contact areas is not expected for smooth, axially symmetric indenters.

*Figure 13*: Schematic illustration of the indentation unloading process [76]
A key and well-known limitation of the Oliver-Pharr method is the underestimation of the contact area when material “pile-up” occurs. The inability to predict this behavior stems from the elastic analysis basis of the method. Using a finite element indentation model, Bolshakov and Pharr [84] concluded that, for bulk materials, pile-up is only a significant source of error in materials which exhibit little work hardening and have a large elastic modulus-to-yield strength ratios. For example, a > 30% underestimation in contact area was observed for an Aluminum-like material without strain hardening, but the error for the same material diminished as strain hardening and yield strength increased [84].

Pile-up can significantly influence hardness measurements on nanolayered composites. Pile-up behavior has been observed in Cu/PdSi [10], Al/TiN [9,64], Cu/Ag
[85], and Cu/Ni [86] systems, but quantitative measurements of contact area and corrections to hardness measurements were made only for Cu/PdSi [10]. Observations in Cu/Ag [85] and Al/TiN [9,64] suggest the tendency to pile-up decreases with decreasing layer thickness—note the stark contrast in residual indent impressions of Cu/Ag at layer thicknesses of 100 and 10 nm shown in Figure 15(a) and (b) respectively. Decreasing pile-up could indicate an increase in strain hardening and/or strength with decreasing layer thickness. Regardless of the cause, quantification of the residual indent area is required for accurate comparisons between the hardness of nanolayered composites.

Since hardness can be influenced significantly by contact area, a better parameter for comparison of nanolayered composites may be $P/S^2$ which is independent of contact area [87]. Combining Equations (8) and (9) shows that $P/S^2$ is directly proportional to hardness:
Although the ability to use $P/S^2$ for comparing hardness as a function of layer thickness is limited since it requires independent knowledge of elastic modulus, it warrants further investigation.

The substrate material which a nanolayered composite film is deposited on can influence hardness. As a rule-of-thumb, maximum indent depth is typically limited to 10% of the total film thickness, yet this may be in error when a hard film is deposited on a softer substrate [88]. Substrate effects are observed in the measured elastic modulus at smaller indentation displacements than hardness since the elastic zone is much larger than plastic zone. Therefore, the indentation depth where substrate effects become apparent can be determined by indenting to a series of indentation depths or by utilizing the CSM technique.

Hardness depends on residual in-plane stress. Not only do nanolayered composites have large residual in-plane stress, but the magnitude of residual stress often varies with layer thickness [66]. However, the effect of residual in-plane stress on hardness of nanolayered composites is unclear. Studies on an aluminum alloy show no effect on hardness when contact area is properly accounted for [89,90], but finite element simulations do predict a dependence—albeit in homogeneous materials—at strengths

\[
\frac{P}{S^2} = \frac{\pi}{(2\beta)^2} \frac{H}{E_r}
\]  

(14)
comparable to those found in nanolayered composites [91]. To this point, no studies, either experimental or computational, have directly addressed the contribution of residual in-plane stress to hardness in nanoscale layered composites.

2.3.2 Micropillar Compression

Unlike indentation with a sharp indenter, micropillar compression generates a nominally uniform, uniaxial stress state allowing direct measurement of the stress-strain curve. And since testing is performed using a nanoindentation system, excellent force resolution (3nN for Agilent’s Nano Indenter G200) is possible. Furthermore, compression does not suffer from the same geometric instability seen in tensile testing, and the volume of material tested is smaller than that used for micro-tensile tests reducing the likelihood of testing an area with fabrication induced flaws [92].

Micropillar compression involves machining of cylindrical, micro/nano-scale pillars into samples followed by compression in a nanoindentation system with a flat-tip punch [93] shown schematically in Figure 16. The load applied to the flat punch, the resulting displacement, and the contact stiffness (if CSM is available), are all continuously recorded during compression. Engineering stress and strain are calculated using the initial dimensions of the pillar and often converted to true stress strain using the assumption of volume conservation. Since strain is calculated using the displacement of the indenter, it requires a correction for the compliance of the tip as well as the material below the pillar. The corrected displacement, \( h_{\text{corr}} \) can be determined using the solution
for a perfectly rigid, circular, flat punch indenting into an isotropic elastic half space provided by Sneddon [94]:

$$h_{corr} = h_m - \frac{(1 - \nu_i^2)}{E_i} \frac{P}{d_t} - \frac{(1 - \nu_b^2)}{E_b} \frac{P}{d_b}$$

(15)

where $h_m$ is the measured displacement of the punch, $P$ is the measured load, $E_i$ and $\nu_i$ are the elastic properties of the indenter, $E_b$ and $\nu_b$ are the elastic properties of the base material and $d_t$ and $d_b$ are the measured pillar diameters at the top and bottom of the pillar respectively.

**Figure 16:** A schematic of the micropillar compression test geometry [53]
The method of fabricating micropillars can affect the measured load-displacement response. One of two Focused Ion Beam (FIB) milling techniques is typically used: lathe milling or annular milling, each potentially affecting the measured response differently [95]. Lathe milling yields pillars with a uniform diameter at the expense of longer ion beam exposure times. Although still debated, evidence suggests that long ion exposure can lead to the generation of surface defects [96,97]. Annular milling trades-off shorter exposure times for a less uniform pillar diameter (taper) and a propensity for rounding at the top of the pillar. A comparison of pillar geometries from a lathe milled, 4 μm Cu/Nb pillar [4] and an annular milled, 1 μm Al/Nb pillar [98] is provided in Figure 17(a) and (b) respectively. Geometric differences make comparing the mechanical behavior between samples worrisome. Select cases suggest, FIB damage could be even more troublesome—a four-fold increase in strength was observed in lathe milled Mg compressed along the [110] axis [95]. In contrast, compression of Al/SiC pillars fabricated by annular milling (4° taper but little rounding) and lathe milling produced similar results [99]. Alternative methods of pillar fabrication including: femtosecond laser machining [100], electroplating [101], and selective etching [102] have shown promise but each has its own limitations.
Figure 17: Effect of FIB milling method on pillar geometry for: (a) a lathe milled, 4 μm diameter Cu/Nb pillar [4] and (b) an annular milled, 1 μm diameter Al/Nb pillar

Straightforward analysis requires a uniform, uniaxial stress state within the compressed pillar which in turn is dependent on the geometry of the pillar and the alignment of the indenter. Finite Element Analysis (FEA) has shown that the fillet radius ($r_c$ in Figure 16), aspect ratio (pillar height/pillar width), and taper (angle between tangent of pillar side wall and pillar center axis) can significantly impact deformation behavior and failure mode [103]. Using FEA, Zhang et al. [103] concluded that: (i) large fillet radius/pillar radius is required to alleviate the stress concentration at the base of the pillar, but small fillet radius/pillar radius is needed to accurately capture material behavior—especially in materials with significant strain hardening. A compromise using a 0.2-0.5 ratio is suggested. (ii) An aspect ratio of $\leq 5$ prevents first mode buckling when using a coefficient of friction equal to 0.03. Generally, an aspect ratio of 2-3 is recommended. (iii) Taper produces errors in elastic modulus calculation and spurious strain hardening behavior, therefore it should be minimized. (iv) Finally, misalignment
between the pillar and the indenter significantly affects the test accuracy and can cause buckling. Misalignment can be minimized experimentally using a goniometric sample holder [93]. The effect of pillar rounding has not been assessed. Apart from geometry, non-uniform deformation can also occur intrinsically in response to crystallographic orientation [104] or a layered structure such as Al/SiC [99].

Pillar size can affect the measured stress-strain results. Much of the initial literature using micropillar compression focused on capturing the effect of pillar size on single crystal deformation in the absence of strain gradients [101,105,106] and is reviewed in Ref. [107]. Zhang et al. [108] observe changes in strength due to both intrinsic (layer thickness) and extrinsic (pillar diameter) size effects in nanolayered Cu/Zr, however, the fact that smaller pillars exhibit a greater degree of taper, have increased pillar rounding, and have relatively more FIB damage are ignored. Since the primary feature of interest in nanolayered composites is often the layer thickness, the pillar diameter should be much larger than the layer thickness to minimize extrinsic sample size effects. Conveniently, the effects of taper and FIB damage are reduced in larger diameter pillars.

Pillar compression tests have been performed in a number of nanolayered composite systems including: Cu/Nb [4,3,109,110,33], Cu/Ni [111], Cu/PdSi [10], Cu/Zr [108,112,113], Al/Nb [98], Al/Pd [114], Al/TiN [115], Al/SiC [99,116], Mg/Ti [41].
Again, comparisons between systems should be made with caution, considering pillar geometry and FIB damage if appropriate.

2.3.3 Tensile Testing

Tensile testing is an attractive method of material testing because it imposes a uniform stress state, and therefore, unlike nanoindentation, provides a direct measurement of the uniaxial stress-strain curve from which properties such as yield strength, strain hardening rate, and failure strain can be determined. However, complications including accurate measurement of strain and premature fracture due to geometric instability can potentially make strength determination unreliable.

In standard macroscale tensile testing, a sample is gripped on opposite ends and elongated to fracture in the tensile direction during which the force to elongate the sample and sample elongation are measured. When testing microscale specimen, measurement of force and elongation becomes more difficult. For example, a specimen with a cross-sectional area of 1 $\mu m^2$ requires a force resolution of approximately 1-10 $\mu N$ [92]. Load cells with this type of resolution are commercially available, however, use of high resolution, low capacity load cells add to the compliance of the test frame making it more difficult to measure elongation directly from grip displacements and possibly affecting fracture behavior [117,118]. Non-contact strain measurement alternatives such as laser interferometry (e.g. a laser extensometer) [119], digital image correlation [120] or in situ x-ray diffraction [60] have been used to resolve strain measurement issues when testing
thin film samples and have the additional benefit of minimizing error if grip slippage occurs.

In the few cases investigated, nanolayered composites typically show little elongation in tension prior to fracture, the amount of which decreases with decreasing layer thickness (see Ag/Cu [121] and Al/Ti [122]). This result would suggest limited ductility, yet deformation to much larger strains has been observed in different loading conditions including cold rolling, >80% [71] and uniaxial compression, 30% [4]. There are two important differences between the loading conditions. The loading direction in tension is parallel to the layers; while in compression and rolling, load is applied perpendicular to the layers. Additionally, in tension, the propensity for geometric instability or localization is greater.

To investigate the onset of geometric instability, consider a ductile bulk specimen pulled in tension. Assuming constant volume, the point of geometric instability (diffuse necking) occurs at the maximum load and is given by [123]:

\[
\frac{d\sigma}{d\varepsilon} = \sigma
\] (16)

For thin tensile specimen, necking is restricted to the thickness direction (i.e. the width of shear band remains constant). Now the point of geometric instability (localized
necking), occurs when the strain hardening rate, $d\sigma/d\varepsilon$ equals half of the true stress $\sigma$ assuming an isotropic sheet specimen [123,p.291–292]:

$$\frac{d\sigma}{d\varepsilon} = \frac{\sigma}{2}$$  \hspace{1cm} (17)

Equation (17) holds as the ratio of width strain to thickness strain approaches zero, and finite element analysis predicts that the width strain decreases as the width to thickness dimension ratio (W/T) increases [124].

The transition in fracture mode is clear upon examination of representative gauge sections of nanocrystalline Ni tensile specimen (grain size = 30 nm), Figure 18 [125]. When W/T > 8, Figure 18(a-b), fracture of the gauge section appears brittle, however once W/T < 8, Figure 18(c-d), fracture transitions to a ductile appearance. Yet, in all cases the fracture surface exhibits ductile dimpling suggesting intrinsic ductility.
**Figure 18**: Representative gauge sections and fracture surfaces from failed nanocrystalline Ni tensile specimen: (a) $T < 0.1$ mm, $W/T > 66$; (b) $T = 0.1-0.5$ mm, $W/T = 13-66$; (c) $T = 0.8-1$ mm, $W/T = 6-8$; (d) $T = 2-2.5$ mm, $W/T = 2-3$ \[125\].

PVD produced Cu/Nb nanolayered composite specimen with a $W/T = 200$ fail in tension at $\sim 3.5\%$ elongation, coinciding with the onset of localized necking, but as in the case of nanocrystalline Ni in **Figure 18**, ductile dimples appear on the fracture surface \[92\]. This result suggests that nanolayered specimen have intrinsic ductility, but elongation is limited due to the specimen geometry, specifically $W/T$ \[126\]. Despite having a $W/T = 10$, ARB produced Cu/Nb also fails at an elongation of $\sim 4\%$ perhaps demonstrating that $W/T < 10$ is needed to avoid localized necking. Indeed, tensile testing of coarse-grained \[118\] and ultra-fined grain Cu \[124\] as well as nanocrystalline Ni \[125\] demonstrate that $W/T < 8$ is needed to prevent localized necking.

Sensitivity to geometric instability can be compounded by sample alignment, inhomogeneities in the film produced during fabrication, surface roughness from sample preparation, and damage caused when removing thin films from their substrate. These
issues call the practice of using tensile elongation as a determinant for ductility in sub-scale tensile specimen into question.

Tensile testing has been performed in relatively few nanolayered composite systems: Al/Ti [122], Cu/Ag [121], Cu/Nb [33,117,60,127,128], and Cu/Ni [23,129–132]. Tensile testing at small scale remains difficult because thicker specimens are needed to avoid geometric instabilities, and yet the probability of fabrication defects in test specimen increases with size. Additionally, the quality of tests is hard to verify externally since tensile testing is performed parallel to the layers while other methods are typically performed with the loading direction perpendicular to the layered direction.

2.4 Strengthening Regimes

In nanolayered composites, strength is a function of layer thickness. Guided by changes in the slope of hardness vs. layer thickness, Misra et al. [17] separated the strengthening behavior of metallic nanolayered composites into three regimes—Hall-Petch, Single Dislocation, and Interface Crossing, Figure 19. Within each regime, Misra et al. [17] suggested a corresponding deformation mechanism. Although each regime has a unique deformation mechanism, macro-yield—large scale deformation—is controlled by the interfacial resistance to dislocation transmission. A discussion on each regime is provided in this section.
2.4.1  

**Hall-Petch Regime**

For most metallic nanolayered composite systems, at layer thickness greater than approximately 50 nm, hardness scales with layer thickness as $H \propto h^{1/2}$ (depicted by the linear fits in Figure 20) consistent with traditional Hall-Petch scaling. Similar to the observations in nanolayered composites, the traditional Hall-Petch theory was motivated by observations that strength increased with decreasing size—grain size, $d$ for conventional materials [133,134]. Furthermore, it was suggested that grain boundaries act as barriers to dislocation motion as they present discontinuities in: (i) slip plane, (ii) Burgers vector, (iii) stress-state, and (iv) modulus [135].
Figure 20: Nanoindentation determined hardness as a function of \((\text{layer thickness})^{1/2}\) for (a) fcc/fcc systems [85] and (b) fcc/bcc systems [36].

The Hall-Petch scaling behavior is derived following Anderson et al. [136]. At an applied stress, \(\sigma_a\), which is large enough to operate a dislocation source but below a critical stress, \(\sigma_{\text{crit}}\), dislocations will be generated and will pile-up against grain boundaries creating a stress concentrator. The number of dislocations in the pile-up scales as \(N_p \propto \sigma_a d\). The force on the leading dislocation at the grain boundary scales as \(f_p \propto \sigma_a^2 d\) and the stress in the vicinity of the pile-up scales as \(\sigma_p \propto \sigma_a d^{1/2}\). Eventually, \(f_p\) reaches a critical value \(f_c\) to push the leading dislocation across the boundary, or \(\sigma_p\) reaches a critical value to activate sources in the adjoining grain. In either case, the critical applied stress, \(\sigma_{\text{crit}}\), scales as the Hall-Petch relation, Equation (18), where \(\sigma_0\) is a reference stress yield strength in the limit \(d \to \infty\), and \(k_{\text{HP}}\) is the Hall-Petch slope.

\[
\sigma_{\text{crit}} = \sigma_0 + k_{\text{HP}} d^{-1/2}
\]  

(18)
For extension to layered materials, grain size \( d \) is simply replaced by layer thickness \( h \), although grain boundaries may still contribute to the strength of polycrystalline layered materials [137,138]. Note: unfortunately, both layer thickness and indentation displacement are given the symbol \( h \) in the literature. To remain consistent, \( h \) is used for both, but the meaning will be specified when used.

The Hall-Petch slope is a function of the interface barrier to dislocation transmission \( \tau^* \), and so, \( \tau^* \) is often estimated by measuring the \( k_{HP} \) assuming the following relationship [17,139]:

\[
\tau^* = \frac{k_{HP}^2 \pi (1 - \nu)}{Gb}
\]  

(19)

where \( \nu \) is the Poisson’s ratio, \( G \) is the shear modulus, \( b \) is the Burgers vector of the plastically weaker constituent. Good agreement between the barrier strength \( \tau^* \) determined using Equation (19) and estimated from peak hardness (using a Tabor factor of \( H \approx (2.7-3)\sigma \) and a Taylor factor of \( \sigma \approx 3\tau^* \)) has been achieved for Cu/Nb [17] and Mg/Ti [41]. However, care must be taken because the barrier strength \( \tau^* \) may be a function of layer thickness. Moreover, as will be shown in Chapter 3, the Tabor factor may also be a function of layer thickness.
2.4.2 Single Dislocation Regime

Hall-Petch scaling ($H \propto h^{-1/2}$) breaks down at layer thicknesses around 50 nm. Still, hardness continues to increase with layer thickness down to a few nanometers, albeit at a reduced rate. The breakdown in Hall-Petch scaling is believed to be a result of layer thicknesses becoming too small to accommodate dislocation pile-ups [140]. Instead, plastic strain is achieved by the slip of Orowan-type, hairpin dislocation loops confined within individual layers until the applied stress is large enough to overcome the interface barrier to dislocation transmission and dislocation loops propagate through interfaces [140]. A schematic of the propagation of an Orowan dislocation loop also called Confined Layer Slip (CLS) is shown in Figure 21.

