MULTISCALE MODELLING AND SIMULATION OF DEFORMATION AND STRENGTH OF NANOSCALE METALLIC MULTILAYER SYSTEMS

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Abstract

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The objective of this research is to investigate the deformation behaviors of two types of NMMs at lower length scales: 1) One dimensional Cu-Ni, Au-Ni nanowires with coherent interfaces and 2) Two dimensional Cu-Nb multilayers with incoherent interfaces.

Using molecular dynamics simulations, different deformation mechanisms governing plastic behavior of the NMMs at lower length scales are investigated. Based on the fundamental physics of deformation captured by these simulations, we propose models that explain the dependence of strength on layer thickness and identify the regions where the deformation is controlled by either dislocation propagation mechanism or dislocation nucleation mechanism.

Deformation mechanisms of Cu-Ni composite nanowires subjected to uniaxial tensile loading are studied using MD simulations. The coupled effects of geometry and coherent interface on the twinning and pseudoelastic behavior of nanowires are investigated. It is shown that nanowires exhibit pseudoelastic behaviors when their layer thicknesses are below a critical thickness. Similar deformation mechanisms are captured through MD simulations of Au-Ni nanoligaments that are assumed as building blocks of composite Au nanofoams with Ni shells.
Deformation behaviour of Cu-Nb NMMs with incoherent interfaces are investigated using MD simulations and the strengthening effect of the weak interfaces interacting with glide dislocations are studied by embedding artificial dislocations inside the layer. In addition, the effects of interfacial discontinuities such as ledges and steps on the strength of the NMMs are investigated.

Next, the strengthening effects of the additional second phase particles inside the same Cu-Nb bi-layers are explored and an analytical model is developed to explain the strengthening effect of the precipitates. The theoretical results show a qualitative agreement with the finding of the atomistic simulations.

In addition, the operative deformation mechanisms are determined at different length scales for Cu-Nb multilayers under biaxial tensile deformation. A unique viscoplastic continuum model is established able to address the macroscale plastic behaviour of bulk NMMs with layer thickness from few nanometers to hundreds of micrometers. An anisotropic yield function is proposed based on the plastic flow potential obtained from biaxial loading of the NMMs.
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Dedication

This dissertation is dedicated to my

Father Goodarz Abdolrahim

Mother Giti Afroozian

Husband Hesam Askari

Brother Koosha Abdolrahim

for always being there for me.
CHAPTER ONE: INTRODUCTION

Nanoscale metallic multilayers (NMM) exhibit very high strength approaching a fraction of the theoretical limit. Their superior properties such as high ductility, morphological stability, radiation damage tolerance, and unusually high fatigue resistance, make them uniquely multifunctional materials. Understanding the deformation mechanisms of such structures and dependency of their behavior on different parameters such as interface structure, chemical composition and morphology, as well as to the underlying dislocation mechanisms, is critical in designing such nanocomposites with desired properties for various applications.

Depending on the geometry of the NMMs, i.e. one or two-dimensional systems, NMMs exhibit completely different mechanical behavior during plastic deformation. Nanowires and nanopillars are one-dimensional systems while thin films are two-dimensional NMMs. Chapters 2 and 3 of this research study the deformation behaviors of nanowires and nanopillars while chapters 4-6 investigate the deformation behaviors of two-dimensional thin films.

Interfaces compose a considerable volume ratio of NMMs and play an important role on defining the deformation mechanism of the multilayers. NMMs can be classified in to two types of interfaces: coherent and incoherent. Coherent interfaces can be fundamentally defined as interfaces between two layers of materials with the same crystallographic structure, but in which there exists a small lattice mismatch that leads to a very strong interface with high coherent stresses. The slip systems are nearly continuous in coherent interfaces, and there is no discontinuity between slip directions of two layers; therefore, dislocations can pass from one layer to another through the coherent or so-called transparent interfaces. High coherency stresses are the barriers that dislocations need to overcome to transmit to the other layers. Incoherent interfaces on the other hand are defined as the interfaces between layers of
different lattice structures or with high lattice mismatch. There is no continuity between the slip systems of the adjacent layers through incoherent or opaque interfaces. These interfaces act as a barrier for slip transmission and entrap approaching dislocations. During loading, an incoherent interface shears easily and attracts gliding dislocations because of its low shear strength relative to the layers. Interacting with interface, dislocations dissociate and create disconnections\(^9\text{-}^{12}\) at the interface. Chapters 2 and 3 study the strengthening effect of the coherent interfaces in fcc-fcc multilayers, while chapters 4 to 6 look at the strengthening effects of the incoherent interfaces in the fcc-bcc multilayers. In addition, the effect of interfacial disconnection and chemical impurities close to interface are being discussed.

Another key parameter in defining deformation behaviors of NMMs is the thickness of the layers. NMMs with various layer thicknesses exhibit fundamentally different deformation behaviors under similar loading conditions. At higher scales, when the thicknesses of layers of NMMs are varied from microns to hundreds of nanometers, the density of dislocations increases rapidly once deformation starts, due to double cross slip and other Frank-Read type multiplication processes. Dislocations pile up at the interfaces or close to internal grain boundaries and it is shown from experimental results that the Hall-Petch relation well describes the strengthening behavior of the NMMs at these length scales:

\[
\sigma_{ys} = \sigma_0 + \frac{k}{\sqrt{h}} \tag{1}
\]

where \(\sigma_{ys}\) is the yield strength, \(h\) is the layer thickness, \(k\) is the Hall-Petch slope and \(\sigma_0\) is the lattice friction to slip. At lower length scales when the layer thicknesses vary to the scale of tens of nanometers, there is no possibility for dislocations to pile up at the interface due to the
restrictive thickness of the nanoscale layers. Then the flow strength of the nanomaterials deviates from the Hall-Petch relation. Misra et al.\textsuperscript{13} showed that at these length scales plastic flow of NMMs features glide of single Orowan-type loops in one layer bounded by two interfaces. Misra et al.\textsuperscript{13} and Akasheh et al.\textsuperscript{14,15} suggested the following model for the confined layer slip (CLS) regime:

$$
\sigma_{cls} = M \frac{\mu b}{8\pi h \left(\frac{4-v}{1-v}\right)} \left[ \ln \frac{\alpha h}{b} \right] - \frac{f}{h} + \frac{C}{\lambda}, \text{ with } C = \frac{\mu b}{(1-v)} \tag{2}
$$

where, $b$ is the burgers vector, $h$ the layer thickness, $\alpha$ is a constant representing the core cutoff parameter and $f$ is a term accounting for the interface stress and is given as the gradient of the interfacial energy ($E_i$) with respect to strain ($\varepsilon$), i.e. $f = E_i + \frac{dE_i}{d\varepsilon}$, and $\lambda$ is the spacing between the interfacial dislocations.

In smaller volumes and as the thickness of layers decreases to less than several nanometers, the volume of the interfaces grows, dislocations annihilate at free surfaces or interfaces, which can lead to dislocation starvation in the bulk. It is also possible that in small-volume materials, the initial configuration does not contain a single dislocation in it. Under these dislocation-starved scenarios, dislocation nucleation is expected to be an important factor in controlling plastic deformation of small-volume materials at low temperature. Less works have been published addressing the governing deformation mechanisms at these small length scales. Chapter 6 looks at dislocation activities of NMMs with very small layer thicknesses of 2~3nm and compares the deformation mechanisms with that of NMMs with larger layer thicknesses. Constitutive equations are developed based on the proposed mechanisms.
The main goal of this research is to study the deformation behaviors in NMMs in physical details using MD simulations and discover the controlling deformation mechanisms of NMMs with different geometries and type of interfaces and with varying layer thicknesses. These deformation mechanisms are either relevant to previously proposed mechanisms or completely new deformation mechanisms not yet suggested in the literature. In addition, predictive models are developed based on the simulation results for general applications that would facilitate the design and analysis of bulk NMMs. This thesis pursues two main objectives as following:

1) Study the deformation behavior of Cu-Ni composite nanowires and the combined effect of coherent interfaces, layer dimensions, and temperature on the competition between slip and twinning deformation mechanisms.

2) Study the deformation behavior of Cu-Nb multilayers and the effect of incoherent interfaces and their chemistry and imperfections, on the governing deformation mechanisms of NMMs with incoherent interfaces.

Metallic nanowires such as Cu, Ni and Au with cross sectional diameters of less than a critical value have a very unique ability of recovering from severe deformations, up to 50% strains, in a very short response time without inducing residual deformation. This behavior is attributed to the high twinnability that these materials exhibit among the fcc metals\textsuperscript{16, 17}. There is a special need to increase the critical dimensions below which these nanowires show pseudoelastic behavior. Tadmor and Hai\textsuperscript{18} developed a criterion for nanocrystalline materials in general for the onset of deformation twinning which quantifies the competition between slip and twinning. The related twinability is given by

\[
\tau_a = \left[ 1.136 - 0.151 \frac{\gamma_{sf}}{\gamma_{ss}} \right] \sqrt{\frac{\gamma_{ss}}{\gamma_{ut}}} \quad (3)
\]
where $\gamma_{sf}$ is the stable stacking fault energy, $\gamma_{us}$ is the unstable stacking fault energy, and $\gamma_{ut}$ is the unstable twinning energy. Although the proposed parameter shows good agreement with the results from experiments in general, it is missing the effect of main parameters such as size and temperature on the twinning behaviors of nanowires.