![Figure 21: Schematic view of Orowan dislocation loop: (a) along the dislocation glide direction and (b) viewed with glide plane edge on [140]](image)

Orowan dislocation loops are generated from existing threading dislocations or nucleate at interfaces during fabrication [139,141,142]. In order for a loop to advance, the work done by the local resolved shear stress, $\tau$, must exceed the energy associated with
depositing dislocation line length, \( w \) at the interface \([139,140]\). This trade-off provides a critical resolved shear stress required to propagate a dislocation loop in CLS:

\[
\tau_{CLS} = \frac{2w}{bh'}
\]

where \( b \) is the slip distance, \( h' \) is the projected layer thickness of the glide plane, and \( w \) represents the interfacial dislocation line energy. As loops propagate, coherency stress is relieved and misfit dislocation structure is deposited at the interface.

The CLS model over predicts strengthening with decreasing layer thickness \( h \) when compared to experimental results.\([17,143]\) To correct for this over prediction, Misra et al. \([17]\) refined the model for incoherent interfaces, specifically for Cu/Nb (an fcc/bcc system), to include: interfacial core spreading, a normalized interfacial energy term, and a term to account for dislocation-dislocation interactions resulting from misfit dislocations. The refined CLS model relies on terms fit from atomistic modeling, namely the core spreading and interfacial energy terms (which are not easily obtained for a generic multilayer system) in addition to a fitting parameter for dislocation-dislocation interactions. Carpenter et al. \([55,144]\) also refined the CLS model but for semi-coherent Cu/Ni interfaces by including a dislocation pinning term and a dependence on interfacial dislocation density as fitting parameters. In both cases, the stress for CLS \( \tau_{CLS} \) as a function of layer thickness \( h \) approximately becomes:
The fitting coefficients (C₁, C₂, and C₃) take slightly different forms in Misra et al. [17] and Carpenter et al. [55,144], but in both cases, experimental verification of the fitting coefficients is difficult.

Dislocation glide via CLS, as presented here, has been observed in Cu-30/Nb-20 nm nanolayered composites during in situ nanoindentation within a TEM, Figure 22 [145]. Curved Orowan dislocation loops within the Cu layers can be observed in Figure 22(a). As the film is loaded, the marked loop glides to the left, Figure 22(a)-(c). Then, during unloading, the loop reverses direction and glides to the right, Figure 22(d)-(f). Glide loops were observed to nucleate at interfaces [145]. Similarly, Kramer and Foecke [146] captured simultaneous CLS in Cu and Ni layers during in situ tensile straining of Cu-35/Ni-55 nm films within a TEM.
Figure 22: Sequence of TEM images taken during *in situ* indentation loading and unloading of a Cu-30/Nb-20 nm film. During loading (a)-(c), the marked dislocation within the Cu layer glides to the left with both ends pinned at the Cu/Nb interfaces. During unloading (d)-(f) the same dislocation reverses direction and moves to the right [145].

2.4.3 Interface Crossing Regime

At layer thickness decreases below $h \approx 5$ nm, a number of systems exhibit a plateau in hardness (see Cu/Cr, **Figure 20b**) or a decrease in hardness with decreasing layer thickness (see Cu/Ni, **Figure 20a**). The plateau has been attributed to the stress for confined layer slip exceeding the barrier for dislocation transmission across the interface $\tau_{CLS} > \tau^*$[21,137] and agrees with simulations of loop expansion using 3D cellular automaton modeling [147,148]. The decrease in hardness has been attributed to nonlinear effects associated with layer thickness on the same order as dislocation core width
Effects of the dislocation core width coupled with the dependence of interfacial dislocation structure on layer thickness, may lead to a decrease in the dislocation transmission barrier at small layer thicknesses. The issue is complex, in that cases with wide dislocation cores, as predicted by atomistic modeling, may show little evidence of a hardness peak while those with narrow cores may display hardness peaks [85,149]. Furthermore, for layer thicknesses $h < 5 \text{ nm}$, the effects of even small amounts of interdiffusion may have a pronounced effect on strength [85].

2.5 Sources of Strengthening

Nanolayered composites derive their properties from a high density of interfaces and the interactions of the interfaces with mobile dislocations. Interfaces have been grouped into two categories: *transparent* if there is continuity of slip across interfaces; and *opaque* if there is no continuity. Both types of interfaces impart significant strength increases to nanolayered composites relative to bulk counterparts, however, evidence suggests the strengthening mechanism is different for each interface type.

2.5.1 Transparent Interfaces

Systems in which there is continuity of slip planes and slip directions across interfaces—such as cube-on-cube Cu/Ni and Cu/Ag—have interface which are termed “transparent” [150]. Dislocations can glide across transparent interfaces and simply leave a step at the interface with minimal residual dislocation content, therefore suggesting that transparent interfaces provide minimal resistance to slip transmission. However, despite
having continuity of slip, Cu/Ni [38] and Cu/Ag [85] still exhibit GPa-level strength due to several factors that restrict dislocations from moving from one layer to the next. Barriers to dislocation transmission are attributed to a difference or “mismatch” in: (i) stress-free lattice parameter $a_0$; (ii) elastic shear modulus $G$ (Koehler barrier); (iii) chemistry (stacking fault mismatch) $\gamma$; and (iv) Burgers vector $b$. Potential strengthening effects due to the formation of intermetallics at the interface will also be discussed. Each effect will be described in terms of how it may contribute to the interfacial barrier to dislocation transmission. The relative contribution of each has been studied primarily through computational modeling of Cu/Ni and to a lesser extent in Cu/Ag.

Atomistic simulations report that lattice parameter mismatch $\Delta a_0/a_0$ is the dominant barrier to slip in systems with transparent interfaces [150]. Lattice mismatch creates alternating compressive and tensile in-plane stress, known as coherency stresses, as atoms stretch or compress to match the lattice parameter of neighboring layers. Tension exists in layers with smaller $a_0$ and compression in layers with larger $a_0$ [149]. Consider now that a superimposed in-plane tensile stress is applied. The superimposed applied stress (e.g., in-plane tension) will tend to increase the magnitude of stress in one layer (e.g., the tensile layer) and decrease it in the other (e.g., the compressive layer). When slip commences, it may be confined by an oppositely signed in-plane stress in the adjoining layers. Macroyield is expected when the applied stress is sufficient to eliminate the alternating signed stress [150]. For layer thicknesses greater than the critical thickness
for CLS to operate and relieve coherency stress, \( h > h_{\text{crit}} \), arrays of misfit dislocations are present and interfaces become semicoherent [151]. Here, unrelieved pockets of large coherency stress between misfit dislocations, as well as the stress field of discrete misfit dislocations serve to increase the barrier to dislocation transmission [149].

Modulus mismatch \( \Delta G/G \) can also be a significant barrier to dislocation transmission. Since the energy/length of a dislocation is proportional to shear modulus \( G \), dislocations are attracted to reside in the lower modulus layer in an A/B system, similar to the attraction of dislocations to free surfaces. The extent of the attractive or repulsive “image” force on the dislocation is dependent on the difference in dislocation line energy in A vs. B layers and thus is proportional to the modulus mismatch [152,153]. Atomistic simulations predict the barrier due to modulus mismatch in Cu/Ni multilayers to be on the order of 0.01 \( G \) and nearly independent of interface orientation and dislocation character [154]. The contribution drops as layer thickness, \( h \), approaches the dislocation core size—for \( h < 10 \) nm [154].

Chemical mismatch \( \Delta \gamma/\gamma \) and Burgers vector mismatch \( \Delta b/b \) contribute significantly less to interface strength. Chemical mismatch is typically studied in terms of the unstable stacking energy \( \gamma \), that is, the maximum energy/area of a slip plane as it is sheared. Dislocation line energy tends to increase with \( \gamma \) [135] so that a mismatch \( \Delta \gamma \) can generate a force as the dislocation crosses an interface. Atomistic calculations suggest the contribution is relatively small (0.003 \( G \)) in Cu/Ni multilayers [154]. A mismatch in
Burgers vector leads to the formation of interfacial line defects (dislocations and disconnections) when dislocations cross the interface. These defects interact with mobile dislocations to hinder successive interface slip on the same or adjacent slip systems, thereby work-hardening the interface and encouraging homogenous deformation [150]. Disconnections are predicted to offer little resistance to the initial dislocation crossing the interface, but do offer resistance to subsequent crossing [155].

The formation of intermetallic compounds at interfaces may also contribute to interfacial barrier strength. The high hardness of Al/Pd nanolayered composites [114] compared to Cu/Ni [38] and Cu/Ag [85] has been attributed to the negative heat of mixing in Al/Pd vs. the positive heat of mixing in Cu/Ni and Cu/Ag [156]. A negative heat of mixing signifies a thermodynamic driving force for intermixing and formation of intermetallics at the interface. The presence of intermetallics in Pd/Al has been shown to increase the barrier to dislocation transmission compared to pure Pd/Al interfaces using atomistic simulations [156].

2.5.2 Opaque Interfaces

Opaque interfaces are present in non-isostructural systems. Although opaque systems tend not to have large coherency stress, their strength tends to exceed that of transparent interfaces, Figure 20 [157]. Here strength is attributed to a low shear strength of the interface and the resulting trapping of mobile dislocations [150]. Weak interfaces can be sheared by the stress field of an approaching dislocation, generating an attractive
force that absorbs the dislocation. The core of the absorbed dislocation spreads into an intricate, non-planar pattern due to the low, non-uniform shear strength of the interface as shown in Figure 23 [158]. Transmission then requires compaction of the dislocation core to nucleate a mobile dislocation in the adjacent crystal [159]. See the recent reviews [160,161] for a more detailed discussion.

**Figure 23**: (lower) Schematic of a Cu/Nb interface with a Kurdjumov-Sachs orientation relation, after a glide dislocation is absorbed into it. Dislocations $b_1$ and $b_2$ depict the extent of core spreading and dislocation $b_r$ depicts residual dislocation. (upper) Plan view of the interface that shows a simulated vector field plot of disregistry across the interface plane. Blue dashed lines show the extent of core spreading and the orange dashed line shows the residual dislocation, from [249].

To restate, interfacial sliding generates an attractive force on mobile dislocations and allows for core spreading in the interface [159,162], thus hindering dislocation transmission [163]. Interfacial sliding is governed by interfacial shear strength and therefore controls the strength of opaque interfaces. Interfacial shear strength is a
function of the bonding of the layer materials at the interface and their atomic arrangement. Using Cu/Nb as a model system and artificially changing the dilute heat of mixing, Wang et al. [162] observed that a larger (more positive) heat of mixing leads to a lower interfacial shear strength and potentially leading to a higher interfacial barrier strength. In a separate study, Wang et al. [159] showed that Cu/Nb interfaces with nearly degenerate energy have unique shear resistance and orientation dependence.

Strength of opaque interfaces may be limited due to dislocation climb. Atomistic simulations show that even at room temperature, dislocation climb can serve to contract dislocation cores and subsequently reduce the barrier to dislocation transmission [164]. Following compaction of the dislocation core, the transmitted dislocation can nucleate at a preferred location and on a slip system not determined only by geometry (Schmid factor) but also by interfacial structure [165,166].

A beneficial consequence of misfit dislocations which are able to easily glide and climb is that they can act as sinks for point defects—for example, those generated by radiation [167]—and facilitate recovery of interfacial dislocations [164], making them attractive as structural materials in high radiation environments. Knowledge of interactions between point defects and interfaces has been expanded to non-planar interfaces and orientation relationships consistent with those formed by severe plastic deformation [168,169], but will not be discussed in detail.
2.5.3 Combining Transparent and Opaque Interfaces

In an effort to optimize nanolayered composite properties, systems combining transparent and opaque interfaces have also been investigated. Yan et al. [170] measured the hardness of Cu/Ni/W and through a comparison with Cu/W and Cu/Ni, suggested that hardness can be increased by including both transparent and opaque interfaces in a nanolayered composite. However, since a comparison to Ni/W hardness was not included, it is not clear if the combination of transparent and opaque interfaces can increase the strength of nanolayered composites beyond the strongest bi-material pair. Molecular Dynamics simulations of Cu/Ni/Nb do not predict strength increases beyond Cu/Nb but do suggest that combining transparent and opaque interfaces results in average properties of the two interfaces types [171]. Specifically, Cu/Ni/Nb nanolayered composites can lead to an increase in the strength over Cu/Ni and an increase in ductility compared to Cu/Nb.

2.6 Summary

Fabrication of nanolayered composites has been demonstrated in each of the techniques discussed—evaporation, sputtering, electrodeposition, and accumulative-roll bonding. Nanolayered composites are most often fabricated by sputtering, but in order to make use of their exceptional mechanical properties in structural applications, bulk processing techniques are required. Severe plastic deformation, specifically accumulative roll-bonding, holds significant promise in producing bulk sheets of metal/metal
nanolayered composites. And since the hardness of Cu/Nb produced by accumulative roll-bonding and sputtering is comparable, sputtering continues to be an ideal method for studying deformation mechanism over an array of systems and for identifying optimal systems for scale-up to bulk processing. Finally, although there is limited research activity in electrodeposition of nanolayered composites currently, electrodeposition could prove to be an effective fabrication method for coating applications.

Understanding the structure of nanolayered composites is necessary to evaluate their mechanical properties and to establish deformation mechanisms, the primary feature that controls strength is layer thickness. XRR measurements produce similar layer thicknesses measurements as observed in TEM images but with far less sample preparation. Still, x-ray and TEM are complementary techniques. TEM images can provide useful, local interface structure, orientation, and grain size information, while XRD provides more global, film-average phase and orientation information. XRD is well-suited for measuring residual stress, which is important because residual stress can play an influential role in interpreting mechanical test results such as indentation.

Evaluation of deformation mechanism in nanolayered composites is reliant on accurate test methods. The primary metric for evaluating the mechanical behavior of nanolayered composites is hardness as determined by nanoindentation through the Oliver-Pharr method. Large errors can be introduced to hardness vs. layer thickness scaling trends by neglecting pile-up and residual stress. In contrast to nanoindentation,
micropillar compression, and tensile testing provide test methods in which material is uniformly strained, but are not without complications of their own. The fabrication of pillars for micropillar compression using focused ion beam milling involves a trade-off between geometric uniformity and ion damage, and the consequences to strength measurements are unclear. Tensile testing of sub-size specimen suffers from limited strain to failure due to early strain localization potentially making strength determination unreliable. Accurate mechanical property characterization should rely on a combination of these testing techniques.

In nanolayered composites, strength is a function of layer thickness. Using the relationship between hardness and layer thickness, deformation mechanism in nanolayered composites are divided into three regimes: Hall-Petch, Single Dislocation, and Interface Crossing. At layer thicknesses $h > 50$ nm, $H \propto h^{-1/2}$ and Hall-Petch behavior is inferred—dislocations pile-up at the interface to overcome the interfacial barrier to dislocation transmission. At smaller layer thicknesses, $5$ nm $< h < 50$ nm, strain is accommodated by Confined Layer Slip—the propagation of single Orowan dislocation loops bound by the confining interfaces. Propagation of Orowan dislocation loops have been observed using in situ TEM. As layer thickness continues to decrease, the stress for CLS becomes larger than the barrier for dislocation transmission across the interface and a plateau or decrease in hardness is observed.
Nanolayered composites derive their strength from a high density of interfaces and the interfaces’ resistance to dislocation transmission. Interfaces have been grouped into two categories: *transparent* if there is continuity of slip across interfaces; and *opaque* if there is no continuity. Systems with transparent interfaces, such as Cu/Ni and Cu/Ag, derive resistance from mismatches in the lattice parameter, shear modulus, stacking fault energy, and Burgers vector of the two constituents. Systems with opaque interfaces, such as PVD-fabricated Cu/Nb derive strength from a weak interfacial shear strength, which serves to attract and trap dislocations. Both types of interfaces result in composites with GPa-level strength when layer thickness is on the order of 10 nm.
Chapter 3: Interpreting Hardness in Nanolayered Composites

3.1 Introduction

Investigations into the strength and deformation mechanisms of nanoscale layered composites predominately rely on hardness determined from nanoindentation, yet hardness is not an intrinsic material property—hardness can depend considerably on the state of the material prior to indentation and on the test method itself, for example on the geometry of the indenter [172]. Despite their significance, complications relevant to nanolayered composites including: relative strength of the composite [173], residual in-plane stress [91], mismatch in the strength of constituent layers [174], and pile-up around the indenter [9,64] have been shown to affect hardness but are often neglected. The consequence is the reporting of inconsistent hardness values between layer thicknesses and A/B composite systems. Moreover, attempts to quantify these contributions to hardness in nanoscale layered composites are currently incomplete.

For understanding material strength, the value of hardness lies in its ease of use and in its correlation to a uniaxial yield stress. The relationship between hardness and uniaxial stress is often given in terms of a constraint or Tabor factor, $c$.
\[ H = c \sigma_y \] (22)

where hardness, \( H \), is defined as load divided by projected contact area. Tabor [74] determined that \( c \approx 3 \) for isotropic, fully work hardened metals assuming a yield stress, \( \sigma_y \), at a strain of 8-10%. Tabor’s work and supporting slip-line field analysis of rigid perfectly-plastic materials [175] give precedent to the use of \( c \) between 2.7 and 3 that is currently assumed in the nanolayered composite literature, but, as Johnson [176] and subsequent finite element results [173,177,178] have demonstrated, the slip-line analysis is valid only if elastic deformation is unimportant—when the ratio of elastic modulus to yield stress is large, \( E/\sigma_y > 200 \) for a Berkovich indenter. And the \( E/\sigma_y \) of nanolayered composites can be significantly less than 200. For example, estimating \( E \) from an isostress rule-of-mixtures [179] and measuring composite yield stress \( \sigma_y \) using micropillar compression [4], Cu/Nb has \( E/\sigma_y \approx 70 \) and \( E/\sigma_y \approx 50 \) at layer thicknesses of 40 and 5 nm respectively. Furthermore, below \( E/\sigma_y \approx 200 \), consistent with Johnson’s theory [176], Marsh [180] found that \( c \) decreased with decreasing \( E/\sigma_y \) taking the form:

\[
c = \frac{H}{\sigma_y} = A + B \ln \left( \frac{E}{\sigma_y} \right)
\] (23)

where Marsh [180] used \( A \) and \( B \) as empirical fitting constants and Johnson [176] derived them using the Hill’s expanding cavity solution [175]. In both cases, they depend on the material and on the indenter geometry.
Large residual in-plane stress has been measured in a number of nanolayered systems and been show to vary with layer thickness [15,66,181]. Although studies on aluminum alloy 8009 showed no effect of residual stress on hardness when contact area was properly accounted for [89,90], finite element simulation predict a transition to residual stress-dependent hardness in homogeneous materials at $E/\sigma_y \approx 200$ [91]. Based on these results, nanolayered composites are expected to display a dependence of hardness on residual stress, however, no studies, either experimental or computational, have directly assessed the contribution of residual in-plane stress on hardness in nanolayered composites.

Finite element simulations suggest that a disparity in the strength of the two constituents in an nanolayered composite may cause a significant reduction in hardness compared to a homogeneous material with the same average properties [174]. Few experiments have attempted to estimate individual constituent strengths, but in one case a ratio of $\sim 2$ is predicted for Cu-20/Ni-20 nm [7], and it is likely that even larger disparity exists in other metal/metal or metal/ceramic composite systems. Previous finite element analyses [174,182,183], however, focus on $E/\sigma_y = 1500$ not at $E/\sigma_y$ comparable to those measured in nanolayered composites and so the magnitude of the potential hardness reduction is difficult to assert. Additionally, no experimental verification has been provided.
Pile-up has been observed in Cu/PdSi [10], Al/TiN [9,64], Cu/Ag [85], and Cu/Ni [86] nanolayered composites, but quantitative measurements of contact area and corrections to hardness measurements were made only made for Cu/PdSi [10]. When performing length-scale comparisons, it is important to note that the degree of pile-up can depend on layer thickness [85] (see Figure 15) and thereby affect the hardness-layer thickness relationship, \( H \propto h^a \). Additionally, in layered materials, hardness may depend on the strength of the top layer, not just the average composite strength [174].

In an effort to elucidate how constituent properties and initial stress state affects the Tabor factor in nanolayered composites, over 64 finite element indentation simulations were performed encompassing a range of composite strengths, constituent strength disparities, and residual stress states. The constituent strength disparity and residual stress were found to be significant effects. Minimal change in the Tabor factor was observed with modulus disparity, friction, and the layer order. To help identify when pile-up may be problematic, effects on contact are also discussed.

### 3.2 Finite Element Model Setup

Indentation behavior of nanolayered composites is modeled using a two-dimensional axisymmetric finite element model constructed in ABAQUS 6.11-1, shown schematically in Figure 24. To save computational time, the 3D Berkovich indenter was modeled as a rigid cone with a half-included tip angle of 70.3° (\( \beta = 19.7^\circ \)) which provides the same depth-to-area ratio as a Berkovich tip indenter (\( A = 24.5h_c^2 \)) and
produces load-displacement curves within 5% of full 3D finite element models for materials with properties comparable to those of interest here [184].

The total dimensions of the layered composite span a radius and height of 5 μm, which was deemed adequate since expansion to 25 μm revealed no change in the load-displacement curve. No displacements along the composite base were allowed in the indentation direction, and no displacements normal to the indentation direction were allowed along the left edge. Individual layers with a thickness of 20 nm were modeled to a depth of 2 μm, below which a “substrate” with the average constituent properties could be used to reduce computational time without changing the results of the simulation. Axisymmetric, four-node bilinear, displacement-temperature coupled elements were used (CAX4T in ABAQUS 6.11-1 [185]) to construct a multi-scale mesh in which 5 nm square elements were used near the indenter while much larger elements were used far from the indenter. The refinement strategy is shown in Figure 24, although element sizes are enlarged to make areas of large refinement visible.
During the displacement-controlled simulations, load and contact area were recorded at each time step. The projected contact area under load was calculated from the contact radius—the distance from the left edge to the last node in contact with the indenter. Hardness is then given by the load, $P$, divided by the actual projected contact area under load, $A_{\text{actual}}$.

$$H = \frac{P}{A_{\text{actual}}} \quad (24)$$
Tangential contact between the indenter and the composite was modeled assuming a conservative estimate of the friction coefficient between polished metallic surfaces and diamond, $\mu = 0.1$ [74,186]. A lower friction coefficient will serve to increase the degree of pile-up and so the effect of friction coefficient will be discussed in Section 3.4.4. Non-penetrating, “hard” contact was assumed in the normal direction.

3.3 Variation in the Tabor Factor

Finite element simulations by Tan and Shen [174] have shown that a mismatch in the strength of the constituents in a layered composite can cause a decrease in hardness compared to a homogenous material even when the average uniaxial strength is constant. However, these and subsequent efforts [182,183] consider composites with strengths much lower than those measured in real nanolayered composites. We expand on previous results to develop the dependence of the Tabor factor on constituent strength mismatch for a range of average, composite strengths.

3.3.1 Constituent and Average Uniaxial Properties

A range of constituent properties are used as inputs, from which, average uniaxial properties are determined using a simple rule-of-mixtures. Bulk, isotropic elastic properties of Ni ($E_{Ni} = 200$ GPa, $\nu_{Ni} = 0.31$) and Cu ($E_{Cu} = 128$ GPa, $\nu_{Cu} = 0.34$) are used. The effect of elastic modulus mismatch will be elucidated in Section 3.3.4, and the effect of anisotropic elastic moduli is given in Section 3.3.5. The average elastic modulus, $E$ is
defined by a rule-of-mixtures in the isostress condition in agreement with the elastic modulus derived from finite element indentation simulations [187]:

\[
E = \left( \frac{V_{Ni}}{E_{Ni}} + \frac{1 - V_{Ni}}{E_{Cu}} \right)^{-1}
\]

(25)

where \( V_{Ni} \) is the volume fraction of Ni, taken here as 0.5. At large strain, the effective uniaxial strength of the composite \( \sigma_y \) is the same considering either isostress or isostrain loading conditions [174], and can be defined as:

\[
\sigma_y = V_{Ni}\sigma_{y,Ni} + (1 - V_{Ni})\sigma_{y,Cu}
\]

(26)

The yield stresses in Equation (26) can be assumed to be equivalent to stresses at a strain of 8%. For power law hardening materials, \( c \) is independent of strain hardening exponent if the yield stress considered is a stress at 8% strain [173], therefore, to simplify the present analysis no strain hardening is considered for the constituent materials.

Previous finite element modeling was restricted to \( E/\sigma_y = 1500 \) [174], here four \( E/\sigma_y \) are examined, and since elastic properties are held constant, they correspond to four reference strength levels with \( \sigma_y \) equivalent to: (i) a typical bulk fcc metal, e.g. Cu with an average grain size of 1 μm [188], \( E/\sigma_y = 500 \), (ii) a Cu-20/Ni-20 nm layered composite, \( E/\sigma_y = 100 \), (iii) a Cu/Ni layered composite with a much smaller bilayer thickness, \( E/\sigma_y = 50 \), and (iv) a superhard material with hardness exceeding 20 GPa,
\( E/\sigma_y = 10 \). At each reference strength level, the constituent yield strengths were adjusted such that \( \sigma_{y,A}/\sigma_{y,B} = 1, 1.5, 3, 5 \) while maintaining a constant average strength \( \sigma_y \).

### 3.3.2 Effect of Constituent Strength Mismatch

The Tabor factor is calculated for each average strength-constituent strength ratio combination and provided in **Figure 25**. No residual stress is considered.

![Figure 25](image.png)

**Figure 25**: The dependence of the Tabor factor \( c \) on average uniaxial strength \( \sigma_y \) and constituent strength ratio \( \sigma_{y,Ni}/\sigma_{y,Cu} \) without residual stress. Elastic properties are held constant.

There are two key features in **Figure 25**. First, the Tabor factor is approximately constant above \( E/\sigma_y \approx 100 \) before decreasing—slowly at first, then rapidly. Second, the
effect of constituent strength mismatch only becomes apparent when the ratio is above 1.5. Moreover, the effect of constituent strength mismatch is nearly independent of average strength $E/\sigma_y$.

The presence of a transition in Tabor factor indicates that the common practice of assuming $c = 2.7$, without considering layer thickness (and thus $E/\sigma_y$), could be inappropriate—using a constant $c = 2.7$ to estimate uniaxial strength could result in an underestimation of composite strength when $E/\sigma_y < 100$. And if $E/\sigma_y$ changes with layer thickness (because $\sigma_y$ increases with decreasing layer thickness), reduced slopes of strength-layer thickness would result. Again using Cu/Nb as an example, based only on $E/\sigma_y$, assuming a constant $c = 2.7$ would result in the underestimation of uniaxial strength by 7.5 and 12.5% for layer thicknesses of 40 ($E/\sigma_y \approx 70$) and 10 nm ($E/\sigma_y \approx 50$) respectively.

The potential error resulting from the disparity in constituent strength is even more significant. Few experiments have attempted to estimate a ratio of constituent strengths, in one case, a ratio of 2 is predicted for Cu-20/Ni-20 nm [7]. Strength derived from nanocrystalline Cu [189] and Ni [190] suggest a ratio in the range of 2-3. An even larger ratio is predicted in other systems, for example, nanocrystalline Cr [191] has approximately 5 times the hardness of nanocrystalline Cu [189]. In such a case, determining uniaxial strength assuming a constant $c = 2.7$ would result in a 23% lower strength. Still larger constituent strength mismatch is likely for metal/ceramic
nanolayered composites such as Al/TiN [64]. Furthermore, if indeed systems have variable constituent strength ratios and a hardness reduction results, hardness comparisons between systems to extract interface properties without accounting for such a difference would be misled. Although it is unclear if the constituent strength ratio is a function of layer thickness, if it is, even comparisons of hardness within a system could lose their meaning.

3.3.3 Effect of Residual Stress

In-plane residual stress was included by displacing the right edge of the composite prior to indentation as done in previous finite element-based studies of residual stress [90,91]. A negative, inward displacement corresponds to development of a net compressive in-plane stress, $\sigma_{ip} < 0$, while a positive, outward displacement results in a net tensile in-plane stress, $\sigma_{ip} > 0$. This step accounts for the net in-plane stress state resulting from coherency stress and the constraint of the Si substrate. The right edge is fixed in the radial direction during indentation to maintain the residual stress. The average residual stress is calculated using the rule-of-mixtures in the isostrain condition:

$$\sigma_{ip} = V_{Ni}\sigma_{ip,Ni} + (1 - V_{Ni})\sigma_{ip,Cu}$$  (27)

To illustrate the effect of a tensile residual stress on Tabor factor $c$, $c$ was calculated for $\sigma_{ip}/\sigma_y = 0.5$ using the same 16 average strength-constituent strength ratio combinations used previously. The results are plotted along with the stress free cases for comparison in Figure 26.
Figure 26: Effect of in-plane tensile residual stress ($\sigma_{ip}/\sigma_y = 0.5$) on the Tabor factor. The residual stress-free cases (dashed lines) are provided as reference.

The impact of tensile residual stress on $c$ depends on $E/\sigma_y$. At $E/\sigma_y = 500$, $c$ is independent of tensile residual stress, but when $E/\sigma_y \leq 100$ the tensile residual stress serves to decrease $c$ significantly compared to the stress-free result. The actual trend between $E/\sigma_y = 500$ and $E/\sigma_y = 100$ is not likely a straight line. In fact, a coupled experimental-finite element investigation showed that residual stress had no effect on hardness for aluminum alloy 8009 (with $E/\sigma_y \approx 200$) when contact area was measured directly [89,90]. No similar experiments have been performed on materials with
$E/\sigma_y < 200$, but independent finite element results confirm that $c$ is reduced when $E/\sigma_y < 200$ in homogeneous materials [91].

![Graph showing the effect of compressive in-plane residual stress ($\sigma_{ip}/\sigma_y = -0.5$) on the Tabor factor. The residual stress-free cases (dashed lines) are provided as reference.](image)

**Figure 27**: Effect of compressive in-plane residual stress ($\sigma_{ip}/\sigma_y = -0.5$) on the Tabor factor. The residual stress-free cases (dashed lines) are provided as reference.

**Figure 27** shows that the effect of compressive residual stress on $c$ is also dependent on $E/\sigma_y$. Like the tensile residual stress, at $E/\sigma_y = 500$, $c$ is independent of compressive residual stress, but now when $E/\sigma_y \leq 100$ the compressive residual stress serves to increase $c$ compared to the stress-free result. Interestingly, a compressive residual stress delays the drop in $c$ with $E/\sigma_y$. $c$ is constant between $E/\sigma_y = 500$ and $E/\sigma_y = 100$ for all constituent strength ratios.
Another way to view the effect of residual stress is to plot $c$ vs in-plane stress $\sigma_{ip}$, the case with $E/\sigma_y = 100$ and a constituent strength ratio of 3 is provided in Figure 28. A linear fit is then used to extract the sensitivity of $c$ to in-plane stress, i.e. the stress sensitivity, $B$.

![Figure 28: Effect of in-plane residual stress on Tabor factor $c$ for $E/\sigma_y = 100$ and a 3:1 constituent strength ratio. A linear fit provides a measure of the in-plane stress sensitivity, $B$.](image)

In-plane stress sensitivity $B$ is determined for each $E/\sigma_y$ and constituent strength ratio combination, Figure 29. It should be noted that although in-plane stress is not precisely linear with $c$ in general [91,192], $(R^2 > 0.9)$ for the levels of in-plane stress used in the current analysis ($-0.5 \leq \sigma_{ip}/\sigma_y \leq 0.5$).
The most alarming result from Figure 29 is that stress sensitivity is a maximum at $E/\sigma_y = 50$, indicating that the effect of residual stress is at a maximum directly in the range of $E/\sigma_y$ expected for nanolayered composites. Additionally, at these high strengths, $B$ is also dependent on the constituent strength ratio. A consequence from this result is that residual stress could affect hardness-layer thickness scaling behavior. Furthermore, since residual stress is likely to vary between nanolayered composite systems, it could also affect comparisons between systems.

To illustrate the potential effect of residual stress, consider the Cu/Cr system, which exhibits a peak residual stress of 1 GPa at a layer thickness of $h = 50$ nm [66], and a...
hardness of 6 GPa at the same layer thickness [38]. The minimum uniaxial strength can be calculated from hardness assuming \( c = 2.7 \). A minimum uniaxial strength will coincide with a maximum in the normalized residual stress \( \sigma_{ip}/\sigma_y = 0.45 \), and thus the maximum effect of residual stress. Assuming these values, the resulting decrease in \( c \), due only to in-plane stress, would be around 0.4, equivalent to underestimating the uniaxial strength by 17%. In contrast to Cu/Cr, measured residual stresses in Cu/Nb are much lower [67] therefore, comparing the hardness of Cu/Cr and Cu/Nb when in-plane stress is not considered will favor Cu/Nb.

### 3.3.4 Effect of Elastic Modulus Mismatch

To this point only an elastic modulus ratio of 1.5—as expected in the Cu/Ni system—has been considered, but the elastic modulus ratio can reach 5 or possibly higher in metal/ceramic systems such as Al/SiC [179]. In order to extend the present analysis past the Cu/Ni system, the effect of modulus ratio on \( c \) is analyzed. Simulations were carried out with a homogeneous elastic modulus, \( E_A = E_B \) and with \( E_A = 5E_B \) for constituent strength ratios of 1 and 5 at four levels of \( E/\sigma_y \), Figure 30. The average elastic modulus was held constant at 164 GPa.
**Figure 30:** Effect of elastic modulus mismatch considering ratios of $E_A/E_B = 1$ and $E_A/E_B = 5$. The average elastic modulus was held constant.

A mismatch in the constituent elastic moduli has minimal effect on the Tabor factor $c$. A reduction in $c$ is observed when $E/\sigma_y \leq 100$, therefore if strength is increased (as layer thickness decreases) to the point where $E/\sigma_y \leq 100$, an error in the conversion from hardness to uniaxial strength will be introduced, but the error in $c$ introduced from an elastic modulus mismatch of 5 at $E/\sigma_y = 100$ is on the order of 5%, negligible considering the same mismatch in constituent strength produces a 33% error.
3.3.5 Effect of Anisotropic Elastic Moduli

To simplify the present analysis, isotropic elastic moduli have been considered, and yet, PVD fabricated nanolayered composites typically have a well-defined texture. An example is a cube-on-cube orientation in which the (100) planes in both Cu and Ni are normal to the film surface [7,55]. The (100) textured films are fabricated on (100) oriented single crystal Si substrates, but if a (110) oriented Si substrate is used instead, a strong (111) fiber texture results [48]. Liu et al. [48] compared (100) and (111) oriented Cu/Ni films and observed higher hardness for the (111) orientation. They concluded that the increase in hardness was due to nanotwin formation within the Ni layers. To verify that hardness cannot be manipulated by elastic anisotropy alone, isotropic finite element simulations are compared with simulations with a (100) orientation and anisotropic elastic moduli. The anisotropic elastic moduli used in the finite element simulations are provided in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>C(_{11}) (GPa)</th>
<th>C(_{12}) (GPa)</th>
<th>C(_{44}) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>168</td>
<td>121</td>
<td>75</td>
</tr>
<tr>
<td>Ni</td>
<td>247</td>
<td>147</td>
<td>125</td>
</tr>
</tbody>
</table>

Figure 31 illustrates that elastic anisotropy has minimal effect on the calculated Tabor factor such that isotropic moduli can be used regardless of orientation for
determination of hardness. Similarly, Vlassak and Nix [78] found that hardness was independent of orientation for single crystal W, Cu, Al, and β-brass. In contrast, Yeap et al. [193,194] found an orientation dependence on hardness in Cu, but it was attributed to the activation of non-interacting slip planes in Cu(100) which are not explicitly considered here. Additionally, a dependence on hardness was only observed for Hertzian contact. That is, although indents were performed with a Berkovich indenter, a maximum indentation depth $h < 50$ nm was used and the Berkovich tips had radii in excess of 100 nm, so the indenter was essentially a spherical indenter.