Performing a large number of MD simulations, we investigated all the parameters that could affect the pseudoelasticity of nanowires including geometrical parameters (such as size, aspect ratio, and cross sectional shape), temperature and strain rate effects. Based on the simulations, we developed a clear understanding of the critical surface to volume ratio that affect the overall behavior of such materials, and designed pseudoelastic composite Cu-Ni nanowires in which the critical thickness of each layer is below the critical value. We showed that due to restrictive thickness of each layer, trailing dislocations and consequently full slip can never happen in the sub layers, while the coherent interfaces between layers make the leading partials in all layers to be coherent. This, in turn, leads to high twinnability and much larger pseudoelastic composite nanowires with multiple numbers of layers compared to single crystalline nanowires. The resulting multilayer nanowires not only can recover from high plastic strains but also show higher yield strengths and better ductility than single crystalline nanowires. Chapters 2 and 3 suggest deformation mechanism maps for composite nanowires and nanoligament of foam structures that accounts for the effect of temperature and size of the individual layers and interfacial effects. The simulation results are compared with experimental results that verifies the proposed deformation mechanisms.

Cu-Nb thin films with incoherent interfaces on the other hand exhibit completely different mechanical behavior than nanowires with coherent interfaces. Several atomistic and experimental studies have addressed the deformation behavior of these kinds of materials, the
effect of the incoherent interfaces on their strengthening behavior, and the interaction of
dislocations with the interfaces. Wang et al\textsuperscript{5, 6} studied the interactions of dislocations with
incoherent interfaces using atomistic simulations. They showed that incoherent interfaces are
very weak in shear, and act as dislocations sinks, resulting in the shearing of the interface. The
results from their simulations indicate that the shear resistance of the Cu-Nb interfaces is: “1)
lower than the theoretical estimations for shear strength for perfect crystals, 2) strongly
anisotropic, 3) spatially non-uniform, and 4) strongly dependent on the atomic structures of
interfaces”. In another work Wang et al\textsuperscript{19} investigated the effect of the temperature on the
interaction of the dislocations and incoherent interface and showed that dislocations could climb
in metallic interfaces at higher temperatures. Dislocation climbs aid the slip transmission from
the interface. Reactions between interfacial dislocations assisted by climb could lead to
annihilation of dislocation content (recovery) and the absorption of discrete pileups in to the
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researches on multilayers, much more investigations need to be performed to fully understand
the strengthening effect of the interfaces. It is yet essential to study the effect of varied interfacial
geometry such as existence of steps and ledges at the interfaces. Chemical composition of the
interface can change its mechanical behavior considerably. Impurities such as oxygen atoms can
be introduced at or close to the interface intentionally or unintentionally during the deposition of
the films. Precipitates of the second phase atoms inside the layers can also affect the interaction
behavior of the dislocations inside the layers with the interfaces. These are all parameters that
have not been fully understood and more numerical simulations are needed to be preformed to
find out their effects on the mechanical behaviors of NMMs. Chapters 3-6 study the mechanical
behaviors of thin films with incoherent interfaces and explore the strengthening effects of the aforementioned parameters.

Experiments and atomistic simulations, although may be expensive and time consuming, can provide important insight on the deformation behavior of nanoscale materials. However, it is also important to be able to express the mechanical behavior of the NMMs in the form of general mathematical models applicable in multiscale modeling of these kinds of materials.

Next step is to develop a multiscale physics based model for determining the plastic behavior of nanoscale metallic multilayers. Most of the current models are built upon phenomenological constitutive equations, which result from assumptions on certain deformation mechanisms derived from limited empirical data. The main issue with these models is the lack of ability to identify the fundamental physics associated with the deformation behavior of NMMs at nanoscales that arise from dislocation motions in small volume. The molecular dynamics (MD) method is a very powerful tool that allows us to capture the operating deformation mechanisms of dislocations at very tiny scales. However, improved multiscale modeling techniques are yet needed that can bridge the information between different material length scales. The results of MD simulations determine the operative deformation mechanisms at different length scales for Cu-Nb multilayers under biaxial tensile deformation. Chapter 6 discusses the difference between deformation mechanisms for varying layer thicknesses. Building on the fundamental physics of deformation as exposed by MD simulations, we established a unique viscoplastic continuum model able to address the macroscale plastic behavior of bulk NMMs with layer thickness from few nanometers to hundreds of micrometers. By applying biaxial in-plane loadings with varying loading ratios, we obtained the plastic flow potential and proposed an anisotropic yield function specific to NMMs. Overall, the state-of-the-art in this study is to bridge the gap between the
scales by developing multiscale material models coupling MD results with crystal plasticity and continuum theories and verify the models by developing experimental techniques.
CHAPTER TWO: DEFORMATION MECHANISMA AND PSEUDOELASTIC BEHAVIORS IN TRILAYER COMPOSITE METAL NANOWIRES

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The deformation mechanisms in Cu-Ni-Cu composite nanowires subjected to uniaxial tensile loading are investigated using Molecular Dynamics simulations. We particularly explore the coupled effects of geometry and coherent interface on the tendency of nanowires to deform via twins and show pseudoelastic behavior. It is found that the critical size to exhibit pseudelasticity in composite nanowires is $5.6 \times 5.6 \text{ nm}^2$, which is 6.5 times greater than single crystalline Cu nanowires. Our results also show that the composite nanowires offer stiffness enhancement compared to the corresponding single crystal Cu nanowires.
2.1 INTRODUCTION

Nanowires are regarded among the most important nanometer materials\textsuperscript{20-22} because of their distinctive structures and properties that can play a critical role in future electronic, optical and nanoelectromechanical systems\textsuperscript{23, 24}. Nanowires are typically single-crystalline, highly anisotropic and semiconducting, insulating or metallic nanostructures that result from rapid growth along one direction. Their cross-section is uniform and much smaller than their length. The result of this is a very high surface to volume ratio, causing the surface atoms to contract towards the core of nanowire in order to minimize their energy by maximizing their local electron density. The surface contradiction results into very high compressive stresses in the nanowires, affecting significantly their mechanical behavior during tensile loading. When the cross-sectional area of single crystal metallic nanowires made of Cu, Ni and Au is smaller than a critical value, the wires can completely recover from severe deformations, up to 50\% strains, in a very short response time without inducing residual deformation\textsuperscript{25-29}. Their unique pseudoelastic behavior, which is very important in the area of self-healing materials used as sensors for bioengineering applications and microelectronics, only exists in nanowires of face-centered-cubic (fcc) metals with high twinnability. This size dependent pseudoelastic behavior is mainly due to the surface-induced internal compressive stress in nanowires, in the order of GPa, which is much higher than in bulk materials and provides the driving force for spontaneous lattice reorientation via twins\textsuperscript{25}. However, measuring the mechanical properties of nanowires is a very difficult task due to their small dimensions. Molecular dynamics (MD) simulations provide a useful tool to investigate the structural, mechanical and thermodynamic properties of these nanoscale materials at the atomic level. Various investigations have been done on single crystalline nanowires and their behaviors\textsuperscript{25-29}. In the present work we particularly use MD to
study deformation mechanisms in composite nanowires and compare their behavior to single crystalline nanowires.

2.2 DEFORMATION MECHANISMS IN NANOWIRES

Previous studies have shown that in defect free fcc single crystalline nanowires made of Cu, Ni and Au, when deformed at strain rate below a critical value\(^{20}\), the deformation behavior is driven by the nucleation of \(1/6<112>\) type dislocation partials at the surface; and whether full type dislocations or twins are formed depends on the stacking fault energy, surface effects, and the size of the nanowire\(^{30-34}\). During tensile loading, at a critical resolved shear stress a leading \(1/6<112>\) partial dislocation nucleates at the surface and propagates in the nanowires. For sizes larger than a critical value, a trailing partial emits on the same plane resulting in the formation of a full dislocation and leading to permanent deformation (slip). Below the critical dimension, a second leading partial nucleates at a slip plane adjacent to the original slip plane, resulting in the formation of a twin boundary. The process of emission of partials repeats itself and moves the twin boundary along the axis of the wire. At sizes lower than the temperature-dependent critical size, an initial configuration with \(<001>\) axis and \{001\} lateral surfaces is unstable due to high surface energies which cause the crystalline structure to undergo spontaneous reorientation to a low energy configuration of \(<110>\) axis and \{111\} closed packed lateral surfaces. The reoriented \(<110>/\{111\}\) wires are found to exhibit pseudoelasticity upon application and subsequent removal of tensile loading\(^{25}\). The pseudoelastic behavior occurs only above a size-dependent critical temperature \(T_{cr}\). For a given wire size if the unloading takes place at temperatures below \(T_{cr}\), the reversible behavior does not occur, leaving the question as to why is the temperature important for the pseudoelastic process. The answer is related to the energetic barrier and the
driving force. To initiate the deformation, partial dislocations nucleate and propagate to accommodate high energy mobile twin boundaries, which constitute an energy barrier for the reversibility of the deformation. Thermal energy can provide the necessary energy for overcoming the barrier. As the wire size increases the surface-induced compressive stress $\sigma$ decreases and, above a critical size, can no longer activate the recovery process. Therefore higher temperatures or external compressive stresses are needed to initiate the reverse process. This size and temperature dependence has been observed in experiments as well as in atomistic simulations\textsuperscript{30, 35}. At room temperature the critical size beyond which the nanowires exhibit pseudoelastic behavior is $1.8 \times 1.8$ nm (5×5 Crystal Lattice Units) for Cu and $1.061 \times 1.061$ nm (3×3 Crystal Lattice Units) for Ni. This behavior is attributed to the high twinnability that these two materials exhibit among the fcc metals\textsuperscript{25, 32}. It should be pointed out that the critical dimensions mentioned above correspond to the initial unstable configurations with $<001>$ orientation, which reorient to stable $<110>$ configurations whose dimensions are $2.19 \times 2.19$ nm for Cu and $1.6 \times 1.6$ nm for Ni.

For many practical applications, and from manufacturability point of view, it is desirable to increase the critical size for pseudoelasticity. Previously Ji and Park\textsuperscript{35, 36} showed that by simply changing the wire cross section from square to rectangle, nanowires with dominant surface facets are created with increased tendency to deform via twinning. Since the twinning is the mechanism responsible for the pseudoelastic behavior, this leads to increased critical size. It is suggested that the asymmetry of the cross sectional geometry of each layer results in an additional driving force for the larger surfaces to reduce their area and therefore their energy by forming twins. Another driving force that can increase the critical size is the addition of internal stresses that result when creating fcc/fcc composite nanowires with coherent interfaces\textsuperscript{37–40}. Within a composite
nanowire, made of a Ni layer sandwiched between two Cu layers, the resulting coherency stresses will add to the already existing surface stresses, thus enhancing the driving force and causing the nanowire to exhibit pseudoelastic behavior at cross-sectional areas larger than the critical value for a single crystalline nanowire. At this juncture it is worth mentioning that it is possible to fabricate nanowires by creating thin films using already established techniques such as sequential sputtering, electrodeposition or electron beam lithography and then thinning them in appropriate dimensions through focus ion beam (or reactive iron etching). In this work, the coupled effects of rectangular geometry and coherent interface on increasing the critical size of nanowires to exhibit pseudoelastic behavior are presented and discussed.

Table 2-1. Cross sectional dimensions of simulated Cu-Ni-Cu composite nanowires. The units are in nm.

<table>
<thead>
<tr>
<th>Case</th>
<th>Overall size</th>
<th>Cu layer</th>
<th>Ni layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.4×2.4</td>
<td>0.8×2.4</td>
<td>0.8×2.4</td>
</tr>
<tr>
<td>2</td>
<td>2.8×2.8</td>
<td>0.93×2.8</td>
<td>0.93×2.8</td>
</tr>
<tr>
<td>3</td>
<td>3.54×3.54</td>
<td>1.18×3.54</td>
<td>1.18×3.54</td>
</tr>
<tr>
<td>5</td>
<td>4.8×4.8</td>
<td>1.6×4.8</td>
<td>1.6×4.8</td>
</tr>
<tr>
<td>6</td>
<td>5.24×5.24</td>
<td>1.82×5.24</td>
<td>1.6×5.24</td>
</tr>
<tr>
<td>7</td>
<td>5.6×5.6</td>
<td>2×5.6</td>
<td>1.6×5.6</td>
</tr>
</tbody>
</table>
2.3 MOLECULAR DYNAMICS SIMULATIONS

The molecular dynamics (MD) simulations were performed using LAMMPS \(^{44}\) with potentials based on the embedded atom method (EAM) \(^{45, 46}\). All simulations were achieved with free surfaces. Composite nanowires were created with surface orientations along \(<11\text{-}2>\), \(<111>\) and \(<1\text{-}10>\), i.e. x, y and z. The temperature of the structure during all the stages of the simulation (relaxation, loading, unloading) was kept constant at 300K. Initially the nanowires were not in equilibrium. They were relaxed keeping the bottom fixed on its plane and the top free to move without applying any load until the final strain of the nanowires reached a steady state. The relaxed nanowires were then subjected to a uniaxial tensile loading by pulling the top by a constant velocity, thus simulating constant strain rate loading conditions. The velocity during all the simulations was kept constant and equal to 0.03 Å ps\(^{-1}\) that corresponds to the strain rate of \(10^8\text{s}^{-1}\), which is at least two orders of magnitude smaller than the critical strain rate (around \(5\times10^{10}\text{s}^{-1}\)) for the initiation of amorphization during the tensile loading\(^{20}\). After the desired strain was achieved, the nanowires were unloaded by simply implementing negative velocity of -0.03 Å ps\(^{-1}\)\(^{32}\). It should be mentioned that the atoms of top surface are constrained to move only along the wire axis by applying velocity in the vertical direction during the loading and unloading periods; they are not free to move in the other two directions. The cross sectional dimensions of the simulated nanowires as well as the size of each single layer are given in table (I).

2.4 RESULTS AND DISCUSSION

The stress-strain curves of a composite nanowire together with the same size Cu nanowire under tensile loading are shown in Fig. 2-1. It is noticed that the presence of the coherent interface
results in an increase in the yield stress from 4.2GPa in the monolithic 2.4×2.4 nm Cu nanowire to 5.28GPa in the same size Cu-Ni-Cu composite nanowire. This is attributed to the coherency compressive stress exerted in the Cu layers in addition to the surface compressive stress, thus increasing the initial stored strain energy and resulting in higher tensile stresses when loading the wire in tension starting from the compressive state. As can be deduced from Fig.2-1, in both cases, fracture starts at strain of about 40% followed by rapid drop in the stress. It should be noted that in the case of single crystalline nanowires we compared our results in Fig 2-1 with similar results found in the literature using the same potential but different computational approach and the results are similar.

The nanowires that correspond to the first five cases (layers with the same thickness) of Table (I) exhibit very good pseudoelastic behavior as can be seen in Figure 2-2 for case 4. Figures 2-2-a through (f) show the reorientation process in a 4.17×4.17 nm tri-layer composite nanowire during loading and unloading at different snapshots together with the section views of the same nanowire according to centrosymmetry parameter. The first twin boundary forms at the strain of 0.039 and as loading is continued it moves along the wire axis and thus changes the original configuration of <110>/<111> to the new configuration of <001>/<001>. This new configuration is not in a stable mode due to the high surface energies. Therefore, upon unloading the unstable <001>/<001> nanowire then reorients back to its original low energy state of <110>/<111> configuration. As it can be seen from the figures, due to the complete coherent interface the twin boundaries traverse the three layers and propagate along the wire axis upon loading and unloading. Since Cu and Ni are in fcc phase, the centrosymmetry contour shows both of them with the same color. Also because of no phase transformation during the reorientation process,
there is no color change between the two configurations of $<110>/\{111\}$ and $<001>/\{001\}$; both are fcc. Figure 2-2(g) shows the resulting stress-strain curve.

Unlike the solid nanowires in which the twins initiate from the sharp edges of free surfaces, in composite nanowires the first twin boundary initiates from the free surface at the interface between Cu and Ni and propagates first in the Ni layer and afterwards expands to the neighboring Cu layers. The reason is that the Ni layer is under high internal coherent tensile stress which makes it easier to overcome the stress barriers to initiate the twin, Fig. 2-3.

The simulation results show that by increasing the thickness of the Ni layer beyond 1.6 nm (which is the critical thickness for single crystalline Ni nanowire) the nanowire starts to fracture after the yield point and no twinning occurs. However, the width of each layer can be increased far beyond this critical thickness, e.g. it is 4.17 nm in Case 5. Therefore, the thickness of the Ni layer was kept at the critical size of 1.6 nm and in the next two cases the thickness of each layer of Cu layers increased up to 2nm, below which the nanowires exhibit pseudoelastic behavior. Beyond the stated thickness, fracture initiates at the primary steps of loading due to the growth of the tensile stress in Ni and reduction of both surface and coherent compressive stress in the Cu layers which contributes to the generation of full dislocations instead of twins.