**Figure 31**: Dependence of Tabor factor $c$ on elastic anisotropy. Comparison between the isotropic elastic case and a (100) orientated case using anisotropic elastic constants.
3.4 Variation in Contact Area

One of the advantages of indentation analysis using the Oliver-Pharr method is that hardness and elastic modulus can be determined without the direct measurement of the indentation area [73,76]. In the Oliver-Pharr method, elastic contact analysis is used to determine contact area through calculation of contact depth. A direct consequence is the inability to account for pile-up resulting in the overestimation of hardness and elastic modulus by as much as 50% [84].

The alternative to the Oliver-Pharr method is to directly measure the indentation area, which can be difficult and time consuming [75]. But direct measurement may be necessary for correct hardness-layer thickness scaling relationships in nanolayered composites since the pile-up can be severe at large layer thicknesses but non-existent at small layer thicknesses [85]. Here, finite element modeling is used to help identify when and to what extent pile-up may occur in nanolayered composites, so that direct measurement can be avoided when possible, and the errors associated with pile-up can be quantified.

3.4.1 Effect of Uniaxial Strength and Constituent Strength Ratio

Bolshakov and Pharr [84] identified that pile-up was greatest in materials with large $E/\sigma_y$ and limited work hardening, therefore pile-up behavior is examined at the 4 previously used strength levels $E/\sigma_y = 10, 50, 100, 500$ at constituent strength ratios of
\[ \sigma_{y,Ni} / \sigma_{y,Cu} = 1, 1.5, 3, 5. \] Since no work hardening is considered, results are indicative of the maximum degree of pile-up.

Following Bolshakov and Pharr [84], pile-up is determined by normalizing the actual contact area measured from the finite element mesh, \( A_{\text{actual}} \) with respect to the indenter shape function, \( A_{sf} \) evaluated at the maximum indentation depth, \( h_{\text{max}} \):

\[
\frac{A_{\text{actual}}}{A_{sf}} = \frac{A_{\text{actual}}}{24.5 h_{\text{max}}^2}
\] (28)

when \( A_{\text{actual}} / A_{sf} > 1 \), pile-up occurs. Consistent with previous finite element analysis on homogeneous materials [84], pile-up only occurs when \( E/\sigma_y > 100 \) as indicated in Figure 32. Above \( E/\sigma_y \approx 50 \), increasing the constituent strength ratio decreases the propensity for pile-up thereby reducing the contact area. Again, since no strain hardening was considered in these simulations, this represents the extreme case—the highest degree of pile-up.
Figure 32: The dependence of contact area on average uniaxial strength and constituent strength ratio. The contact area determined from finite element simulations, $A_{\text{actual}}$, is normalized by the area given by the indenter shape function evaluated at the maximum contact depth, $A_{sf}$.

Comparison of the result in Figure 32 and pile-up measurements in the Cu/Ag system [85] suggests that other factors may affect the degree of pile-up. Since the peak Tabor factor is $c = 2.7$, the minimum strength can be calculated from hardness using $c = 2.7$. Furthermore, using this minimum strength, a maximum $E/\sigma_y$ at a given layer thickness can be estimated assuming bulk elastic constants. The maximum $E/\sigma_y$ for Cu/Ag at a layer thickness of $h = 100$ is approximately $E/\sigma_y \approx 100$, and yet pile-up is significant (see Figure 15). The discrepancy could be due to the ideal, conical indenter geometry used in the present analysis, a large compressive residual stress, or a friction coefficient lower than $\mu = 0.1$. 

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3.4.2 Effect of Residual Stress

Bolshakov et al. [90] observed that compressive in-plane stress could also lead to pile-up. The dependence of pile-up on in-plane tensile and compressive residual stresses for $\sigma_y,N/\sigma_y,Cu = 1$ is shown in Figure 33. Above $E/\sigma_y \approx 50$, the degree of pile-up is increased with a compressive in-plane residual stress and is reduced with a tensile in-plane residual stress, as expected. Below $E/\sigma_y \approx 50$, however, the contact area, and thus the degree of pile-up, has a weak dependence on residual stress. This result indicates that, to avoid errors related to pile-up, contact area should be measured for materials with $E/\sigma_y > 100$ and compressive in-plane residual stress.
Figure 33: The dependence of contact area on tensile and compressive in-plane residual stress for a constituent strength ratio of 1. The contact area determined from finite element simulations, $A_{\text{actual}}$, is normalized by the area given by the indenter shape function evaluated at the maximum contact depth, $A_{\text{sf}}$.

3.4.3 Effect of the Topmost Layer

Previous finite element simulations on nanolayered composites has suggested as much as a 10% increase in hardness is possible when the stronger layer is used as the topmost layer compared to when the weaker layer is used as the topmost layer due to changes in contact area [174]. In practice, Cu/Ni nanolayered composites are often fabricated with Cu—the expected weaker layer—as the topmost layer. The effect of the topmost layer is examined here with $E/\sigma_y = 100$ and a constituent strength ratio of 5, Figure 34.
Figure 34: Effect of topmost layer for the case of $\frac{\sigma_{y,Ni}}{\sigma_{y,Cu}} = 5$ and $\frac{E}{\sigma_y} = 100$. Cu and Ni layer thicknesses are both 20 nm.

Figure 34 shows that using the stronger layer as the topmost layer produces a 5% increase in hardness at the maximum indentation depth (25 layers), which is on the order of the experimental error in hardness measurements of Cu/Ni nanolayered composites [55]. But at shallow indentation depths, the difference can be significant (25% at $h = 100$ nm or 5 layers deep), despite nearly identical load-displacement curves. The reduction in hardness is due to the dependence of pile-up on indentation depth.
Contact profiles at indentation displacements of (a) $h = 100$ nm and (b) $h = 500$ nm are provided in Figure 35. At $h = 100$ nm, considerable pile-up is observed when the
weaker layer is on top, but no pile-up is observed at a displacement of 500 nm. This result suggests that pile-up is controlled in large part by the properties of the topmost layer. The impact of this result is twofold. First, nanolayered composites could exhibit pile-up even when the average, composite properties would suggest they would not pile-up. For example, even when $E/\sigma_y < 100$ and without residual stress, pile-up could still develop (see Section 3.4.3). Second, nanolayered composites may exhibit indentation depth-dependent pile-up, such that hardness could depend on depth when the topmost layer is the weaker layer. A relevant case is Al/SiC, where depth dependent hardness has been observed [195], but since residual indent impressions were not measured as a function of depth, pile-up cannot be confirmed as the cause.

Simulation time is another consequence of the topmost layer. The effect of topmost layer on simulation time can be significant as illustrated in Table 2. Using the stronger layer on top reduces computational time by half, furthermore, when the stronger layer resides on top, the hardness saturates quickly, allowing shallower indentation depths to be used, leading to larger reductions in computational time (16hr → 1hr).
Table 2: Effect of topmost layer and indentation depth on computational time

<table>
<thead>
<tr>
<th>Topmost Layer</th>
<th>Indentation Depth (nm)</th>
<th>Simulation Time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weak (Cu)</td>
<td>500</td>
<td>~30</td>
</tr>
<tr>
<td>Strong (Ni)</td>
<td>500</td>
<td>16</td>
</tr>
<tr>
<td>Strong (Ni)</td>
<td>200</td>
<td>1</td>
</tr>
</tbody>
</table>

3.4.4 Effect of Friction

Increasing friction between the indenter and the sample has been shown to effect the Tabor factor of homogenous materials through a reduction in the contact area [172,186]—a decrease in the propensity to pile-up. Mata and Alcalá [186] measured a Coulomb friction coefficient, $\mu = 0.15$ consistent with the range reported by Tabor [74,p.42], $\mu = 0.1 - 0.15$. Moderate friction, $\mu = 0.1$ was used in all previous simulations. To assess the role of friction, additional simulations were performed considering two additional cases: frictionless contact and $\mu = 0.15$.

In agreement with results on homogenous materials [186], the Tabor factor of nanolayered composites is dependent on the friction coefficient at higher $E/\sigma_y$, Figure 36. A maximum deviation (16%) from the frictionless case occurs at $E/\sigma_y = 500$. Although, the friction coefficient is not expected to change drastically between indentation experiments, it may affect the hardness-layer thickness scaling relationship since, for example the transition from $E/\sigma_y = 100$ to $E/\sigma_y = 50$ is steeper when friction is higher.
Figure 36: Dependence of Tabor factor on friction coefficient. Frictionless ($\mu = 0$) and high friction ($\mu = 0.15$) cases are provided.

The increase in Tabor factor with increasing friction is a result of decreasing contact area, Figure 37, with no change in normal load. Friction opposes the slip of material at the indenter leading to a decrease in contact area. Consistent with these results, Buaille et al. [172] and Harsono et al. [196] both noted that the load-displacement behavior is relatively independent of friction when the included angle of the conical indenter was larger than $\sim$60°. Here, the included angle was 70.3°. Friction is more important when materials are more likely to pile-up—cases including $E/\sigma_y > 100$, lower working hardening, or sharper indenters.
Figure 37: Dependence of contact area on friction. The contact area determined from finite element simulations, $A_{\text{actual}}$, is normalized by the area given by the indenter shape function evaluated at the maximum contact depth, $A_{sf}$.

3.5 Optimizing Hardness

Finite element simulations that incorporate independent constituent strengths have elucidated a new route to optimizing nanolayered composite hardness based on minimizing the constituent strength mismatch between the individual constituents. This result is illustrated in Figure 25 where, for a constant average strength, Tabor factor, $c$, is shown to decrease as constituent strength ratio increases. However, the cause of the Tabor factor decrease has not been described.
Generally speaking, $c$ is greater than 1 (hardness $>$ uniaxial strength) because during uniaxial compression the free surface allows the edge of the sample to expand freely, but during indentation, material outside of the indented area restricts the motion of the deformed material. The constraint that the surrounding material imposes creates a large in-plane compression during indentation thereby requiring higher normal stresses to cause plastic deformation. It follows that processes serving to lower the indentation generated in-plane compressive stress will lower $c$. An example is a superimposed tensile, in-plane, residual stress as shown in Section 3.3.3 and in Ref. [91].

In-plane stresses within select Cu and Ni elements are compared for constituent strength ratios of $\sigma_{y,N}/\sigma_{y,Cu} = 1, 1.5, 3$ and 5, maintaining $E/\sigma_y = 100$ and assuming an initially stress free sample, Figure 38. To simplify analysis, all layers are defined to be elastically homogeneous. The presence of a weaker constituent decreases the in-plane compression in the stronger constituent as well as the average in-plane compression. For this particular pair of elements, the average in-plane stress is 13% lower than the homogeneous case when $\sigma_{y,N}/\sigma_{y,Cu} = 5$. Correspondingly, a reduction in the maximum normal load to reach a given displacement is observed.
Figure 38: Indentation generated in-plane stress (stress normal to the indentation direction) in select Ni and Cu elements near the indentation surface at the maximum indentation depth ($h_{\text{max}} = 200$ nm).

During indentation, material in the softer constituent flows away from the center of the indent, reducing the in-plane compression in the stronger constituent compared to the homogeneous case. This behavior can be visualized by distortions in the finite element mesh, Figure 39. Note the meshed sample is much larger than what is shown in Figure 39, only a fraction of the mesh is provided.
Figure 39: Deformed mesh for the case where $\sigma_{y,N}/\sigma_{y,Cu} = 5$ and $E/\sigma_y = 100$. Only a fraction of the mesh is provided.

Figure 40 depicts the percent difference in maximum load, contact area and Tabor factor from the homogenous case as a function of constituent strength ratio. Although both maximum load and contact area are decreasing, the reduction in maximum load is larger leading to the overall decrease in Tabor factor.
The dependence of hardness on constituent strength ratio complicates the conversion of hardness to uniaxial strength and decreases the attainable hardness of nanolayered composites, but a fortuitous consequence of the constituent strength ratio dependence is that by coupling simulations with the measurement of an experimental Tabor factor, individual constituent strengths can be extracted. A case study outlining the procedure for extracting the individual Cu and Ni strengths in a Cu-20/Ni-20 nm sample is provided in Chapter 4.
3.6 Summary and Conclusions

Strength comparisons of nanolayered composites across layer thickness and between composite systems rely on the conversion of hardness measurements to uniaxial strength using a Tabor factor. To facilitate accurate comparisons, Tabor factors—hardness/uniaxial strength—have been calculated for nanolayered composites encompassing a large range of constituent properties, initial stress states, and indentation conditions. A finite element indentation model was used to compute hardness while the rule-of-mixtures was used to determine uniaxial strength. The ratio of individual constituent strengths and residual stress were found to be the dominate effects. Friction exhibited a moderate change in the Tabor factor while elastic modulus mismatch and the layer order showed minimal effect.

Maintaining isotropic Cu and Ni elastic properties, four levels of average, uniaxial strength $\sigma_y$ were considered: (i) a typical micro-grained fcc metal, $E/\sigma_y = 500$, (ii) a Cu-20/Ni-20 nm layered composite, $E/\sigma_y = 100$, (iii) a Cu/Ni layered composite with a smaller bilayer thickness, $E/\sigma_y = 50$, and (iv) a superhard material, $E/\sigma_y = 10$. At each average, uniaxial strength, four constituent strength ratios were investigated: $\sigma_y, Ni / \sigma_y, Cu = 1, 1.5, 3, \text{ and } 5$. At low average, uniaxial strength ($E/\sigma_y > 100$), Tabor factor is nearly independent of $\sigma_y$; however, at large $\sigma_y (E/\sigma_y < 100)$, Tabor factor decreases significantly with increasing $\sigma_y$. In contrast, the effect of constituent strength ratio is relatively independent of the average uniaxial strength. When $\sigma_y, Ni / \sigma_y, Cu > 1.5$, the disparity in constituent strengths causes a significant decrease in the Tabor factor that
increases with the extent of the disparity. The consequences of these results for nanolayered composites are three-fold. First, strength-layer thickness scaling relationships based on hardness measurements may be in error if $E/\sigma_y < 100$ and/or if the constituent strength ratio is large ($\sigma_A/\sigma_B > 1.5$). Additionally, both may depend on layer thickness. Second, strength comparisons—based on hardness measurements—between composite systems with different $E/\sigma_y$ and/or constituent strength ratio could be inaccurate. Finally, a fortuitous consequence is that measurement of experimental Tabor factors will allow for estimation of individual constituent strengths.

Accurate comparison of hardness across multiple layer thicknesses and between composite systems requires measurement of in-plane residual stress. To determine the effect of in-plane residual stress, indentation simulations were performed with tensile and compressive residuals stress states at a magnitude of half the average uniaxial strength. Compared to the stress free case, tensile residual stress lowers the Tabor factor while a compressive residual stress increases it, but when $E/\sigma_y = 500$ the Tabor factor is independent of residual stress. The Tabor factor is most sensitive to residual stress when $E/\sigma_y = 50$, directly in the range of $E/\sigma_y$ expected for nanolayered composites with layer thicknesses on the order of 10 nm.

Both mismatch in elastic moduli and elastic anisotropy have minimal effect on the Tabor factor when $E/\sigma_y > 50$, but the effect of mismatch in elastic moduli can become significant at very high strength $E/\sigma_y \approx 10$ whereas, due to the multiaxial stress state
underneath the indenter, at low $E/\sigma_y$, the effect of elastic anisotropy is minimal. Therefore, in systems with large elastic moduli mismatch and very high strength—such as metal/ceramic nanolayered composites—the elastic modulus mismatch may result in additional reduction in the Tabor factor.

Increasing friction can decrease the Tabor factor; minimizing sliding at the indenter-sample interface serves to decreasing contact area. Results on nanolayered composites are comparable to homogeneous materials—reductions in the Tabor factor are more significant at lower strength ($E/\sigma_y = 500$) and negligible at high strength ($E/\sigma_y = 10$).

Error in hardness measurements and thus hardness-layer thickness scaling relationships can result from the occurrence of pile-up. Contact area determined from finite element modeling indicates that pile-up is more severe at lower strength ($E/\sigma_y = 500$) giving cause for the observation of pile-up at large layer thicknesses but not at lower layer thicknesses. Pile-up is increased with compressive residual stress and decreased with tensile residual stress. Furthermore, when the weaker layer is the topmost layer, hardness can be depth-dependent—hardness will increase with increasing depth due to changes in contact area.

Although the common practice of using a constant Tabor factor $c = 2.7$ may introduce errors in the predicted uniaxial strength, the results here support the use of
\( c = 2.7 \) as a maximum Tabor factor. Therefore, if hardness is measured, \( \frac{H}{2.7} \) can be used to calculate a minimum uniaxial strength, and normalizing by the average elastic modulus will provide a maximum \( \frac{E}{\sigma_y} \) from which the relative magnitude of the various effects discussed can be assessed.
Chapter 4: Extracting Constituent Strengths: An Indentation-Based Method

For nanolayered composites, the average composite mechanical response is often measured rather than that of the individual constituents. Examples include nanoindentation [36,140,197], micropillar compression [4,98,112], and tensile testing [117,121,122]. Yet, a better understanding of the constituents—particularly in confined geometries—is needed to foster intelligent composite design. Nanolayered composite strength is attributed the strength of the interfaces, but interface strengthening is not experimentally quantified. Instead, interface strengthening is inferred from comparisons between layer thicknesses or composite systems. This practice is problematic since both the constituent materials and the layer thicknesses dictate the interface structure, and so both interface structure and constituent strength influences the average, composite mechanical response. Therefore, access to individual constituent strengths will allow for isolation of the interface strength.

The key observation is that hardness of layered materials depends not only on average, composite material properties, but also on individual constituent properties. When a disparity in the strength of the individual constituents exists, hardness is decreased, whereas the composite strength determined through uniaxial testing is
unaffected. A consequence of this observation is that individual constituent strengths can be determined by first measuring uniaxial strength, in-plane residual stress state, elastic modulus, and hardness and then comparing the experimentally determined Tabor factor to a parametric finite element analysis (like that in Chapter 3). The coupled experimental/computational, indentation-based method to extract constituent strengths is outlined, and the method is applied to the Cu-20/Ni-20 nm system to extract individual Cu and Ni strengths.