In Table (II) we summarize the yield properties of the composite nanowires of the different sizes at the temperature of 300K. Since smaller wires have higher surface-to-volume ratios, they have higher strain energies and consequently are stronger than larger wires. Therefore, by increasing the size of the wire the yield stress decreases. Although the overall behavior of the composite nanowires is comparable to single crystalline nanowires, the composite nanowires have higher yield stress when compared to similar monolithic Cu nanowires (Fig 2-1). The interesting result
is that even composite nanowires with larger size of 3.54×3.54 nm have higher yield stresses than the 2.4×2.4 nm Cu nanowire. Since the temperature is a key parameter in pseudoelastic behavior of nanowires, by varying the temperature the results shown in table II will change. Also we investigated the effect of strain rate within the range of $10^7 \text{s}^{-1}$ to $10^9 \text{s}^{-1}$. The result shows that there is an effect on the yield properties, as expected, but not on the pseudoelastic behavior, Fig 2-4. We also performed analysis under quasi-static loading conditions and the results show that the pseudoelastic behavior doesn’t change although there is a significant drop in the yield stress. These results are not surprising since the pseudoelastic behavior is driven by surface and coherency stresses while the yield stress can be strain rate dependent.

Table 2-2. Yield parameters of simulated pseudoelastic Cu-Ni-Cu composite nanowires at $T=300\text{K}$.

<table>
<thead>
<tr>
<th>Case</th>
<th>Wire size</th>
<th>$\varepsilon_y$</th>
<th>$\sigma_y (\text{GPa})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.4×2.4</td>
<td>0.048</td>
<td>5.28</td>
</tr>
<tr>
<td>2</td>
<td>2.8×2.8</td>
<td>0.056</td>
<td>5.09</td>
</tr>
<tr>
<td>3</td>
<td>3.54×3.54</td>
<td>0.05</td>
<td>5.01</td>
</tr>
<tr>
<td>4</td>
<td>4.17×4.17</td>
<td>0.039</td>
<td>4.13</td>
</tr>
<tr>
<td>5</td>
<td>4.8×4.8</td>
<td>0.045</td>
<td>4.38</td>
</tr>
<tr>
<td>6</td>
<td>5.24×5.24</td>
<td>0.038</td>
<td>4.1</td>
</tr>
<tr>
<td>7</td>
<td>5.6×5.6</td>
<td>0.044</td>
<td>4.12</td>
</tr>
</tbody>
</table>

Fig. 2-4 shows the stress-strain curve for the composite nanowire with the critical size of 5.6×5.6 which still shows good pseudoelasticity. Increasing the size of the wire beyond this critical size
leads to the formation of full dislocations instead of the initiation and propagation of twins across the wire axis.

2.5 CONCLUSIONS

In conclusion by utilizing molecular dynamics simulations, we have shown that below a critical size composite trilayer nanowires deform via twinning and exhibit pseudoelastic behavior. We have shown that because of the coupled effects of coherent interface and rectangular geometry of layers, the critical size is 6.5 times greater than that for single crystalline Cu nanowires. Moreover the composite nanowires have higher yield stresses than similar single crystalline nanowires which indicate that composite nanowires also offer stiffness enhancement compared to the corresponding monolithic Cu nanowires.

ACKNOWLEDGMENTS

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References


Figure 2-1 Comparison of the stress-strain curve for a $<110>/\{111\}2.4 \times 2.4$nm composite Cu-Ni-Cu nanowire with the same size single crystalline nanowire at the temperature of 300K.
Figure 2-2. Steps (a) to (f) show the snapshots of 4.17nm×4.17nm composite nanowire with the original configuration of <110>/\{111\} during loading and unloading at the temperature of 300K accompanied with their matching section view according to the centrosymmetry parameter. Curve (g) shows the corresponding stress-strain curve. (Note: This figure requires double column space)
Figure 2-3. Snapshot of overlapping both the geometry of nanowire and the related centrosymmetry parameter simultaneously exactly after the initiation of the first twin at the strain of $\varepsilon = 0.039$. The top pictures show the cross sectional view and the bottom show the side view.

Figure 2-4. Stress-strain curve of a <110>/<111> 5.61×5.63nm composite nanowire during loading and unloading at the temperature of 300K.
CHAPTER THREE: THE MECHANICAL RESPONSE OF CORE-SHELL STRUCTURES FOR NANOPOROUS METALLIC MATERIALS

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3.1 Abstract

Nanoporous gold (NP-Au) exhibits microscale plasticity, but macroscopically fails in a relatively brittle manner. This current study suggests that a core-shell structure can increase both ductility and strength of NP-Au. A core Au foam structure was created using conventional dealloying methods with average ligament size of 60nm. Nickel was then electroplated on to the NP-Au with layer thicknesses ranging from 2.5nm to 25nm. Nanoindentation demonstrated a significant increase in the hardness of the coated Np-Au, to about five times of that of the pure Np-Au, and a decrease in creep by increasing the thickness of the coated Ni layer. Molecular Dynamics simulations of Au-Ni ligaments show the same trend of strengthening behavior with increasing Ni thickness suggesting that the strengthening mechanisms of the Np-Au are comparable to those for fcc nano ligaments. The simulations demonstrate two different strengthening mechanisms with the increased activity of the twins in plated Au-Ni ligaments, which leads to more ductile behavior, as opposing to the monolithic Au ligaments where nucleation of dislocations govern the plasticity during loading.
3.2 Introduction

Nanoporous noble metals, such as gold, can be formed from the selective de-alloying of a sacrificial element (such as silver or copper) from a solvent metal [1-3]. The resulting structure has been well characterized in the literature as a three dimensional array of interconnected pores and ligaments[4]. The porosity of the alloy is determined from the base chemistry of the precursor alloy, while the ligament size (or pore size) is controlled by the de-alloying conditions (such as rate) and any subsequent annealing to coarsen the structure[5]. Nanoporous metals have been noted as viable candidates for materials in catalysts[6-8] and sensors and actuators [9-11].

One common drawback of nanoporous metals is their limited macroscopic ductility[12-14] and low macroscopic strength[15], and as such a common method to evaluate the strength of nanoporous metals is to use indentation methods, either with conventional indentation geometries[12] or using micropillar compression[16]. When bulk materials are used as the base material, significant shrinkage (10% in each dimension) during the de-alloying process can occur; in a constrained system this leads to large stresses and in a freestanding system non-uniform de-alloying can lead to local stresses that develop into cracks and macroscopic flaws[17]. It is possible, through judicious selection of an adhesion layer and controlled de-alloying, to create thin films of nanoporous gold which exhibit almost no lateral contraction and little, if any, residual stresses in the film[18]. However, this structure, while exhibiting significant strength in a given ligament due to the small size and defect free structure, still has macroscopically limited ductility because of the lack of strain hardening capability. In situ compression testing of nanoporous gold during transmission electron microscopy has documented the motion of dislocations at ligaments and joints; this deformation appears to occur
by the motion of complete dislocations moving across a ligament from sources which are likely caused by the complex loading conditions during compression of foam structures[19].

Multilayer metallic materials are well documented in the literature as having strengths in excess of either bulk constituent. Additionally, in some cases, the ability to strain harden can be enhanced due to the complex interactions that dislocations have with interfaces at small length scales[20]. The confined layer slip (CLS) model suggests that in some cases having layer thicknesses on the order of 20 nm will lead to dislocation motion being constrained to individual layers, due to the dissimilar elastic properties of the layers, rather than allowing dislocations to propagate across interfaces[21]. Furthermore, in certain structures such as Cu-Ni, a nanowire consisting of a copper core with a Ni shell can exhibit pseudoelasticity at large strains due to twinning[22-24]. Therefore, it may be possible to increase strength or relative ductility in nanoporous materials by synthesizing ligaments that consist of a core-shell structure of a nanolayered metal; a composite foam, if it behaves like a metallic multilayer, should exhibit more strain hardening capacity than the single material system[20]. In addition, if layer thicknesses were small enough, the ligaments could develop pseudoelastic properties. The added benefit of the addition of a second metal in a core-shell foam would be the addition of a broader range of elements which could be formed in the nanoporous structure. As de-alloying typically limits the system to the more noble metal, the addition of a less noble and more reactive metal may provide additional design outlets not possible from the conventional processing for these materials, as has recently been demonstrated for battery materials using tin over NP-copper [25].

The purpose of the current study was to experimentally produce a core-shell nanoporous material via electrodeposition of a second metal onto a nanoporous foam, and then determine the
mechanical response of the resulting structure. The experimental results will be compared to a computational simulation of a ligament of the same material system.

3.3 Procedures

3.3.1 Experimental fabrication and testing

To create nanoporous gold films on silicon substrates an Ag-Au film was sputtered onto a copper adhesion layer that had previously been deposited on a commercial silicon wafer. Dealloying was employed to obtain the nanoporous gold (NP-Au) template used in this study. The composition of the original alloy was 30.5 at.% Au - 69.5 at.% Ag. 300 nm thick NP-Au films were created on silicon substrates, with average pore and ligament sizes on the order of 40 and 60 nm respectively. The procedures for growth and de-alloying are described in detail in [18].