Experimental tabor factors have been calculated previously in Al/TiN [115], Cu/PdSi [10], Al/SiC [116], and Cu/Nb [4], and therefore, in principle, the present method could be applied. However, in all these cases, hardness and uniaxial strength measurements are not performed at comparable strain rates. Specifically, pillar compression tests are typically performed at strain rates on the order of $10^{-4}$/s while indentation tests are performed at rates two orders of magnitude faster. To compound the impact of this rate disparity, work on face-centered cubic nanocrystalline materials show that strain rate sensitivity increases with decreasing grain size [198]. Therefore, it is reasonable to hypothesize that strain rate sensitivity of these nanolayered composites could be large and could be a function of layer thickness. Strategies to measure strain rate sensitivities in thin films and their impact on the measured Tabor factor will be discussed.
4.1 Fabrication and structure

The Cu/Ni nanolayered composite films used in this and previous studies [7,55,111] were grown at the Center for Integrated Nanotechnologies (CINT) at Los Alamos National Laboratory. Films were sputtered on unheated, HF-cleaned <100> Si substrates. After initial deposition of a 100 nm thick, single crystal Cu buffer layer, layers were alternated to a total film thickness of 5 µm and capped with a final Cu layer. Low deposition rates (5-6.5 Å/s) and Ar pressures of 6.5 and 5 mTorr were used for Cu and Ni respectively.

Selected area diffraction [111] and grazing incidence x-ray diffraction [18] reveal “cube-on-cube” epitaxial layers where the layers are single-crystal with an in-plane orientation relation: [001]_{Cu,Ni} \parallel [011]_{Si} with the substrate. Transmission electron microscopy confirmed that measured layer thicknesses are within 1 nm of the nominal layer thicknesses [55].

4.2 In-Plane Residual Stress

In-plane lattice spacings were measured through x-ray diffraction from a grazing incidence (88-89° from the surface normal) using a PANalytical X’Pert Pro MRD 4-axis x-ray diffractometer, coupled with a hybrid monochromator and a 0.27° parallel plate collimator at the Center for Nanophase Materials Sciences at Oak Ridge National Laboratory [7].
Cu and Ni diffraction peaks were simultaneously fit using a pseudo-Voigt profile function in PANalytical HighScore Plus v3.0 software. The fitted peak positions, $2\theta$ furnished average in-plane interplanar lattice spacings, $d_{ip}$ in Cu and Ni through Bragg’s Law:

$$d_{ip} = \frac{\lambda}{2\sin\theta}$$  \hspace{1cm} (29)$$

where $\lambda$ is the source wavelength (for Cu K$_{\alpha}$, as used here, $\lambda = 1.54184$ Å). In-plane lattice true strains, $\varepsilon_{ip}$ were calculated using bulk lattice parameters, $a_0$ provided in Table 3:

$$\varepsilon_{ip} = \ln\left(\frac{d}{d_0}\right), \quad d_0 = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}$$  \hspace{1cm} (30)$$

For a single crystal thin film with a (100) plane in the plane of the film and under equi-biaxial strain, in-plane stress can be calculated using an effective biaxial modulus [199,p.169]:

$$\sigma_{ip} = \left(C_{11} + C_{12} - 2\frac{C_{12}^2}{C_{11}}\right)\varepsilon_{ip}$$  \hspace{1cm} (31)$$

where anisotropic elastic moduli, $C_{ij}$ for Cu and Ni are provided in Table 3. The resulting room temperature, in-plane stresses for the Cu-20/Ni-20 nm sample are measured to be
1750 ± 42 and -508 ± 28 MPa in Ni and Cu respectively. Values are the average of four separate 10 min, 2θ-scans and their corresponding standard deviation. Based on the isostress rule-of-mixtures, the average in-plane residual stress is tensile with a magnitude of $\sigma_{ip} = 623 \pm 28$ MPa.

Table 3: Physical properties used for determination of in-plane stress; lattice parameters are from Cullity and Stock [157], anisotropic elastic constants are from Courtney [160].

<table>
<thead>
<tr>
<th></th>
<th>$a_0$ (Å)</th>
<th>$C_{11}$ (GPa)</th>
<th>$C_{12}$ (GPa)</th>
<th>$C_{44}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>3.615</td>
<td>168</td>
<td>121</td>
<td>75</td>
</tr>
<tr>
<td>Ni</td>
<td>3.527</td>
<td>247</td>
<td>147</td>
<td>125</td>
</tr>
</tbody>
</table>

4.3 Uniaxial Flow Stress

Micropillars were prepared using a lathe-milling technique [93] on a Nova NanoLab 600 focused ion beam-scanning electron microscope [18]. Nominally, pillars were 2 μm in diameter and 5 μm tall with a taper of approximately 1-2°. A representative pillar is shown in Figure 41(a). Additional details on the fabrication of the pillars can be found in Refs. [18,111].
Figure 41: Micropillar compression: (a) fabricated pillar and (b) plot of true stress vs. true strain from a load-unload cycled pillar compression test at a nominal strain rate of $10^{-4}$/s [18]. The uniaxial yield stress, $\sigma_y$, used for calculation of the experimental Tabor factor is marked.

Compression of the Cu-20 nm/Ni-20 nm micropillar was performed using a 10 µm flat punch indenter tip on the Nanoindenter XP at Wright-Patterson Air Force Base. Alignment was achieved using a custom built goniometric sample holder. Within the compression test, multiple load-unload cycles were carried out under displacement control at a nominal strain rate of $10^{-4}$/s.

Force-displacement data was continuously measured and engineering stress-strain curves were calculated using the initial pillar dimensions measured from Scanning Electron Microscope (SEM) images. The pillar diameter at half the total height was used for the cross-sectional area. A Sneddon correction was applied to account for the compliance of the pillar base, consistent with previous micropillar compression tests.
[99,101,112]. Then, assuming volume conservation, engineering stress-strain curves were converted to true stress-strain curves, Figure 41(b).

Although the uniaxial stress at a strain of 8% should be used to provide a Tabor factor independent of strain hardening [173] and allow for comparison with simulations, micropillar compression on Cu-20/Ni-20 nm was only performed to a maximum strain of ~3.5%. Error may be introduced by using the stress at 3.5% strain instead of 8% strain, but the error is expected to be marginal since the stress appears to be saturating with strain. Assuming that minimal strain hardening occurs between 3.5 and 8% strain, the stress at 3.5% strain, $\sigma_{3.5\%} = 1550$ MPa, will be used to approximate the stress at 8% strain, $\sigma_{3.5\%} \approx \sigma_{8\%} = \sigma_y$.

4.4 Elastic Modulus

Instrumented nanoindentation tests were performed on an MTS Nanoindenter XP with Continuous Stiffness Measurement (CSM) applied at 45 Hz over a harmonic displacement range of 2 nm. Films were attached to SEM stubs with Ag paste and fixed in a specially designed sample holder—essentially a hard plastic puck with a hole to accommodate the SEM stub and a set screw to prevent the stub from moving.

After calibrating the tip area function of the sharp Berkovich tip (tip radius < 50 nm) using a silica standard, indentation tests were performed to a depth of 500 nm (10% of the nominal film thickness). Figure 42 shows that elastic modulus was constant
with depth, indicating minimal effect of the substrate [88] or mounting compliance [200]. The average elastic modulus between depths of 100-500 nm for 5 separate tests was 157 ± 4 GPa, in good agreement with the composite elastic modulus calculated using the rule-of-mixtures and isotropic elastic moduli for Cu (128 GPa) and Ni (200 GPa). Note that the same isotropic elastic moduli were used in the finite element modeling in Chapter 3. Subsequent tests showed that modulus was constant to a depth of at least 2000 nm, which is 40% of the nominal film thickness. The proximity of the measured elastic modulus to the expected elastic modulus of the Si substrate (130-170 GPa [201]) likely results in minimal substrate effect [88].

**Figure 42:** Elastic modulus as a function of indentation depth for Cu-20/Ni-20 nm. Two curves are shown to illustrate the general consistency of the measurements.
4.5 Hardness

In addition to CSM, load-displacement curves were measured using standard indentation to depths of 250, 500, 750, 1000, and 2000 nm. A minimum of 5 indents were made at each depth. Representative load-displacement curves are provided in Figure 43. Little scatter was observed between tests at a given depth and between the CSM and standard indentation load-displacement curves.

![Figure 43: Representative load-displacement curves for indentation into Cu-20/Ni-20nm to maximum displacements of 250, 500, 750, 1000, and 2000 nm.](image)

Hardness was calculated from the load-displacement curves using standard Oliver-Pharr analysis [73,76] at each depth, Figure 44. To distinguish from hardness measured from the actual indentation area, it is designated $H_{OP}$. Since hardness is
relatively independent of indentation depth, an average hardness is calculated, 
\[ H_{OP} = 4.23 \pm 0.13 \text{ GPa}. \]

![Graph showing hardness as a function of indentation depth with an average hardness of 4.23 ± 0.13 GPa.](image)

**Figure 44:** Hardness as function of indentation depth measured using standard Oliver-Pharr analysis. To distinguish from hardness measured using the actual contact area, it is designated \( H_{OP} \).

4.5.1 Contact Area Measurement

As previously mentioned, the Oliver-Pharr method does not account for pile-up, and therefore measurement of hardness could be overestimated by as much as 50% [84]. To verify that hardness determined using the Oliver-Pharr method is accurate for Cu-20/Ni-20 nm, residual indentation impressions were imaged using an FEI/Philips Sirion Field Emission SEM. An image of 500 and 2000 nm deep indents used for contact
area measurement are provided in Figure 45(a) and (b) respectively. The straight edges of the triangle indicate that significant pile-up is not observed at any indent depth measured. Although SEM images can provide quantitative measurement of projected contact area, they provide only qualitative determination of pile-up height. If a quantitative determination of pile-up height is desired Atomic Force Microscopy (AFM) provides a more suitable technique [75].

![Figure 45](image)

**Figure 45:** Residual indentation impression in Cu-20/Ni-20 nm at indentation depths of: (a) 500 nm and (b) 2000 nm

Careful measurement of the projected contact areas—the area of the triangle in Figure 45(a,b)—was performed using ImageJ, an open-source image processing software. Hardness calculated using the measured contact area $H_{\text{meas}}$ is in good agreement with the hardness determined using the Oliver-Pharr method as shown in Figure 46. It should be noted that the Oliver-Pharr method estimates the projected contact area under
load while measurement of the residual indent impressions clearly provides the unloaded contact area. Regardless, in this case, good agreement is observed.

![Graph](image)

**Figure 46:** Comparison of hardness calculated from the contact area determined using the Oliver-Pharr method $H_{\text{OP}}$ and SEM images of the actual contact area $H_{\text{meas}}$. Results are shown for Cu-20/Ni-20 nm.

4.5.2 Strain Rate Sensitivity

Standard indentation testing is typically performed at high loading rates to avoid errors due to thermal drift; where thermal drift is a general term to describe all forms of spurious displacements that occur during indentation, for example displacements resulting from thermal expansion/contraction. Thermal drift is measured in units of nm/s, and since test time increases as loading rate is decreased, short test times are used to minimize effects of thermal drift.
Yet high indentation loading rates are also problematic because they do not allow for direct comparison to micropillar compression tests which are commonly performed at much lower rates. To rectify this discrepancy, strain rate sensitivity for Cu-20/Ni-20 nm is calculated using a range of indentation loading rates, and steps are taken to minimize thermal drift.

First, an indentation strain rate needs to be defined. Indentation strain rate can be determined by differentiating the definition of hardness [202], and, provided that hardness is independent of indentation depth, $h$, indentation strain rate can be approximated by $\frac{1}{2} \frac{\dot{P}}{P}$ [202]:

$$\dot{\varepsilon}_{\text{ind}} = \frac{\dot{h}}{h} = \frac{1}{2} \left( \frac{\dot{P}}{P} - \frac{\dot{H}}{H} \right) \approx \frac{1}{2} \frac{\dot{P}}{P}$$

Indentation strain-rate sensitivity, $m_{\text{ind}}$, is then inferred as $d(\ln H)$ divided by $d(\ln \dot{\varepsilon}_{\text{ind}})$:

$$m_{\text{ind}} = \frac{d \ln H}{d \ln \dot{\varepsilon}_{\text{ind}}}$$

Although the strain state beneath an indenter is not uniform, and therefore all of the material underneath in indenter is not strained at the same rate, agreement between rate sensitivity determined using traditional uniaxial testing and indentation testing has
been achieved for nanocrystalline Ni so long as effects of thermal drift are reconciled [203].

Constant rate indentation tests are performed, but to circumvent thermal drift, the displacement measurements are disregarded entirely and instead contact area is calculated from an assumed elastic modulus, $E$ and the measured harmonic contact stiffness, $S$ [204,205]. Since elastic modulus is expected to be constant with rate, the elastic modulus measured at a higher strain rate where thermal drift is minimal can be used. Rearranging the standard indentation equation presented previously, Equation (9), to solve for contact area provides:

$$A_E \pi \beta^2 \frac{S^2}{4 E_r^2} = 1$$

Equation (34)

$S$ and $P$ are measured and expected to be relatively insensitive to thermal drift, and thus a thermal-drift insensitive hardness can be calculated by dividing load by the contact area determined using Equation (34) [204,205]. The advantages of this method are that it uses a single rate so that rate-specific residual contact areas can be measured. Moreover, it is applicable to indents of any depth so rate sensitivity in thin films can be measured while avoiding substrate effects.

Results from the constant rate method applied to Cu-20/Ni-20 nm appear in Figure 47. Indentation tests were performed at constant $\dot{\varepsilon}_{ind}$ spanning $10^4$ /s to $10^2$ /s up
to a maximum load of 100 mN. It is worth noting that in order to maintain consistent indentation depths in the presence of large thermal drifts (spurious displacements), a maximum load should be prescribed instead of a maximum displacement. A constant $E = 157$ GPa, consistent with the $E$ measured at $\dot{\varepsilon}_{\text{ind}} = 0.025$, was assumed to calculate a drift-insensitive contact area $A_E$. The resulting $H$ is plotted as $\ln(H)$ vs. $\ln(\dot{\varepsilon}_{\text{ind}})$ following Equation (33) to calculate strain rate sensitivity, $m_{\text{ind}}$.

![Graph showing ln(H) vs. ln(\dot{\varepsilon}_{\text{ind}}) for Cu-20/Ni-20 nm](image)

$m_{\text{ind}} = 0.032 \pm 0.001$

**Figure 47:** Indentation strain rate sensitivity for Cu-20/Ni-20 nm using the constant indentation strain rate test method. Values are the average of 5 indents, error bars representing the standard deviation in $\ln(H)$ between tests are smaller than the data points.

The measured strain rate sensitivity for Cu-20/Ni-20 nm is $m_{\text{ind}} = 0.032 \pm 0.001$ using constant rate indentation. In contrast, Zhu et al. [13] found $m_{\text{ind}} = 0.5$ (reported as
stress exponent, $1/m_{ind}$) for Cu-20/Ni-20 nm, but for films with a (111) texture not a (100) texture as used here. Moreover, Zhu et al. [13] determined $m_{ind}$ by measuring displacement during 10 min constant load holds which could be significantly affected by thermal drift [204] such that the value of $m_{ind}$ might be exaggerated. Carpenter et al. [111] took a different approach, measuring $m$ in the same Cu-20/Ni-20 nm films used in the present study, but using micropillar compression jump tests. An average $m = 0.014$ was reported by Carpenter et al. [111], however, it was noted that $m$ increased with increasing strain (up to 3%), therefore it is possible, in addition to the different loading conditions, the larger $m_{ind}$ determined here may be a result of the larger strains underneath the indenter. Interestingly, the $m_{ind}$ measured here is in good agreement with the average $m_{ind}$ of nanocrystalline Cu ($m_{ind} = 0.04$) [206] and Ni ($m = 0.016$) [207] at a similar size scale (20 nm grain size). More work is required to determine how size scale and interface structure affect strain rate sensitivity.

### 4.5 Extraction of Constituent Strengths

Now that uniaxial strength, in-plane residual stress state, elastic modulus, and hardness (at the same strain rate used for determination of uniaxial strength) have been experimentally measured, constituent strengths can be estimated through comparison with the parametric finite element analysis from Chapter 3. For reference, the experimental results are provided in Table 4.
Table 4: Experimentally determined in-plane residual stress, $\sigma_{ip}$, uniaxial strength, $\sigma_y$, elastic modulus, $E$, and hardness, $H$ for Cu-20/Ni-20 nm.

<table>
<thead>
<tr>
<th></th>
<th>$\sigma_{ip}$ (MPa)</th>
<th>$\sigma_y$ (MPa)</th>
<th>$E$ (GPa)</th>
<th>$H$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-20/Ni-20 nm</td>
<td>$623 \pm 30$</td>
<td>$1550$</td>
<td>$157 \pm 4$</td>
<td>$4.17 \pm 0.1$</td>
</tr>
</tbody>
</table>

First, the computational results for the Tabor factor as function of elastic ratio and constituent strength ratio (Figure 25) must be shifted to include the effect of the measured tensile in-plane residual stress, $\sigma_{ip}/\sigma_y = 0.40$ as provided in Figure 48. Now, the experimental data point for Cu-20/Ni-20 nm can be added to Figure 48 by calculating the experimental elastic ratio, $E/\sigma_y = 100$ and Tabor factor, $H/\sigma_y = 2.26$ from the data presented in Table 4.
Figure 48: Computationally determined Tabor factor as a function of $E/\sigma_y$ and constituent strength ratios. Curves shifted to account for the measured tensile residual stress $\sigma_{ip}/\sigma_y = 0.4$. Plotting experimental results for Cu-20/Ni-20 nm allows extraction of a constituent strength ratio equal to 3.

Location of the experimental data point in Figure 48 suggests that Cu and Ni in the Cu-20/Ni-20 nm nanolayered composite have a strength ratio of ~3. Although the stronger constituent cannot be determined directly with this method, bulk [208] and nanocrystalline [209] strength measurements indicate that Ni is expected to be the stronger constituent. Assuming then that Ni is the stronger constituent and using the average uniaxial strength from the micropillar compression test, the individual Cu and Ni strengths can be estimated as $\sigma_{y,Cu} = 770$ MPa and $\sigma_{y,Ni} = 2320$ MPa respectively.
If the Tabor factor is determined in the typical fashion, using hardness at 
\( \dot{\varepsilon}_{\text{ind}} \approx 0.025 \) instead of at the same rate as the micropillar compression test, the computed Tabor factor equals 2.70—the exact Tabor factor expected for bulk, coarse grain metals. Clearly inconsistent strain rates can mask the subtle effects of disparate constituent strengths and in-plane residual stress.

### 4.6 Summary and Conclusions

A coupled experimental/computational, indentation-based method for estimating constituent strengths in nanolayered composites is outlined. The method requires experimental measurement of in-plane residual stress, uniaxial flow strength, elastic modulus, and hardness. The experimental measurements are used to locate an experimental data point on a computationally determined Tabor factor \((H/\sigma_y)\) vs. elastic ratio \((E/\sigma_y)\) plot that encompasses a range of constituent properties and has been adjusted for the measured in-plane residual stress.

The indentation-based method has been applied to a Cu-20/Ni-20 nm nanolayered composite. A tensile in-plane residual stress with magnitude of \(\sigma_{ip} = 623 \pm 28\) MPa was measured using in-plane x-ray diffraction. Uniaxial flow strength was determined using micropillar compression testing, and at a maximum strain of 3.5% the flow strength reaches \(\sigma_y = 1550\) MPa. Elastic modulus and hardness were measured using nanoindentation. Elastic modulus was constant with indentation depth and in good agreement with the average of Cu and Ni isotropic elastic constants, \(E = 157\) GPa.
Minimal pile-up was observed thus contact areas calculated using the Oliver-Pharr method and directly from SEM images of the residual indents were comparable. Indentation tests performed at strain rates between $10^{-4}$/s to $10^{-2}$/s revealed a strain rate sensitivity of $m_{ind} = 0.032 \pm 0.001$. Consequently, large errors (~20%) in the Tabor factor are generated when hardness and uniaxial strength are determined at different strain rates.

The experimentally determined Tabor factor $H/\sigma_y = 2.26$ and elastic ratio $E/\sigma_y = 100$ correspond well with the simulated results assuming a constituent strength ratio $\sigma_{y,Ni}/\sigma_{y,Cu} \approx 3$. From the ratio and the average uniaxial strength, the Cu and Ni strengths can be estimated as $\sigma_{y,Cu} = 770$ MPa and $\sigma_{y,Ni} = 2320$ MPa respectively. Further discussion on the extracted constituent strengths is presented in Chapter 6.
Chapter 5: Extracting Constituent Strengths: A Diffraction-Based Method

The indentation-based method (Chapter 4) provides a unique method to calculate the individual constituent strengths in nanolayered composites; however, it estimates a single value of stress and accordingly offers no information about how constituent strengths and interface structure evolve during deformation. X-ray diffraction affords an established method to measure the constituent (phase)-independent evolution of lattice strains during deformation, furnishing a useful compliment to the indentation-based method. Diffraction-based techniques have been applied to Cu/Nb nanolayered composites ex situ to examine micropillars pre and post compression testing [109] as well as in situ during tensile testing of freestanding Cu/Nb films [60], but remain under-utilized.

A diffraction-based method is developed and applied to Cu/Ni nanolayered composites. To strain the films the difference in thermal expansion coefficient of the Si substrate and metallic layers is utilized. Similar straining methods have been used to extract the in-plane stress-strain response of single layer films by measuring the curvature of the film-on-substrate assembly during heating and cooling [210–212]. However, the curvature techniques provide only the average film response rather than that of the
individual constituents. Instead, we use *in situ* x-ray diffraction during heating/cooling, and by employing x-ray diffraction from a grazing incidence, direct measurement of in-plane lattice parameters—which furnish in-plane elastic strain (and stress)—are obtained. This method was established for single layer metallic films on substrates [213–216] as an alternative to curvature measurements, and for Al [215] and Cu films [217] on Si substrates, it provides values of film stress comparable to curvature measurements. But heated *in situ* x-ray diffraction has not been reported for layered composites.

5.1 **Fabrication and Structure**

The Cu/Ni nanolayered composite films used in this and previous studies [7,55,111] were grown at the Center for Integrated Nanotechnologies (CINT) at Los Alamos National Laboratory. Films were sputtered on unheated, HF-cleaned <100> Si substrates. After initial deposition of a 100 nm thick, single crystal Cu buffer layer, layers were alternated to a total film thickness of 5 µm and capped with a final Cu layer. Low deposition rates (5-6.5 Å/s) and Ar pressures of 6.5 and 5 mTorr were used for Cu and Ni respectively.

Selected area diffraction [111] and grazing incidence x-ray diffraction [18] reveal “cube-on-cube” epitaxial layers where the layers are single-crystal with an in-plane orientation relation [001]$_{Cu,Ni}$ $\parallel$ [011]$_{Si}$ with the substrate. Transmission electron microscopy confirmed that measured layer thicknesses are within 1 nm of the nominal layer thicknesses [55].

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5.2 Experimental Procedure

5.2.1 Measurement Setup

In-plane x-ray diffraction from a grazing incidence was performed during heating and cooling of the Cu-20/Ni-20 nm samples, with semi-coherent interfaces, used previously, as well as Cu-10/Ni-10 nm films with more coherent interfaces. A PANalytical X’Pert Pro MRD 4-axis x-ray diffractometer, coupled with a hybrid monochromator and a 0.27° parallel plate collimator, was used at the Center for Nanophase Materials Sciences (CNMS) at Oak Ridge National Laboratory. An Anton Paar DHS 900 heated stage regulated the sample temperature under vacuum. Performing heating under vacuum served to minimize oxidation and the associated effects on the measured stress-temperature behavior [218]. No evidence of oxidation was observed in the diffraction patterns after thermal cycling.

The sample orientation is shown in Figure 49(a), with an angle of incidence $\Psi = 88-89°$ from the film surface normal. Penetration depths of $\sim 350-1000$ nm are expected [40]. A full in-plane rotation, $\phi$-scan, was performed to determine $\phi$ with the greatest diffraction intensity, corresponding to alignment of the (200) pole parallel to the diffraction axis n. This $\phi$ was used in subsequent scans. The samples were heated by 50°C increments to 325°C, then cooled by 50°C decrements to room temperature. At each temperature, four separate 20 scans were taken at a rate of 0.4°/min ($\sim$10 min/scan). Each scan provided sufficient intensity to identify in-plane (200) diffraction peaks. The four
scans were used to quantify changes in (200) diffraction peaks with time at a given temperature.

Diffraction peaks were simultaneously fit using a pseudo-Voigt profile function in PANalytical HighScore Plus v3.0 software. The fitted peak positions furnished average (200) interplanar lattice spacings \(d_{\text{Cu}}(T)\) and \(d_{\text{Ni}}(T)\). Figure 49(b) and (c) show example intensity vs. \(\theta\) in-plane scans and fitted profiles for Cu-10/Ni-10 nm and Cu-20/Ni-20 nm samples, respectively. A single peak at lattice spacing between those of Cu and Ni is observed in Figure 49(b) consistent with coherent Cu/Ni interfaces. The Cu and Ni peaks then separate as layer thickness increases as seen in Figure 49(c) since the lattice mismatch can no longer be accommodated elastically. Although both samples were tested under the same conditions, the same duration, and with the same optics, the Cu-10/Ni-10 nm sample shows significantly less intensity. The lower intensity leads to a less favorable signal to noise ratio as seen in Figure 49(c). The source of this variance is unknown but may be related to the greater number of interfaces in the Cu-10/Ni-10 nm sample or slight misalignment.
Figure 49: (a) Film geometry for x-ray diffraction at a grazing incidence; (b) measured 2θ diffraction pattern (jagged curve) and best fit (smooth curve) of the in-plane, coherent [020] peak for the Cu-10/Ni-11 nm film at 125°C; (c) measured 2θ diffraction pattern (smooth curve) and best fit (overlying curve) of in-plane [020] peaks for the Cu-20/Ni-20 nm film at room temperature.

5.2.2 Calculation of In-Plane Stress and Strain

At a given temperature, the fitted peak positions, 2θ furnished average in-plane interplanar lattice spacings, \( d(T) \) in a given layer type (Cu or Ni) through Bragg’s Law:

\[
d(T) = \frac{\lambda}{2 \sin \theta}
\]

where \( \lambda \) is the source wavelength (for Cu K\textsubscript{α}, as used here, \( \lambda = 1.54184 \text{ Å} \)). In-plane elastic lattice true strains, \( \varepsilon_{el} \) were calculated using bulk lattice parameters, \( a_0 \) provided in Table 5:

\[
\varepsilon_{el}(T) = \ln \frac{d(T)}{d_0(T)}, \quad d_0 = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}
\]
where \( d(T) \) is the measured interplanar spacing at the elevated temperature \( T \) and \( d_0(T) \) is the corresponding stress-free value. The in-plane, direct component of thermal strain in a given layer is:

\[
\varepsilon_{\text{th}}(T) = \ln \frac{d_0(T)}{d_0(T_0)} = \alpha(T - T_0) \tag{37}
\]

where \( d_0(T) \) and \( d_0(T_0) \) are the stress-free interplanar spacings at the elevated and reference (room) temperatures, and \( \alpha \) is the coefficient of thermal expansion of the layer. Combining Equations (36) and (37) elicits a more convenient form for the elastic strain:

\[
\varepsilon_{\text{el}}(T) = \ln \frac{d(T)}{d_0(T_0)} - \alpha(T - T_0) \tag{38}
\]

The quantities \( d(T) \) and \( T \) are experimental measured and \( d_0(T_0) \) and \( \alpha \) are furnished from literature values reported in Table 5. The direct component of stress in the in-plane <200> directions, at a given temperature is provided by the anisotropic, elastic constitutive equation:

\[
\sigma_{\text{el}}(T) = \left( C_{11} + C_{12} - 2\frac{C_{12}}{C_{11}} \right) \varepsilon_{\text{el}}(T) \tag{39}
\]

where \( C_{11}, C_{12} \) are the anisotropic elastic moduli of the layer, reported in Table 5.
The in-plane, direct components of plastic strain are obtained by first noting that the layers and the Si substrate are oriented so that the in-plane directions $[200]_{\text{Cu}} \parallel [200]_{\text{Ni}} \parallel [220]_{\text{Si}}$. In the idealized reference case, the interfaces are coherent, so that the reference (200) interplanar spacing $d_{0}(T_{0})$ of Cu is stretched to the current (220) interplanar spacing $D_{0}(T)$ of the thick (essentially stress-free) Si substrate. In that case, Cu layers experience a total in-plane strain:

$$\varepsilon_{\text{tot}}(T) = \ln \frac{D_{0}(T)}{d_{0}(T_{0})}$$

(40)

An identical counterpart expression holds for coherent Ni layers. In reality, the deformation is too large to be accommodated by elastic and thermal strains. Instead, plastic deformation in the form of threading dislocation motion occurs (see inset Figure 54a). For the case of face-centered cubic (fcc) layers with a [001] interface normal, threading dislocation motion can form arrays of misfit dislocations with line directions along orthogonal in-plane <110> directions [141]. The in-plane plastic strain is therefore the total strain minus the elastic and thermal strains:

$$\varepsilon_{p}(T) = \varepsilon_{\text{tot}}(T) - \varepsilon_{\text{el}}(T) - \varepsilon_{\text{th}}(T) = \ln \frac{D_{0}(T)}{d(T)}$$

(41)
The second equality is obtained by substituting Equations (36) and (37) for $\varepsilon_{\text{el}}(T)$ and $\varepsilon_{\text{th}}(T)$, respectively. Since $D_0(T)$ is not measured directly, a useful quantity is the change in plastic strain during heating:

$$
\Delta \epsilon_p(T) = \epsilon_p(T) - \epsilon_p(T_0)
= \Delta \epsilon_{\text{tot}}(T) - \Delta \epsilon_{\text{th}}(T) - \Delta \epsilon_{\text{el}}
= (\alpha_{\text{Si}} - \alpha)(T - T_0) - \Delta \epsilon_{\text{el}}
$$

(42)

This is independent of $D_0(T)$ and is readily calculated in terms of $\alpha_{\text{Si}}, \alpha$, and the measured values of $d$ at $T_0$ and $T$, respectively. Physically, it states that the mismatch in thermal strain between the substrate and layer must be accommodated by elastic and plastic strain in the layer.
Table 5: Physical properties used for stress analysis; lattice parameters are from Cullity and Stock [219], thermal expansion coefficients for Cu and Ni are from Krishnan [220] and for Si from Watanabe et al. [221]. Anisotropic elastic constants are from Courtney [222].

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<th>a₀</th>
<th>α</th>
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<th>C₁₂</th>
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<td>166</td>
<td>64</td>
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</tbody>
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5.2.3 Calculation of Interface Dislocation Density

The interfacial dislocation density produced during straining is \( \rho_{\text{interface}} = 2/S \), where \( S \) is the in-plane, perpendicular spacing between dislocations (see upper inset, Figure 55). \( \rho_{\text{interface}} \) is therefore the line length of interfacial dislocations per area of interface. For fcc metals with a [100] interface normal, the resulting in-plane plastic strain in the layer is \( \epsilon_p = b_e/S \), where \( b_e = 0.5 \) is the in-plane edge component of 60° interfacial dislocations [141]. Since both Cu and Ni layers can deform plastically, the net interfacial dislocation density depends on the difference in plastic deformation in Ni vs. Cu layers:

\[
\rho_{\text{interface}}(T) = \frac{2}{b_e} \left( \epsilon_{p,Ni} - \epsilon_{p,Cu} \right) = \frac{2}{b_e} \ln \frac{d_{Cu}(T)}{d_{Ni}(T)} \tag{43}
\]
Thus, the interfacial dislocation density at temperature $T$ depends on the measured interplanar spacings in Cu and Ni at that $T$. The case $\rho_{\text{interface}} = 0$ occurs in the coherent limit where the Cu and Ni interplanar spacings are equal.

The relevant room temperature lattice parameters, thermal expansion coefficients and anisotropic second order elastic constants for Cu, Ni and Si are reported in Table 5. Room temperature values were used since estimates of $\sigma_{ip}(T)$ changed < 12% compared to those based on $T$-dependent expansion coefficients and elastic constants over the experimental $T$ range. Bulk values of thermal expansion coefficients were used since no direct measurements were available from these experiments. This assumption is supported by x-ray diffraction studies over the range 100-400°C, showing that 720 nm Al films on Si substrates have < 9% difference in thermal expansion coefficient compared to bulk [223]. However, a 60% decrease in thermal expansion coefficient for 0.3 μm vs. 1.7 μm thick Al films was observed using a microcantilever approach [224]. Such conflicts regarding the size-dependence of thermal expansion coefficients have not been resolved [214].

5.3 Results and Discussion

5.3.1 In-Plane Stress vs. Temperature

Figure 50(a) and (b) show in-plane biaxial stresses, $\sigma_{\text{Ni}}(T)$ and $\sigma_{\text{Cu}}(T)$, respectively, for the Cu-10/Ni-10nm sample. Ni layers are in tension (2.9 GPa) and the Cu layers are in compression (1.4 GPa) at room temperature since $d_0$ is smaller for Ni vs.
Cu. These large in-plane stresses are on the order of the stress (~2 GPa) expected for completely coherent Cu/Ni interfaces [149], but here, the stresses in Cu and Ni are not equal and opposite due to the presence of the Cu seed layer and Si substrate. During heating, the metals expand more than the Si substrate since $\alpha_{\text{Cu}}$ and $\alpha_{\text{Ni}} > \alpha_{\text{Si}}$. Therefore, $\sigma_{\text{Ni}}$ becomes less positive and $\sigma_{\text{Cu}}$ becomes more negative during heating. The dashed line in each plot shows the predicted slope $d\sigma/dT$ for each layer assuming they deform thermo-elastically (i.e., no plasticity). The slope is obtained by differentiating Equation (39) to get $d\sigma/dT$, where $d\varepsilon_{\text{el}}/dT = (\alpha_{\text{Si}} - \alpha)\Delta T$ from Equation (42). This approximation captures the experimental measurements to within an average of 4% error.
Figure 50: Average in-plane biaxial stress (a) $\sigma_{Ni}$ and (b) $\sigma_{Cu}$ vs. temperature for the Cu-10/Ni-10 nm multilayer sample. The dashed lines and governing equations are predictions combining Equations (39) and (42) assuming no inelastic deformation (i.e., thermo-elastic only).

Figure 51(a) and (b) show in-plane biaxial stresses $\sigma_{Ni}(T)$ and $\sigma_{Cu}(T)$, respectively, for the Cu-20/Ni-20 nm sample. The initial stresses in both layers are smaller than those in the Cu-10/Ni-10 nm film, indicating a less coherent interface, and as before, the stresses in the Cu and Ni layers are not equal and opposite due to the Cu seed layer and Si substrate. Noticeable deviations from thermoelastic behavior are apparent,
implying $\varepsilon_p(T) \neq 0$. In Ni, the deviation occurs only upon cooling. In Cu, the deviation occurs for heating above 200°C, as well as over most of the cooling range. After a thermal cycle, $|\sigma_{\text{Ni}}|$ is ~10% lower and $|\sigma_{\text{Cu}}|$ is 40% lower. This relaxation may reflect dislocation-based plasticity, interdiffusion between layers [15,225], or diffusion-mediated processes such as constrained diffusional creep observed in single phase thin films [212,226].
Figure 51: Average in-plane biaxial stress (a) $\sigma_{\text{Ni}}$ and (b) $\sigma_{\text{Cu}}$ vs. temperature for the Cu-20nm/Ni-20nm multilayer sample. The dashed lines and governing equations are predictions combining Equations (39) and (42) assuming no inelastic deformation (i.e., thermo-elastic only).