A Watts bath consisting of 24 g nickel sulfate, 3 g nickel chloride, and 3 g boric acid in 125 mL of deionized water was used to plate the NP-Au films with nickel. A nickel rod was used as the anode, while the cathode was the NP-Au. The plating temperature was held at 58°C, and a voltage between 1 and 6 V was applied to reach a nominal current density of 0.05 A/cm² for a given sample. The plating time was between 1 and 5 seconds to grow films of the desired nominal thicknesses of 2.5 nm, 5 nm, 8 nm, 15 nm, and 25 nm (depending on the measured current density). The thickest plating still had pores present when observed with electron microscopy, but it was not possible to determine if the pores in the thickest layers still had completely interconnected porosity.

Several of the Ni-plated samples were imaged with a JEOL 2010F field emission transmission electron microscope (TEM) operated at 200 kV. High-angle annular dark field
imaging (Z-contrast imaging) was performed to observe the core-shell structure of the Ni-plated NP-Au. Scanning transmission electron microscopy (STEM) mode was used to acquire images and energy-dispersive x-ray spectroscopy (EDS) line scans, with a spot size of 1 nm, camera length of 50 mrad, and linescan step size of 2 nm.

A Hysitron Triboindenter with a cube corner tip was used to perform the indents. A depth-controlled load function was used on all the samples, and the maximum indentation depth on each sample was approximately 50 nm. An array of 25 indents was performed on each of the Ni-plated foams, as well as on an unplated NP-Au film. The reported mechanical properties are those measured at the maximum indentation depth, and they represent the average values of these properties as measured from the 25 indents. The majority of tests were carried out in depth control.

### 3.3.2 Atomistic simulations of core-shell ligaments

Molecular dynamics (MD) simulations were performed using LAMMPS[26, 27] with potentials based on the embedded atom method (EAM) for gold and nickel[28]. The potentials were chosen for their accurate representations of the stacking fault energy (SFE) in both materials. While it is possible to directly simulate a nanofoam structure within a limited volume, cylindrical ligaments with Au as the core and Ni as the shell were simulated to increase the efficiency of the calculations. Our expectation is that the ligament junctions will alter the local stress state but the trends in yield behavior should be similar between experimental tests of a foam and simulations of individual ligaments. The advantage of using this unit structure, rather than a complex foam, is that choice of the ligament sizes and relative thickness of the Ni on the underlying Au core can be tailored to closely match the experimental conditions. The implicit
assumption here is that the deformation in a ligament will reflect the overall deformation of the foam structure. Free boundary conditions were applied on the surfaces to consider the effect of surface stress on the equilibrium shape of realistic models and periodic boundary conditions were considered along the axis of the ligaments to simulate the reasonable length to the cross section ratio of ligaments and avoid surface effects on the top and bottom surfaces that are not free and are connected to other ligaments. The structure is created with surface orientations along \( \langle 112 \rangle \), \( \langle 111 \rangle \) and ligament axis along \( \langle 1 \overline{1} 0 \rangle \) that is reported as the predominant crystallographic orientation in the Au nanofoams\[29\]. It should be noted that ligaments are arranged in all directions inside the porous media and the stated orientation is just used as a first order estimate of the behavior. The lattice parameter of Ni is 0.352 nm and for Au is 0.408 nm. Although there is a relatively large lattice mismatch in this system, they form coherent interface, which corresponds to experimental results in the literature\[30, 31\]. Coherency strains were calculated according to linear elasticity for both Au and Ni layers and applied in the structure. The diameter of the Au core was fixed at 30nm and the thickness of Ni coatings varied from 2nm to 6nm to match a portion of the experimental conditions. The total number of atoms from this simulation is on the order of 3,500,000. In order to bring the structure to the equilibrium configuration, the ligaments were allowed to relax for some time. The temperature of the structure was kept constant at 10 K during relaxation and loading by rescaling atomic velocities. While this temperature is lower than the experiments, simulations run at 300 K generally exhibit the same trend with lower yield points due to thermal activations, but at 10 K the mechanisms are more distinct and not obscured by thermal fluctuations. The structure was then subjected to tensile loading via constant strain rate of \( 10^9 \text{ s}^{-1} \).
3.4 Results

A scanning electron micrograph of a typical Ni plated NP-Au structure is shown in figure 3-1.a, while a TEM image of the same system shown in figure 3-1.b demonstrates a free standing ligament with a layer thickness of approximately 10-15 nm of Ni on a 30-40 nm thick ligament. An elemental profile across the ligament (figure 3-1.c) clearly shows the core-shell structure with Ni uniformly coating the ligament and forming a distinct interface. This ability to form a distinct interface is critical for generating the strengthening effect observed in the CLS model; a diffuse interface would lead only to solid solution strengthening.

Nanoindentation of the nanoporous films produces load-depth curves that exhibit significant creep. As shown in figure 3-2 for the unplated NP-Au and nominal plating thicknesses 8, 15, and 25 nm there is a characteristic “loop” in the partial unloading experiments, indicative of creep and viscoplastic deformation. This is likely a result of the bending of ligaments at the edge of the elastic-plastic boundary in the indentation; this will result in elastic modulus measurements that are upper bound or over-estimates of the stiffness of the system. Of particular interest in the load-depth curves is that the hardest films are not always the thickest plated films. After a rapid rise in the hardness with the presence of a few nm’s of Ni on the underlying Au, the hardness does not continue to increase as rapidly. The change in creep behavior can be seen in figure 3-3.a where the load during the second hold segment, normalized by the maximum load at the hold, significantly decreases for even a 2.5 nm coating of Ni on NP-Au. The hardness of the films as a function of indenter penetration (i.e. contact radius normalized by film thickness, in this case 300 nm) is shown in figure 3-3.b, demonstrating that it is possible to determine properties prior to significant substrate effects in this material. Error bars
in Figure 3-3.b indicate the standard deviation associated with each value. The similarity between the 15 and 25 nm thick coatings may be indicative of the closing of completely interconnected porosity, and therefore for further comparisons to the atomistic simulations we will concentrate on the thinner plating layers where the pores are most likely still interconnected.

The resulting stress-strain curves for the tensile behavior from the MD simulations of the core-shell structures are shown in figure 3-4. Pure gold ligaments of 30 and 38 nm diameter exhibit the same stress-strain behavior; there appears to be no size effect over the range of diameters in this study and as such any differences in strength of the resulting core-shell foams should be due to the layered structure or relative density, not the difference in the size of the ligament. From the stress-strain curves the maximum stress which can be supported is easily identified; this will be the first order estimate of the yield stress for these materials. Table 1 describes the maximum stress supported for each of the simulated structures. Additionally, a simple volumetric rule of mixtures based on the maximum yield conditions for pure Au and pure Ni is shown. The fact that the simple rule of mixtures underestimates the simulation indicates that deformation mechanism changes between the monolithic material and the core-shell structure, and that the core-shell strengthening may be based on the mechanism of deformation and not solely a thickness effect.

The atomistic simulations show the initiation of plasticity via nucleation of the dislocation from the Au-Ni interface and the propagation of dislocations to both core and shell layers, figure 3-5. The peak point in figure 3-4 corresponds to the nucleation of dislocations from the interface, coinciding with the onset of plasticity in these materials. In the pure metal, the
partial dislocations rapidly move across the ligament, and there is no significant dislocation storage mechanism. This is similar to experimental observations [13, 19] that show dislocation motion, once started, is confined to a particular ligament. However, in the core-shell structure, due to the elastic mismatch at the coherent interface, partial dislocations are continuous in both the core and shell layers. Due to the restrictive thickness of the Ni layer there is no space for the trailing partials to nucleate inside the Ni layer upon continuation of loading. Therefore the Ni layer tends to exhibit twinning behavior by nucleating more leading partials adjacent to the initial partials, instead of trailing partials. The nucleated partials inside the Ni shell move along the wire axis and force their counterpart partials inside the Au layer to move with them. This results in the accommodation of the plastic deformation via motion of twins within the ligaments, even though the size of the Au core is far beyond the critical thickness to avoid the formation of trailing partials and twinning to occur, Figure 3-6. The stress-strain curves of Figure 3-4 shows that the addition of the Ni layer increases the yield and flow strength of the material. However, after the initiation of plasticity in the simulations subsequent deformation occurs at substantially lower stresses, though still higher than the pure metal ligaments. Comparing the dislocation configuration of the Au core in the composite Au-Ni ligament with dislocation configuration in pure Au, figure 3-6.b and Figure 3-7, shows that fewer slip planes are activated in Au-Ni composite ligaments. This is because of significant twinning deformation mechanism accommodating plasticity in Au-Ni ligaments while the nucleation of dislocations is primarily responsible for plastic deformation in pure Au ligaments. This suggests that twinning is a viable mechanism to accommodate plastic deformation beyond conventional dislocation motion in the core-shell structure, and that there is a likelihood that additional work hardening may be viable within ligaments, leading to a more macroscopically ductile film. Additionally, as twinning is a
requirement for pseudoelasticity in core-shell nanostructures [23], there exists the possibility of generating pseudoelastic nanoporous metals if ligament diameters can be subsequently reduced.

Table 3-1. Yield conditions of ligaments of Ni plated Au from MD simulations.

<table>
<thead>
<tr>
<th>Ni shell thickness D_{Au}=30nm</th>
<th>MD yield stress, GPa</th>
<th>Yield stress using a volumetric rule of mixtures, GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 – Pure Gold (D=30&amp;38nm)</td>
<td>2.1</td>
<td>2.1</td>
</tr>
<tr>
<td>2 nm</td>
<td>2.7</td>
<td>2.6</td>
</tr>
<tr>
<td>4 nm</td>
<td>3.7</td>
<td>3.2</td>
</tr>
<tr>
<td>6 nm</td>
<td>4.1</td>
<td>3.5</td>
</tr>
<tr>
<td>Pure Ni (D=38nm)</td>
<td>7.1</td>
<td>7.1</td>
</tr>
</tbody>
</table>

Traditionally the strength of foams is represented by the Gibson-Ashby model[32], where foam strength is related to the bulk strength of the fully dense solid by a power law relationship involving the relative density. However, as the core-shell NP structure likely does not have an equivalent bulk strength, and the actual density will vary with plating thickness, it is not appropriate to invoke the traditional Gibson-Ashby scaling law for the experimental data. It is more instructive to determine the strength of the solid relative to the material density as a whole.
Assuming that the NP foam can be described to the first order as a cubic array of ligaments, the core-shell structure can be given a representative unit cell size, \( a \), which is constant for all conditions and based on the initial NP-Au film, and an average ligament diameter, \( d \), and a plating thickness \( t \). The density of pure gold (19.3 g/cm\(^3\)) and pure Ni (8.9 g/cm\(^3\)) can then be used to determine the film density, as a function of plating thickness by

\[
\rho = \frac{V_c (\rho_c - \rho_s) + V_{c+s} \rho_s}{a^3}
\]

(1)

Where \( V \) is the volume of the ligaments, and \( \rho \) the density, while subscripts \( c \) and \( s \) refer to core and shell. The respective volumes are (for nominal porosities of about 50%)

\[
V_c = 3ad^2 - 2d^2; \quad V_{c+s} = 8 \left( \frac{d}{2} + t \right)^3 + 12 \left( \frac{d}{2} + t \right)^2 \left( a - (d + t) \right)
\]

(2), (3)

While this will be non-physical once the plating thickness is larger than the ligament size, it is instructive to examine hardness versus film density rather than relative density.

For the simulation, it is indeed possible to extract a “bulk” flow stress (Table 1) and then use the Gibson and Ashby scaling relationships [32] to predict strength. Assuming that the hardness is 2.8 times the yield strength via the Tabor relationship, then

\[
H = 0.84\sigma_y \left( \frac{\rho_f}{\rho_b} \right)^{1.5}
\]

(4)

where \( \rho_b \) is the strength predicted from the MD simulation and the relative density of the foam (with respect to bulk density) will be determined as above. The resulting hardness from the measurements and predictions for films with nominal plating thicknesses between 0 and 15 nm are shown in Figure 3-8, assuming the ligament size is on the order of 35 nm and the cell size is on the order of 90 nm (i.e. a relative density of the pure NP-Au of 33%). In general, the agreement between the MD predictions and experimental measurements is good, and lends
credence to the observations in the simulations that the deformation mechanisms in a core-shell nanoporous foam differ from monolithic NP-Au.

3.5 Conclusions

The ability to increase the overall strength of a nanoporous material by forming a core-shell structure has been demonstrated. Adding thin layers of Ni onto a NP-Au foam can increase the strength of the film by approximately five times, from a hardness of 400 to 2000 MPa in the core-shell foam. The addition of Ni does not only impact the hardness, but also significantly decreases creep during the indentation process. An atomistic model of core-shell nanowires has been used to explore the differences in the deformation mechanisms with the addition of the plated Ni, and suggests that twinning plays a larger role in a core-shell structure, whereas a similar size structure in a monolithic material is primarily dominated by the nucleation of dislocations. The use of atomistic simulations in conjunction with conventional models of the strengths of foams shows that the predicted performance of the foam using the simulation is within 15% of the experimental data for relatively low density foams.

Acknowledgements

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References


Figure 3-1. (a) Scanning electron micrograph of the typical morphology of core-shell Ni-plated NP-Au. (b) TEM image of a free standing ligament showing the core-shell structure and (c) the
corresponding composition profile of a section noted in (b) showing the Ni plating is on the order of 10-15 nm on a 30-40 nm diameter core. Lines in (c) are smooth fits to guide the eye only.

Figure 3-2. Typical load-depth curves for indentations into NP-Au and Ni plated NP-Au for nominal plating thicknesses of 8, 15, and 25 nm on a ligament size of nominally 30 nm.
Figure 3-3.a) Load relaxation during the second hold period (nominal depth of 30 nm) for an unplated NP-Au and one with a 2.5 nm Ni plating. Load is normalized by the maximum load at the start of the hold .b) Hardness as a function of indentation size, demonstrating no substrate
effects. Two different samples plated with a thickness of 25 nm are shown to demonstrate reproducibility.

Figure 3-4. Stress-strain curves from simulated tensile behavior of pure Au and Au-Ni ligaments. Ligaments of pure Au at 30 and 38 nm diameter, as well as 30 nm of Au with plating thicknesses of 2, 4, and 6 nm are shown. There is no size effect demonstrated for pure Au; the behavior is independent of ligament thickness.
Figure 3-5. a) Nucleation of dislocations from the interface of Au-Ni composite ligaments. b) and c) nucleation and propagation of dislocations in both Au and Ni layers. d) Just Ni layer shown at the same strain as c). ($D_{Au} = 30nm, t_{Ni} = 4nm$). Atomistic configuration are shown according to centro symmetry parameter.
Figure 3-6. a) Formation of twins. b) Movement of twins (twinning) upon loading. ($D_{Au} = 30nm$, $t_{Ni} = 4nm$). Atomistic configuration are shown according to centro symmetry parameter.
Figure 3-7. Dislocation configuration of pure Au

Figure 3-8. Hardness as a function of film density for nominal plating thicknesses of 2.5, 5, 8, and 15 nm. The experiments with plating thickness of 25 nm, which may close off regions of porosity are not included in this figure.
CHAPTER FOUR: INFLUENCE OF THE INCOHERENT INTERFACE AND ITS DISCONNECTIONS (IMPERFECTIONS) ON THE STRENGTH PROPERTIES OF FCC/BCC NANOSCALE MULTILAYERS

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Keywords: Nano metallic multilayers, Interface, Strength, Atomistic simulation

4.1 Abstract

Incoherent interfaces in Cu-Nb nanoscale metallic multilayers (NMM) provide strengthening mechanism by impeding dislocation motion. Due to discontinuity of slip systems, interfaces shear easily and act as barriers for slip transmission between layers; meaning that these interfaces have relatively, low shear strengths and high potentials in attracting and entrapping glide dislocations. Using MD simulations, we studied the deformation mechanism of the interaction of the interface with upcoming glide dislocations by embedding artificial dislocations inside the layer. The interface slip barrier evolves continuously during deformation by absorbing dislocations, leaving disconnections at the interface. Disconnections, which basically can be defined as the composition of a dislocation within the interface and a step, act as extra barriers for slip transmission. Quantifying the slip barriers of the interface are in strong need for analytical solutions and developing a hardening law for NMM with incoherent interfaces. We provide a method for quantification of interfacial barriers by developing energy maps for a sheared interface. This achieved by computing the interfacial strain energy change for a various dislocation configurations and as dislocations dissolved in the interface. Moreover, the
contribution of disconnections on the strengthening mechanisms of nanolayers is investigated. MD simulations have shown that disconnections cause work hardening and boost the effect of the interface in strengthening the structure. The barrier strength of the disconnection increases with increasing disconnection height. In addition, existence of several disconnections at the interface could increase this effect.

4.2 Introduction

Experimental and computational studies have shown that nanoscale metallic multilayers (NMM) can exhibit very high strength levels and ductility\textsuperscript{48-50}. Their strengthening mechanisms are completely different from those of bulk materials when their thickness becomes less than a certain value (~8nm)\textsuperscript{4, 13}. Hall-Petch relation, which is based on dislocation pile ups at the interface\textsuperscript{51, 52}, is no more able to address the deformation behavior at these length scales. There is no possibility for dislocations to pile up at the interface due to the restrictive thickness of the nanoscale layers. Therefore the operative strengthening mechanism becomes dependent on the interaction of the glide dislocations with interface and its barrier properties to slip transmission across the interface\textsuperscript{1, 53}. Our focus in this paper is to study the role of the interfaces and their imperfections on the deformation mechanisms of the NMMs. Two types of interfaces can be classified at this scale level: coherent and incoherent.