5.3.2 Deviation from Thermoelastic Prediction

To determine if dislocation plasticity or other forms of inelastic deformation are the cause of the observed stress relaxations, four consecutive diffraction scans were measured at each temperature. The resulting $\sigma_{\text{Ni}}(T)$ and $\sigma_{\text{Cu}}(T)$ for the Cu-20/Ni-20 nm are given in Figure 52(a) and (b) respectively. Each scan took ~10 min with ~2 min intervals between scans to reposition the goniometers. At each temperature, no evidence
of uniform, time-dependent stress relaxation is observed from the first to fourth scans. The data for Ni at 275°C (heating) and Cu at 325°C do show monotonic decreases in stress of 12% and 7%, respectively, over these 40 min isothermal intervals, but the amount of decrease between consecutive scans is irregular. Overall, the aggregate of data supports time-independent plastic deformation rather than creep as the inelastic deformation.
Additional evidence for dislocation plasticity-based stress relaxation is provided by post-thermal cycle TEM analysis. Figure 53 shows TEM micrographs of the Cu-20/Ni-20 nm sample after the thermal cycle. The layer structure remains intact (a) and layer thickness is unchanged (b), suggesting large-scale diffusion and morphological instability does not occur [227]. The initially planar Si-Cu seed layer interface becomes nonplanar and nearby region become polycrystalline (c), suggesting formation of copper...
silicides as in Ref. [228]. Diffusion between Si and the Cu seed layer is aided by lack of an appropriate barrier layer. Nevertheless, this region is small compared to the overall film thickness and is not expected to account for the observed changes in $\sigma_{Cu}$ or $\sigma_{Ni}$.

Two additional x-ray diffraction-based techniques were used to supplement the evidence that minimal interdiffusion occurred. The first is the calculation of stress-free Cu and Ni lattice parameters in the Cu-20 nm/Ni-20 nm film using the $\sin^2\Psi$-method. Following a procedure similar to Daniels et al. [15], the Cu and Ni lattice parameters changed by $<0.2\%$ after the thermal cycle. This small change suggests minimal

Figure 53: Bright-field TEM micrographs of the Cu-20/Ni-20 nm after a single thermal cycle showing: (a-b) layer structure is maintained, with significant dislocation content at interfaces; (c) evidence that the Cu seed layer has reacted with the Si substrate but represents a small fraction of the overall film thickness.
interdiffusion. The second technique makes use of the satellite peaks in the out-of-plane diffraction pattern. Since satellite peaks are not observed for the Cu-20 nm/Ni-20 nm film, the Cu-10 nm/Ni-10 nm film was used. DuMond and Youtz [49] as well as Cook and Hilliard [50] found that the diffracted satellite peak intensity is proportional to the square of the Fourier transform of the composition variation. Therefore, satellite peak intensity can be measured to estimate the change in amplitude of the composition variation. Here, a < 4% change in the relative intensity of the (200) Cu and Ni satellite peaks was observed post-heating indicating that the change in composition amplitude is < 2%. Furthermore, the interdiffusivity in nanolayered composites is expected to decrease with increasing layer thickness [229], and therefore the amount of interdiffusion is expected to be even less severe in the Cu-20/Ni-20 nm film. Overall, the lack of significant diffusion suggests a time-independent inelastic mode of deformation such as confined layer slip—glide of single Orowan-type dislocation loops bounded by two interfaces [139,230].

5.3.3 In-Plane Stress vs Plastic Strain

If dislocation-plasticity is assumed, then the deviation of the measured strain from the thermoelastic predicted strain is related to an increment in plastic strain, Equation (42), allowing Figure 51 to be re-plotted as $\sigma_{\text{Ni}}$ vs. $\Delta \varepsilon_{p,\text{Ni}}$ and $\sigma_{\text{Cu}}$ vs. $\Delta \varepsilon_{p,\text{Cu}}$ given for Cu-20/Ni-20 nm in Figure 54(a) and (b) respectively. During heating, $\sigma_{\text{Ni}}$ decreases with $\Delta \varepsilon_{p,\text{Ni}} \approx 0$, consistent with elastic unloading. During cooling, $\sigma_{\text{Ni}}$ increases linearly by ~500 MPa as plastic strain increases by $\Delta \varepsilon_{p,\text{Ni}} \approx 0.1\%$. Gaps in the unloading
vs. loading traces have been observed in conventional [231,232] and nanocrystalline metals [233] following complete unloading and/or stress reversal under isothermal conditions. But here, the Ni layers are unloaded to only 60% of the initial stress. The elastic unloading indicates that dislocation loops in Ni (see inset, Figure 54a) are unable to reverse direction during unloading, yet they readily move forward upon reloading. A possible explanation is that deformation in adjoining Cu layers has altered interfacial structure during unloading, thereby lowering the threshold for yield in Ni layers.

A peculiar feature is the large increase in stress $\Delta \sigma_{\text{Ni}} \sim 500$ MPa during the initial plastic strain increment $\Delta \varepsilon_{\text{p,Ni}} \approx 0.1\%$. For comparison, 1 $\mu$m Ni thin films show $\Delta \sigma \sim 200$ MPa [216], nanocrystalline Ni (29 nm avg. grain size) shows $\sim 240$ MPa [234], and conventional grain size Ni shows $\sim 5$ MPa [208]. For consistency, these values are all measured during the initial 0.1% increment in plastic strain. The large value in the present experiments reflects that continued motion of existing dislocations or activation of new sources requires extraordinary increases in stress. Numerical and analytic calculations document strong interactions between threading and misfit dislocations [235,236] in nanolayered thin films. Also, dislocation models of the work to increase interfacial misfit dislocation density [237] in nanolayered thin films support such large experimental values.
Figure 54: Average in-plane biaxial stress (a) $\sigma_{Ni}$ and (b) $\sigma_{Cu}$ vs. increment in plastic strain in the Cu-20/Ni-20 nm multilayer sample. (a) Ni layers unload elastically during heating and reload plastically during cooling. Inset shows forward confined layer slip of dislocations in Ni. (b) Cu layers load plastically during heating, unload elastically during initial cooling from points H6 to C1, then unload plastically during continued cooling. Inset (right) shows forward confined layer slip during heating and inset (left) shows reverse confined layer slip during continued cooling.
Figure 54(b) shows $\Delta \sigma_{\text{Cu}} \approx 200$ MPa during heating. $\sigma_{\text{Cu}}$ plateaus at $\approx 740$ MPa (compression). During initial unloading (cooling), Cu layers unload elastically by 80 MPa (Point H6 to C1 in Fig. 6b). Then reverse plastic deformation commences with continued unloading. Here, $\Delta \sigma = -400$ MPa over the increment $\Delta \varepsilon_{p,\text{Cu}} \approx 0.1\%$. This magnitude of stress change is comparable to those in loading/unloading of passivated Cu films (thickness = 340 nm) during plane-strain bulge tests [238]. Although the changes in $\Delta \sigma_{\text{Cu}}$ and $\Delta \sigma_{\text{Ni}}$ are large in this initial plastic regime, corresponding changes in the macro-stress on the Cu-20/Ni-20 nm film, measured by micropillar compression, is only $\Delta \sigma \approx 100$ MPa [18].

An unusual feature in Figure 54(b) is the linear recovery of plastic strain over a large (300 MPa) unloading range. Xiang and Vlassak [238, 239] also observe plastic strain recovery in Cu layers (340-890 nm) using plane-strain bulge tests; Keller et al. [218] report similar effects using substrate curvature tests. Both groups report large plastic strain recovery only if the Cu layer is passivated. Like the present work, the Xiang and Vlassak study reports plastic strain recovery prior to a reversal in the sign of applied stress. They attribute it to back stresses from dislocation pile-ups at the passivation/film interface. However, the nanoscale layers in the present study are more than an order of magnitude thinner, so that they are too small for significant pile-ups [140]. Rather, the phenomena can stem from the driving force to remove dislocation line length at interfaces. This process is depicted in Figure 54(b) insets and it has been observed in
microscopy [139,142,146,240], simulations [148,235,241–243], and perhaps most clearly during in situ nanoindentation of Cu/Nb nanolayered composites [145].

As dislocation loops deposit and remove dislocation line length at the interface, the interfacial dislocation density changes. Figure 55 shows interfacial dislocation density $\rho_{\text{interface}}$ (Equation (43)) vs. T for the Cu-20/Ni-20 nm film. During heating, $\rho_{\text{interface}}$ increases ~22% as Cu layers plastically compress and deposit dislocation content while Ni layers remain elastic (“Heat” inset, Figure 55). During cooling, $\rho_{\text{interface}}$ ~ constant as Cu and Ni layers co-stretch by comparable plastic strain. Here, existing or new dislocation loops in Ni advance by forward slip while loops in Cu layers retract by reverse slip (“Cool” inset, Figure 55).
Carpenter et al. [55] conclude that accumulation of interfacial dislocation content can serve to pin forward/reverse motion. It can also reduce the pinning dimension $S$ for dislocations to bow-out from interfaces, thus impeding dislocation nucleation into adjoining layers. The average pinning strength in Cu can be estimated by comparing the biaxial stress for forward (heating) and reverse (cooling) modes (Figure 54b):

$$
\sigma_{\text{Cu, forward(heat)}} = \frac{2w}{b_c h} + \sigma_{\text{Cu, pin}}; \quad \sigma_{\text{Cu, backward(cool)}} = \frac{2w}{b_c h} - \sigma_{\text{Cu, pin}}
$$

These equations are derived from dislocation models of confined layer slip, where dislocations with average energy per unit length $w$ are deposited at interfaces. The local
stress provides the available work, $\sigma_{\text{Cu}} b \epsilon h$, to create the increase, $2w$, in dislocation line energy when the loop advances [139]. Equating these work and energy terms furnishes the contribution $2w/b \epsilon h$ in Equation (44). $\sigma_{\text{Cu, pin}}$ is the additional stress required to overcome pinning obstacles—e.g., existing interface dislocations with average spacing $S$. For the cool/backward mode, the pinning stress opposes the backward motion and thus has the reverse sign.

Estimates of the pinning stress and average line energy are provided by applying Equation (44) to the difference in stress $\sigma_{\text{Cu, forward}} = 690 \pm 24$ MPa at point H6 vs. $\sigma_{\text{Cu, reverse}} = 609 \pm 15$ MPa at point C1 (Figure 54b). The unloading is elastic, suggesting there is a difference in stress to move the same dislocation structure in the forward vs. backward direction. An estimate $\sigma_{\text{Cu, pin}} = 41 \pm 20$ MPa is calculated using $\sigma_{\text{Cu, pin}} = 0.5(\sigma_{\text{Cu, forward}} - \sigma_{\text{Cu, reverse}})$ from Equation (44). Similarly, an estimate $w_{\text{Cu}} = 0.85 \pm 0.03$ nJ/m is obtained using $w = 0.25b \epsilon h(\sigma_{\text{Cu, forward}} + \sigma_{\text{Cu, backward}})$ from Equation (44), with $b_{\epsilon<101>/2} = 0.125$ nm (averaged between Cu and Ni) and layer thickness $h = 21$ nm. Thus, $w_{\text{Cu}}$ is smaller than typical estimates of bulk line energy $0.5C_{44,Cu}b^2 = 2.4$ nJ/m [135]. This is consistent with the belief that interfaces lower dislocation line energy, thereby trapping the dislocation [244].

The trends in pinning strength and line energy during heating and cooling are complicated by the interplay between temperature and interfacial dislocation density. During heating, interfacial dislocation density $\rho_{\text{interface}}$ is estimated to increase by 22%
(Figure 55), corresponding to a decrease in average misfit dislocation spacing S from 41 to 34\(b_c\). During the process, the Cu flow stress increases by 180 MPa (35\%), despite potential softening induced by the temperature increase. During cooling, reverse flow occurs incrementally over a \(~300\) MPa decrease in |\(\sigma_{\text{Cu}}\)|, Figure 54(b). Similar trends are observed in electrodeposited nanocrystalline Ni and are attributed to a wide grain-to-grain distribution in critical stress for slip [245]. In the context of Figure 54(b), the large increase in |\(\sigma_{\text{Cu}}\)| upon heating may reflect that regions with favorable values of residual stress or relatively low threshold stress for slip are able to deform initially, thus redistributing stress to less favorable regions. Similarly, the unloading region with a decrease in |\(\sigma_{\text{Cu}}\)| may reflect a wide distribution of internal stress and critical threshold for reverse motion.

The corresponding trends for Ni show that during heating/unloading, show no reverse plasticity. This implies a large resistance to reverse plasticity (\(\sigma_{\text{Ni, pin}}\)), which is estimated using the form of Equation (44) to be \(\sigma_{\text{Ni, pin}} > 0.5(\sigma_{\text{Ni,25°C}} - \sigma_{\text{Ni,325°C}}) \sim 340\) MPa. During cooling/reloading, it is remarkable that Ni readily undergoes forward yield, without any prior reverse yield. A hypothesis is that the increase in interfacial dislocation density (\(\rho_{\text{interface}}\)) during heating has introduced new sources that readily operate upon reloading. Thus, heating appears to work harden Cu layers but soften Ni layers.
5.3 Summary and Conclusions

To summarize, this work extends the use of heated in-plane x-ray diffraction to investigate constituent deformation behavior in nanolayered composite films. The Cu-10/Ni-10 nm multilayer with more coherent interfaces displayed negligible plastic deformation even though $\sigma_{ip, Ni} \sim 2.9$ GPa and $\sigma_{ip, Cu} \sim 1.8$ GPa was achieved during heating/cooling. The Cu-20/Ni-20 nm case with semicoherent interfaces did plastically deform, revealing peculiar features:

- Enhanced reverse yielding in Cu layers, where reverse plastic flow occurs without changing the sign of average stress in Cu layers;
- Large changes in flow stress, $\Delta \sigma_{ip, Ni} = 500$ MPa and $\Delta \sigma_{ip, Cu} = 200-400$ MPa, during initial forward vs. reverse yield. This feature is interpreted in terms of a large spatial distribution in residual and/or critical stress for confined layer slip within layers;
- Estimate of line energy $\sim 0.8$ nJ/m for dislocations deposited at [001] Cu/Ni interfaces during fully plastic flow. This estimate is $\sim 1/3$ typical line energy estimates ($\frac{1}{2}C_{44,Cu}b^2$) for bulk Cu, suggesting that on average, dislocations may be readily attracted to [001] Cu/Ni interfaces;
Chapter 6: Method Assessment and Comparisons

Access to individual constituent strengths allows for comparisons between nanolayered composites of various layer thicknesses and constituent materials revealing how interfaces control strength. In this chapter, the Cu and Ni strengths extracted from Cu-20/Ni-20 nm films using the indentation-based method and the diffraction-based method are compared to the strength of monolithic Cu and Ni thin films, nanocrystalline Cu and Ni as well as single crystal Cu and Ni nanowires. Comparison of nanolayered composite strength to monolithic films is most common but neglects scale dependent strengthening making them difficult to interpret. Instead, by comparing layer constituent strengths to nanocrystalline Cu and Ni at the same size scale insight into the barrier strength of homophase grain boundaries vs. heterophase interfaces is provided. Finally, comparisons with single crystal nanowires expound on the relative strengthening derived from abundant source, limited propagation case of heterophase interfaces vs. limited source, unrestricted propagation case of single crystal nanowires.

6.1 Layer Strength vs. Monolithic Films

In an effort to exemplify the high strength of nanolayered composites, measured hardness is often compared to the hardness of monolithic thin films made of the same constituents. For example, Lui et al. [48] compares the hardness of the Cu/Ni nanolayered
composites to monolithic Cu and Ni, pointing out that the peak hardness (over a range of layer thicknesses) in the Cu/Ni nanolayered composite is greater than both the Cu and Ni monolithic films. Similar observations have been made in Cu/Co [246] and Cu/Ag [85]. However, these comparisons cannot be treated quantitatively because they are not at a consistent size scale—the monolithic films are on the same size scale as the entire nanolayered composite film, approximately 1-5 μm. The thickness of the monolithic films is need to be on the order of μm because true hardness values of monolithic films on the scale of 10’s of nm would indentation depths below the capabilities of current nanoindentation equipment.

6.2 Layer Strength vs. Nanocrystalline Strength

The individual constituent strengths extracted using the indentation and diffraction-based methods are compared to the strength of pure nanocrystalline Cu and Ni which has been determined in two ways. The first is by extrapolating Hall-Petch scaling behavior down to grain sizes of 20 nm using Hall-Petch scaling coefficients derived from tests on micro-grained samples and provided in Table 6. The second is by converting the hardness of nanocrystalline Cu [189] and Ni [190] to uniaxial flow strength using appropriate Tabor factors determine from finite element indentation simulations [173]. It should be noted, however, that indentation strain rates were not reported for Cu or Ni in these studies. If normal indentation strain rates, $\dot{\varepsilon}_{\text{ind}} \approx 0.025$ and rate sensitivities on the upper end of the expected range, $m_{\text{ind}} \approx 0.04$ [198] are assumed, then the strengths reported here could be as much as 300 MPa too high.
**Table 6:** Coefficients for Hall-Petch scaling behavior in bulk Cu and Ni

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<th></th>
<th>$\sigma_0$ (MPa)</th>
<th>$k_{HP}$ (MPa $\cdot$ m$^{1/2}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>25</td>
<td>0.112</td>
<td>[222]</td>
</tr>
<tr>
<td>Ni</td>
<td>11.2</td>
<td>0.371</td>
<td>[209]</td>
</tr>
</tbody>
</table>

Good agreement between the extracted layer strengths and the strength of pure nanocrystalline Cu and Ni is observed, **Figure 56**, with the exception of Ni determined using the diffraction-based method. During the diffraction-based method, the Cu-20/Ni-20 nm film is initially strained in compression, and because the Ni layers were initially in tension, it is not clear if the Ni layers were at yield at the reported stress. In contrast, the indentation-based and the nanocrystalline strength correspond to well-developed yield stresses (stress at ~8% strain).
The strength measured using the diffraction-based method requires further elaborating. The strength reported for Cu is the peak strength during straining, occurring at a temperature of 275°C. The equivalent stress at room temperature is ~200 MPa larger assuming the temperature dependence of bulk Cu [247] (shown by the shaded box in Figure 56). Furthermore, using the diffraction-based method, strength is probed in the plane of the film, while in indentation, the direction of loading is normal to layers.
While it is common to see reports of nanolayered composites exhibiting strengths far exceeding the strength of either constituent, these statements are often based on comparisons between nanolayered composites and monolithic films where the size scale—which controls strength—is much different. In contrast, the strengths here are compared at the same size scale, and the observed agreement suggests that the strengthening behavior due to heterophase Cu/Ni interfaces is inherently similar to homophase grain boundaries in single-phase Cu and Ni.