Coherent interfaces can be fundamentally defined as interfaces between two layers of materials with the same crystallographic structure, but in which there exists a small lattice mismatch that leads to a very strong interface with high coherent stresses. The slip systems are nearly continuous in coherent interfaces, and there is no discontinuity between slip directions of two
layers; therefore, dislocations can pass from one layer to another through the coherent or so-called transparent interfaces\textsuperscript{2, 54}. High coherency stresses are the barriers that dislocations need to overcome to transmit to the other layers. Incoherent interfaces on the other hand are defined as the interfaces between layers of different lattice structures or with high lattice mismatch. There is no continuity between the slip systems of the adjacent layers through incoherent or opaque interfaces. These interfaces act as a barrier for slip transmission and entrap approaching dislocations\textsuperscript{5-7, 55}. During loading, an incoherent interface shears easily and attracts gliding dislocations because of its low shear strength relative to the layers. Interacting with interface, dislocations dissociate and create disconnections\textsuperscript{9-12} at the interface. Disconnections are composed of two parts: an in-plane dislocation that shears the interface locally and an out of plane step or ledge that cannot transmit to the other layer due to discontinuous slip systems. Disconnections expedite the process of the initiation of the plasticity slightly due to additional stress concentration\textsuperscript{56}. On the other hand, they add extra barriers to slip transmission due to extra interface-dislocations interactions. As a result, disconnections increase the strain hardening effect of the interface and strengthen the structure.

In the present work, we investigate the interaction of the incoherent interface in Cu-Nb system with multiple dislocations, and develop a map for the interfacial energy as a function of dislocation contents. We particularly use MD simulations to introduce dislocations inside the layers and calculate the interfacial energy variations during loading as dislocations interact with interface. In addition, the effects of some interfacial defects such as steps and ledges on the strength properties of NMMs are explored.
4.3  Molecular Dynamics Simulations

The MD simulations were performed using LAMMPS\textsuperscript{44, 57} with potentials based on the embedded atom method\textsuperscript{58-61} The structure is composed of a Nb-Cu-Nb trilayer as shown in Figure 4-1.a. Since the main reason of this simulation is to study the interaction mechanisms of Cu layer interior dislocations with the interface, the second Nb layer at the bottom was added to avoid any dislocation- free surface interactions. The structure is created based on Kurdjumov–Sachs (KS\textsubscript{1})\textsuperscript{1} crystallographic orientation such that \( (111)_{\text{Cu}} \parallel (110)_{\text{Nb}} \) and \( (110)_{\text{Cu}} \parallel (111)_{\text{Nb}} \). The lateral dimensions are 197.4×9.7 nm in x and z directions with applied periodic boundary conditions. These dimensions are specifically selected to assure periodic boundary conditions with minimum stresses at equilibrium. The thickness along y direction is 7 nm for Cu layer and 2 nm for Nb layers. The boundary conditions are free along this direction. The structure then brought to minimal energy by allowing all atoms to adjust their coordinates until the maximum force applying on any atom does not exceed \( 2 \times 10^{-9} \) N\textsuperscript{57}[57][58][57][56][54][52][50][49]. Figure 4-1.b shows KS\textsubscript{1} crystallographic orientation of interfacial atoms after relaxation according to the centro symmetry parameter\textsuperscript{62}. All the simulations carried out at the equilibrium temperature of 0K since we are just interested in deformation mechanisms in this research and need to avoid thermally activated processes.

There are five (110) type planes in Nb and three (111) type planes in Cu layer that are non-parallel to the interface\textsuperscript{5}. Only one set of these planes has the common trace of intersection at the interface plane, \((11\overline{1})/(01\overline{1})\), Figure 4-2.a. This set has the highest probability for dislocations.
residing on a glide plane in one layer to transmit to another glide plane in the other layer. In
order to create a gliding dislocation on a specific plane a half plane of atoms perpendicular to the
corresponding plane need to be removed. Since we want the dislocation to glide on (111), the half
plane is removed from (112) plane that is perpendicular to the desired glide plane. However, the
Cu layer is confined between the two Nb layers, thus it is not possible to remove a semi-infinite
half plane completely. Instead taking a rectangular plate of atoms on (112) plane and
minimizing the energy of system leads to formation of a dipole consisting of two dislocations
each composed of two partials, Figure 4-2.b. The resulting dislocation composed of two partials
where the leading partial meets the interface right after the relaxation due to lower energy
levels at the interface. It is a mixed dislocation since the dislocation line sense is in the z
direction i.e., (110), while the Burgers vector of the full dislocations is on (101).

The structure is then subjected to tensile stress parallel to the interface. Dislocations start to
move toward the interface spontaneously once the load is applied. This sudden movement of
dislocations in the direction of interface is predictable owing to the comparatively lower shear
strength of the interface than of layer itself. Furthermore, later on in this paper, we will show that
the interfacial atoms have lower energy levels than other atoms in the bulk; hence, dislocations
tend to accommodate themselves to the lower energy levels at the interface. Interfaces attract
dislocations and act as a sink for the approaching dislocations. Figure 4-3 shows the movement
of dislocations during loading. Upon entering the interface, dislocations dissociate in to two
parts. One part is the interfacial dislocation that shears the interface locally and spreads in the
interfacial plane easily. The second part is the out of plane step portion that is immobile and as
will be shown later in this paper cannot be transmitted to the Nb layer, even at high applied
stresses of 9.8 GPa. The combination of these two, the interfacial dislocation and the step, is
called a disconnection\textsuperscript{10}. For the dislocation configuration examined, it is the screw component of the dislocation that causes the interface to shear since it could glide from one closed packed plane, \((1\overline{1}1)\), to another at the interface \((111)\), while the step fraction that remains unmoving at the interface is the edge component. A closer view of the intersection of the dislocation with the interface is shown in Figure 4-4.a. Disregistry analysis\textsuperscript{5, 6, 63} are performed to identify the in plane slipped region. The technique is based on the calculating relative amount of position vectors for interfacial pairs of atoms that are placed at both sides of the interface with regard to reference and sheared configuration. Figure 4-4.b illustrates the in plane disregistry of the interfacial planes. The highlighted region with arrows exhibits the sheared region caused by the intersecting dislocation. The amount of in-plane shear is about ten times higher than the out of plane, demonstrating the very low shear resistance of the interface and its ability to attract glide dislocations towards itself.

4.4 Results an Discussion

4.4.1 Interfacial energy calculations

As dislocations enter into and shear the interface, the interfacial properties change. This property change is reflected directly in the interfacial energy of the interfacial atoms. Tracking the variation of the interfacial energy once interface interacts with dislocations provides a good insight of the driving mechanisms of the interface in absorbing glide dislocations and how the evolution of interfacial properties contribute to the strengthening mechanisms of the NMMs. In the present work, we calculated the variation of the interfacial energy for several cases with
different number of embedded dislocations in the simulation cell and developed energy maps as a function of interface dislocation content.

In order to measure the change of interfacial energy associated with the absorption of dislocations, first we need to identify the atoms at the boundary between two crystalline layers that are affected by the interfacial energy, i.e. their energy is in excess of the intrinsic energy of bulk lattices. Computing the energy values of different laminates of atoms revealed that only energy of those laminates that straddle right at the interface between two layers, i.e. one Cu and one Nb atomic plane, differs from the other laminates in the bulk. The interfacial energy did not influence any other atoms inside the layers. Thus these two plane of atoms are considered as interfacial laminates and the interfacial energy can be defined as the difference between the total energy of an internal laminate without interfacial effect and energy of the interfacial laminates,

\[ E_{\text{interface}} = \sum_{i=1}^{N_A} (e_A^i - e_A^{\text{bulk}}), \quad E_{\text{int}} = \sum_{i=1}^{N_B} (e_B^i - e_B^{\text{bulk}}) \]  

(1)

Where \( N_A \) and \( N_B \) are the number of interfacial atoms in Cu and Nb layer, \( E_{\text{interface}} \) is the resulting interfacial energy and \( e^i \), \( e^{\text{bulk}} \) are the total energy of an atom at the interface and in the bulk lattice respectively. The structure is subjected to loading until dislocations are completely absorbed by interface. In order to measure the change of interfacial energy after loading and absorption of embedded dislocations, we define the relative interfacial energy as the subtraction of the initial interfacial energy from the interfacial energy of the sheared configuration

\[ E_{\text{relative}} = E_{\text{interface}}^1 - E_{\text{interface}}^0 \]  

(2)
Where $E^{\text{interface}}_1$ is the interfacial energy of the sheared configuration and $E^{\text{interface}}_o$ is the initial interfacial energy. Variation of interfacial energy is calculated for several sets of embedded dislocations. Figure 4-5 shows the results for Cu interfacial laminate, Nb interfacial laminate and the total variation of interfacial energy that is defined as the sum of the two stated laminates. It should be noted that the spacing between dislocations were set in a way to avoid mutual interactions of dislocations. Namely, the spacing between the dislocations varied between 9 nm and 12 nm. Consequently, the sheared regions at the interface were well separated and didn’t superpose on each other. (Placing dislocations closer than this spacing makes other slip planes to be activated and some extra dislocations are nucleated from other sites that are not of interest of this part of work). The simulations were carried out for up to ten dislocations, that is equal to the dislocation density of $2.5 \times 10^{15} (m/m^3)$. Comparing the values of relative interfacial energies for the Cu and Nb interfacial planes as well as the total relative interfacial energy shows that the absolute values of relative interfacial energy increases for all cases with varying amount of dislocations. The negative energy values for the Cu interfacial plane indicates that the energy of the Cu interfacial plane is less than the bulk interior ones ($E^{\text{Bulk}}_{\text{Cu}} > E^{\text{interface}}_{\text{Cu}}$), explaining why the dislocations inside the Cu layer are favored to enter the interface. The high positive energy values for the Nb interfacial plane of atoms reveals that the energy of the Nb interfacial plane is higher than the bulk interior ones ($E^{\text{interface}}_{\text{Nb}} > E^{\text{Bulk}}_{\text{Nb}}$). This elucidates that it is not as easy for dislocations inside the Nb layer to enter the interface. As Wang et al reported in their paper, there is a critical distance for dislocations in Nb layer to enter the interface. Beyond that critical distance, the Koehler repulsive forces avoid the dislocations to move towards the interface. Nb high positive energy values also clarify that the Cu gliding dislocations need to overcome high
energy levels to pass through the Nb layer. Overcoming these high energy levels is not easily achievable unless a high amount of stress is applied.