Although there is agreement at 20 nm for Cu and Ni, the indentation-based and diffraction-based methods need to be extended to additional layer thicknesses and new composite systems to determine if the relative strength of heterophase interfaces and homophase grain boundaries is dependent on layer thickness and interface type of the nanolayered composites.

6.3 Propagation Limited Layers vs. Source Limited Nanowires

When a large number of interfaces exist, dislocation sources are abundant but dislocation propagation is limited. High strength can be achieved with a high density of interfaces (or grain boundaries) as evidenced by nanolayered composites and nanocrystalline materials. In contrast, high strength can also be achieved in single crystal materials where dislocation sources are limited but dislocation propagation is unrestricted. To compare the relative strengthening that is achievable for these two cases,
the Cu and Ni strengths extracted from the Cu-20/Ni-20 nm nanolayered composite are compared to the strength of single-crystal Cu and Ni nanowires.

A peak tensile stress of 6.5 GPa was observed in 75 nm diameter Cu ~defect-free nanowires [248], nearly an order of magnitude larger than those reported in Figure 56, and approaching the theoretical strength of Cu. This discrepancy suggests that the source limited case, where nucleation of dislocations is difficult, requires significantly higher stresses to cause plastic deformation than the abundant source, propagation limited nanolayered composite case.

Although Ni nanowire experiments have also been performed, peak stresses reach only 2.5 GPa for 100 nm diameter wires [249], much lower than the theoretical strength of Ni, and on the order of Ni in nanolayered composites. The low nanowire strength was attributed to the dominance of crack initiation over dislocation activity [249]. In agreement with theoretical strengths however, Molecular Dynamics simulations suggest that defect-free Ni nanowires are expected to have even higher peak stresses than Cu nanowires [250]. In summary, the strength of source limited single-crystal nanowires are expected to withstand significantly higher stress prior to plastic deformation than the abundant source, propagation limited nanolayered composites.
Chapter 7: Outcomes and Future Directions

7.1 Primary Outcomes

The primary outcomes of this work are two new methods that can be used to determine individual constituent strengths in nanolayered composites. The methods are complimentary. The first, the indentation-based method, couples finite element indentation simulations with experimental nanoindentation and micropillar compression. The indentation-based method can be applied to all types of nanolayered composites including non-crystalline systems. The second, the diffraction-based method, uses heated x-ray diffraction and provides useful external verification of the first method. Although the diffraction-based method is limited to crystalline systems on substrates, when it can be utilized, it provides unique information about the evolution of stress within the individual constituent. As elaborated in this thesis, the access to individual constituent strengths provides new insight into the role of interface strengthening and how to optimize it.

The key observation that enables use of the indentation-based method is that the Tabor factor—hardness/uniaxial flow strength—decreases with increasing disparity in constituent strengths. Thus, hardness is maximized in systems with similar individual constituent strengths. The dependence on constituent strength, in addition to the observed
decrease in the Tabor factor in higher strength materials (small $E/\sigma_y$) and those with residual in-plane stress, however, draws into question the common use of a constant Tabor factor equal to 2.7. Since the individual constituent strengths, the average uniaxial strength, and the in-plane residual stress can all change with layer thickness and with the constituent material-type, comparisons across a range of layer thickness and between composite systems based on hardness testing can contain large errors. Finite element simulations support the use of a Tabor factor equal to 2.7 only to estimate the minimum uniaxial strength from hardness measurements; but determination of accurate uniaxial strengths still requires uniaxial testing.

Both the indentation and the diffraction-based methods are applied to the Cu-20/Ni-20 nm system. Application of the indentation-based method reveals a constituent strength ratio of 3 in the Cu-20/Ni-20 nm system. It also indicates that the experimentally measured Tabor factor can be overestimated by as much as 20% when using hardness and uniaxial flow strength that are not determined at the same strain rate because of large strain rate sensitivities. Moreover, if strain rate sensitivity changes with layer thickness and constituent phases, comparisons across layer thickness between composite systems comparisons could be heavily influenced by the strain rate at which testing was performed. Furthermore, accurate comparison of experimental and computational hardness measurements requires direct measurement of contact area when pile-up is present.
Application of the diffraction-based method to Cu-20/Ni-20 nm divulges a number of peculiar features including: reverse yielding, work hardening on the order of half the elastic modulus ($E/2$), and evidence that plastic flow in Cu layers facilitates flow in the Ni layers. When layer thickness is reduced to 10 nm (Cu-10/Ni-10 nm), interfaces become coherent and elastically accommodate the deformation imposed by the thermal expansion differences between the film and the substrate. Cu-10/Ni-10 nm shows thermal stability up to 325°C for >1 hr.

The strength of the indentation and diffraction-based methods is the ability to compare extracted constituent strengths to other interface types. Here Cu and Ni layer strengths are compared to single phase, nanocrystalline, and single crystal nanowire Cu and Ni strengths, thereby elucidating the relative magnitude of interface strengthening. Cu and Ni strengths in the Cu-20/Ni-20 nm are comparable to the strength of 20 nm, nanocrystalline Cu and Ni, suggesting that—in this specific case—homophase grain boundaries and heterophase interfaces provide a similar barrier to dislocation transmission. However, defect-free single crystal Cu nanowires can sustain an order of magnitude higher stresses because dislocation sources are not as abundant as in nanolayered and nanocrystalline materials; instead, dislocations must be nucleated. The outlined methods allow for the quantification of interface strength which can facilitate purposeful interface design and optimization.
7.2 Future Directions

A key future direction is the extension of both methods to new nanolayered composite systems. Extension to Cu-20/Nb-20 nm for example can clarify how the barrier strength of opaque Cu/Nb interfaces compares to transparent Cu/Ni interfaces. Additionally, a range of layer thicknesses can be investigated to refine strength vs. layer thickness relationships, and examine how interface strength scales with layer thickness. Application of the indentation-based method to metal/metallic glass systems could provide unique insights into the heavily debated size-scale dependence of metallic glasses, and explore strength in confined layer where shear band formation is inhibited.

Replacing micropillar compression testing with additional indentation testing would not only decrease cost required for implementing the indentation-based method, but it would also significantly increase throughput. Currently, micropillar compression provides the average uniaxial strength while indentation testing provides hardness, but indentation testing conveys additional unused information including the load-displacement curve. This leaves indentation testing under-utilized. Reverse indentation analysis, that is, the estimation of flow strengths using the indentation load-displacement curve, has been successfully demonstrated in Aluminum alloys [173] as well as plastically-graded materials [251,252]. Coupling of simulated and experimental load-displacement curves provide enough material information to replace micropillar compression testing. Standard Berkovich indentation could also be supplemented by additional sharp [172,253] or spherical indenters [254].
Refinements including interfacial shear strength, plastic anisotropy, and extension to 3D can be made to the indentation finite element model. Currently, the model enforces compatibility at interfaces, and yet evidence suggests that interfacial shear strength may be low in some nanolayered composite systems [116]. Interfacial shear strength can be modeled by imposing varying degrees of friction at the interface [116]. It is also likely that layers are plastically anisotropic. Dislocation motion parallel to the interfaces (in-plane) should be much easier than dislocation motion normal to the interfaces potentially leading to large plastic anisotropy. Aspects of plastic anisotropy can be investigated by incorporating an anisotropic yield criterion such as the quadratic Hill yield criteria [255], or crystal plasticity into the finite element modeling. Finally, deviation in contact area calculated using a pyramidal indenter and a conical indenter suggests that a 3D finite element model may be required for accurate contact area determination and comparison with experiments [256].

The diffraction-based method can be adapted to incorporate multiple heating/cooling cycles or cooling/heating cycles. To this point, the diffraction-based method has only been applied to a single heating/cooling cycle, but additional stress evolution information could be gained through use of multiple heating/cooling cycles as illustrated by experiments in monolithic Cu and Ni thin film experiments [212,216]. Using a cryogenic stage [257] to perform a cooling/heating thermal cycle, where the film is cooled below room temperature before being heated back to room temperature, would
enable one to monitor stress evolution while the film is strained in tension. Additionally, concerns of interdiffusion would be minimized.

In the present work, a lab source x-ray diffractometer with a point detector was used, limiting the number and resolution of diffraction peaks that can be monitored. If instead, a synchrotron x-ray source with an area detector is utilized, full diffraction rings can be monitored continuously [60,258]. As a result of the high flux synchrotron source exposure time can be reduced, allowing for better temperature resolution [259], and tilting experiments which can provide estimation of stress-free lattice parameters [258] which, as a function of temperature, convey the thermal expansion coefficients of the individual constituent. Not only will this work provide direct measurement of thermal expansion coefficients which can bring clarity to the debate on their dependence on size-scale and confinement, but it can develop rigorous guidelines for optimizing material properties by controlling interfaces.
Appendix A: Extension to Cu/PdSi Nanolayered Composites

The indentation-based offers a novel way to examine the size-scale and confinement dependent strength of amorphous metallic glass materials. The indentation-based method has been applied to crystalline Cu/amorphous Pd$_{0.77}$Si$_{0.23}$ (Cu/PdSi) nanolayered composites. Previous work on the same samples by Knorr et al. [10] estimated Cu layer strengths on the order of 2 GPa by performing micropillar compression tests on a range of layer thicknesses and volume fractions. However, estimation required the assumptions that the strength of PdSi was scale independent and unchanged by the confinement of Cu layers. The indentation-based method allows testing of those assumptions.

Uniaxial flow strength and hardness is already available for Cu/PdSi nanolayered composites [10]. Application of the indentation-based method therefore only requires measurement of in-plane stress and strain rate-sensitivity as described here.

A.1 In-plane Residual Stress

X-ray diffraction indicates Cu exhibits a strong (111) texture normal to the film surface while no distinct peak for the amorphous PdSi layers was observed consistent with previous reports [10,260]. In-plane residual stress in the Cu layers was determined
using the $\sin^2\psi$-method, paralleling work done on other (111)-textured nanolayered composites [15,53]. Lattice parameter measurements from the Cu-20/PdSi-20 nm film for different \{hkl\} planes (at the same $\phi$ angle) are given in Figure 57.

![Figure 57: Lattice parameters of Cu in a Cu-20/PdSi-20 nm layered composite from measured \{hkl\} interplanar spacings for analysis using the sin$^2$ψ-method.](image)

In-plane residual stress is determined by the slope of the linear fit to the measured \{hkl\} planes. Assuming a biaxial stress state and Reuss (isostress) average elastic properties:

$$a_\psi = \left( \frac{2S_{11} + 4S_{12} - S_{44}}{3} + \frac{S_{44}}{2} \sin^2 \psi \right) \sigma_\psi a_0 + a_0$$ \hspace{1cm} (45)
The resulting in-plane residual is compressive $\sigma_{ip} = -390$ MPa. Note that the $\sin^2\psi$-method is used here instead of the direct in-plane ($\psi \approx 90^\circ$) because the $\sin^2\psi$-method is much less sensitive to the stress-free lattice parameter. The stress-free lattice parameter can be calculated by first setting $\sigma_{ip} = 0$ in Equation (45) to calculate a stress-free angle $\psi_0$:

$$
\sin^2 \psi_0 = \frac{-4S_{11} - 8S_{12} + 2S_{44}}{3S_{44}}
$$

(46)

Then, the stress-free angle $\psi_0$ is inserted in the linear fit equation to calculate the stress-free lattice parameter $a_0$. For Cu-20/PdSi-20 nm, $a_0 = 3.620$ nm. In-plane stress and stress-free lattice parameter were also calculated for Cu-90/PdSi-90 nm and are provided in Table 7.

<table>
<thead>
<tr>
<th>$\sigma_{ip, Cu}$</th>
<th>$a_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(MPa)</td>
<td>(Å)</td>
</tr>
<tr>
<td>Cu-20/PdSi-20 nm</td>
<td>-390</td>
</tr>
<tr>
<td>Cu-90/PdSi-90 nm</td>
<td>-177</td>
</tr>
</tbody>
</table>

Table 7: In-plane residual stress $\sigma_{ip}$ in the Cu layers and stress free lattice parameter $a_0$ for Cu in Cu/PdSi films determined using the $\sin^2\psi$-method.
A.2 Strain Rate Sensitivity

Strain rate sensitivity of the Cu-20/PdSi-20 nm film was determined using the same constant rate method described in Section 4.5.2. Indentation tests were performed at constant $\dot{\epsilon}_{\text{ind}}$ spanning $10^{-4}$ /s to $10^{-2}$ /s limited to a maximum load of 30 mN ($h_{\text{max}} \approx 500$ nm). A constant $E = 118$ GPa, consistent with the $E$ measured at $\dot{\epsilon}_{\text{ind}} = 0.025$ /s [10] was assumed to calculate a drift-insensitive contact area $A_E$. The resulting hardness $H$ is plotted as $\ln(H)$ vs. $\ln(\dot{\epsilon}_{\text{ind}})$ following Equation (33) to calculate strain rate sensitivity, $m_{\text{ind}}$ in Figure 58. For Cu-20/PdSi-20 nm, $m_{\text{ind}} = 0.008\pm0.001$, therefore $< 3\%$ error is introduced by calculating the Tabor factor using uniaxial strength from micropillar compression at $\dot{\epsilon} = 0.001$ /s and hardness at $\dot{\epsilon}_{\text{ind}} = 0.025$ /s as reported in Ref. [10].
Figure 58: Indentation strain rate sensitivity for Cu-20/PdSi-20 nm using the constant indentation strain rate test method. Values are the average of 5 indents, error bars representing the standard deviation in $\ln(H)$ between tests are smaller than the data points.

A.3 Extraction of Constituent Strengths

As done for Cu-20/Ni-20 nm in Chapter 4, the in-plane residual stress state, uniaxial strength, elastic modulus, and hardness (at the same strain rate used for determination of uniaxial strength) are used to estimate individual constituent strengths through comparison with the parametric finite element analysis from Chapter 3. For reference, the experimental results are provided in Table 8.
Table 8: Experimentally determined in-plane residual stress $\sigma_{\text{ip}}$, uniaxial strength $\sigma_y$ (at $\varepsilon = 8\%$ from [10]), elastic modulus $E$, and hardness $H$ for Cu-20/PdSi-20 nm.

<table>
<thead>
<tr>
<th></th>
<th>$\sigma_{\text{ip}}$</th>
<th>$\sigma_y$ (at $\varepsilon = 8%$)</th>
<th>$E$</th>
<th>$H$</th>
<th>$H$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(MPa)</td>
<td>(MPa)</td>
<td>(GPa)</td>
<td>(GPa)</td>
<td>(GPa)</td>
</tr>
<tr>
<td>Cu-20/PdSi-20 nm</td>
<td>$390 \pm 22$</td>
<td>$2140 \pm 30$</td>
<td>$118 \pm 3$</td>
<td>$4.17 \pm 0.1$</td>
<td>$4.06 \pm 0.1$</td>
</tr>
</tbody>
</table>

Note: $\sigma_{\text{ip}}$ is only measured in the Cu layers

First, the computational results for Tabor factor as function of elastic ratio and constituent strength ratio (Figure 25) are shifted to include the effect of the compressive in-plane residual stress, $\sigma_{\text{ip}}/\sigma_y = -0.20$ measured in the Cu layers, Figure 59. The experimental data point for Cu-20/PdSi-20 nm can be added to Figure 59 by calculating the experimental elastic ratio, $E/\sigma_y = 55$ and Tabor factor, $H/\sigma_y = 1.90$ using Table 4.
Figure 59: Computationally determined Tabor factor as a function of $E/\sigma_y$ and constituent strength ratios. Plotting experimental results for Cu-20/PdSi-20 nm allows extraction of a constituent strength ratio equal to 5.

The location of the experimental data point in Figure 59 suggests that Cu and PdSi in the Cu-20/PdSi-20 nm nanolayered composite have a strength ratio of ~5. Assuming that PdSi is stronger than Cu, and using the average uniaxial strength determined from micropillar compression testing, the individual Cu and PdSi strengths can be estimated as $\sigma_{Cu} = 710$ MPa and $\sigma_{PdSi} = 3570$ MPa respectively. These values assume that the in-plane residual stress in Cu is equal to the average in-plane residual stress (i.e. PdSi is equally stressed). If instead the film is assumed to be stress-free (i.e. if PdSi is strained in tension) the constituent strength ratio is ~4 and Cu and PdSi strengths are $\sigma_{Cu} = 860$ MPa and $\sigma_{PdSi} = 3420$ MPa. Substrate measurements would be better suited to determine residual stress of the film since it is not limited to crystalline systems [69].
The strength of PdSi estimated using the indentation-based method is much larger than predicted in micropillar compression tests (1.5 – 2 GPa) although the layers are much smaller than the tested pillars [261]. The strength of PdSi may be increased in confinement due to the suppression of shear bands. Interestingly, however, the strength of Cu is comparable to the strength of Cu extracted from Cu-20/Ni-20 nm films.
References


40. Birkholz M. Thin Film Analysis by X-Ray Scattering. Wiley; 2005.


204. Maier V, Merle B, Göken M, Durst K. An improved long-term nanoindentation creep testing approach for studying the local deformation processes in


228. Chang C-A. Formation of copper silicides from Cu(100)/Si(100) and Cu(111)/Si(111) structures. Journal of Applied Physics. 1990 Jan;67:566–569.