Entering more dislocation to the interface leads to the formation of more disconnections at the interface. Formation of disconnection increases the total interfacial energy \( E_{interface} > E_{o}^{interface} \). This is really interesting result since it explains the reason that interfacial disconnections add extra barriers for dislocations to nucleate. The total relative interfacial energy increases by increasing the disconnection density at the interface, hence the barrier effect of the interfacial disconnections raises with increasing their density. This observation indicates that the disconnections cause work hardening and boost the strengthening effects of the interface. On the other hand increasing the density of embedded dislocations to more than \( 2.5 \times 10^{15}(m/m^3) \) in this case, thus reducing the spacing between dislocation to less than 9 nm, results in dislocation-dislocation interactions and activation of other slip systems within the Cu layer instead of travelling to interface.

4.4.2 Effect of interfacial imperfections on NMMs strength properties

In previous section, our aim was to understand the deformation mechanisms of NMMs via energy calculations, while gliding dislocations interact with interface. Disconnections that form at the interface after the absorption of dislocations increase the energy levels and add extra barrier for slip transmission to next layer. The barrier strength of the disconnections depends on different parameters. Here in this section we investigate the effect of some of these parameters such as disconnection’s height and position.
All the MD simulations are similar to the previous settings except that instead of initial embebedded glide dislocations inside the layer, we introduce some imperfections at the interface. So the layers are defect free initially and all we have are some defects at the interface. The structure is loaded under the same loading conditions as previous and stress-strain curves are exploited to illustrate the effect of such imperfections on the strengthening mechanisms of NMMs.

Figure 4-6.b shows the resulting stress-strain curves for a NMM with a defect free interface and interfaces with steps of height=0.5, 1 and 1.4nm (figure 4-6.a). Steps with different heights basically equal to the passing of several gliding dislocations from the same spot at the interface. There are two obvious peak points in the related curves in figure 4-6.b. We here call them as first and second yield point. The first yield point corresponds to the nucleation of first dislocation in the softer layer that is Cu in this case. At first yield point plasticity initiates in the Cu layer while the Nb layer still deforms elastically. The second yield point on the other hand corresponds to inception of plasticity in the Nb layer as well as the Cu layer, associated with the nucleation of dislocation in the Nb layer. Therefore, the plastic yielding in the whole NMM corresponds to the second yield point.

Comparison of the two yield points in the related curves reveals that the existence of a step drops the first yield point a little bit. Nucleation starts from Cu layer at the stress of 5.32 GPa for the NMM with perfect interface and at 5.1 GPa for the one with step height of 1nm. This is mainly because of increasing stress concentration at the steps edges. On the contrary, the second yield point increases up due to the extra barrier that the disconnection adds to the transmission of slip to the neighboring layer. The required stress for initiation of plasticity in Nb layer for the NMM with perfect interface is 9.86 GPa while it is 10.7 GPa for the interface with step height of 1nm.
The barrier strength of the disconnections increases with increasing disconnection height up to a critical limit. Increasing the height of the steps further than this limit doesn’t affect the overall yield stress anymore, (figure 4-6.b).

Strengthening effect of other types of interfacial imperfections such as ledges are also explored. Ledges of height 1 nm and length of 6 nm are introduced at the interface as shown in Figure 4-7.a. Corresponding results in figure 4-7.b shows that ledges have a decreasing effect on the first yield point and an increasing effect on the second yield point due to same reasons explained for steps. Increasing the amount of ledges to more than 2 in this case, drops the the overall yield stress due to high stress concentrations at the ledges that dominates the barrier effect of the ledges and helps the dislocations to nucleate easier in the Nb layer.

4.5 Conclusion

MD simulations were performed to quantify the strengthening mechanisms of the incoherent interface in Cu-Nb layers. We introduced several number of glide dislocations inside the Cu layer and computed the change of interfacial energy associated to the absorption and dissolving of the dislocations towards the interface. Interacting with interface, dislocations leave disconnections at the interface that are composed of a dislocation that spreads easily within the interface, and a step that is entrapped by the interface and cannot pass through the Nb layer until high stress is applied. The resultant energy maps showed that layer disconnections increase the total energy of the system due to the extra interface and dislocation strain field contributions. Disconnections add extra barriers to slip transmission and increase the strength of the interface. Corresponding stress-strain curves reveal that the barrier strength of the disconnections boosts with increasing disconnection height up to a certain limit. A single step with the depth of 1 nm
could increase the strength of the NMM up to 8%. Effects of the existence of other interfacial imperfections such as ledges are also investigated. They exhibit the same strengthening mechanisms as interfacial disconnections.

These kinds of fundamental studies are useful in designing NMMs with desired properties for various applications. Yet the effects of other aspects of interfacial imperfections such as geometry (obtuse or acute) of the steps or ledges are issues that are being examined.

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references


S. Shao and S. N. Medyanik, Modelling and Simulation in Materials Science and Engineering 18, - (2010).


Figure 4-1. a) KS1 crystallographic orientation of the Nb-Cu-Nb trilayer (Cu: $x|\{1\bar{1}2\}$, $y|\{111\}$, $z|\{\bar{1}0\}$, Nb: $x|\{\bar{1}12\}$, $y|\{1\bar{1}0\}$, $z|\{111\}$). b) Atomistic configuration of interfacial atoms, shown according to centro symmetry parameter.
Figure 4-2. a) Side view of the layers with the slip planes (11\overline{1})/(01\overline{1}) that have common trace of intersection at the interface plane, atoms of (\overline{1}\overline{1}\overline{2}) plane removed. b) Formation of leading $\frac{\alpha}{6}$ [112] and trailing partial $\frac{\alpha}{6}$ [2\overline{1}1] after relaxation of the system.
Figure 4-3. (a) to (d). Snapshots of atomistic simulation of the interaction of gliding dislocation with the interface. Atoms are coloured according to the centro-symmetry parameter (atoms in perfect crystallographic configuration are not shown.

Figure 4-4.a) Side view of the interface, showing step portion of the disconnection, after intersecting with glide dislocation. b) disregistery plot from the top view of the interface showing the amount of the shear due to dislocation spreading within the plane of the interface.
Figure 4-5. Relative interfacial energy as a function of interfacial dislocation content

Figure 4-6. a) Interface with 1nm step. b) Stress-strain behavior of a NMM with a defect free perfect interface and others with interfacial steps of height=0.5 and 1 and 1.4nm
Figure 4-7. a) Ledges at the interface b) Stress-strain behavior of a NMM with a defect free perfect interface and others with one, two and three interfacial ledges. Dislocations start to nucleate close to ledges due to stress concentration.
Nanostructured metallic material (NMM) composites are a new class of materials that exhibit high structural stability, mechanical strength, high ductility, toughness and resistance to fracture and fatigue; these properties suggest that these materials can play a leading role in the future micromechanical devices. However, before those materials are put into service in any significant applications, many important fundamental issues remain to be understood. Among them, is the question of the strengthening of NMM using second phase particles and if the addition of precipitates will strengthen the structures in the same manner as in bulk crystalline solids. This issue is addressed in this work by performing molecular dynamics simulations on NMM with precipitates of various sizes and comparing the results with the same structure without precipitates. In this view, Cu/Nb bilayer thin films with spherical Nb particles inside the Cu layer were examined using molecular dynamics simulations and show to exhibit a significant improvement on their...
mechanical behavior, compared to similar structures without particles. Furthermore, an analytical model is developed that explains the strengthening behavior of an NMM that has precipitates inside one layer. The theoretical results show a qualitative agreement with the finding of the atomistic simulations.

Keywords: Dislocations, precipitation, nanocomposites

5.1 Introduction

In recent years, the mechanical behavior of NMM has been investigated both theoretically and experimentally. Theoretical studies feature molecular dynamics [1–3] (MD) and dislocation dynamics [4] (DD) simulations. Experimental techniques include, among others, nanoindentation and bulge testing. The results have shown that NMM composites exhibit high yield strength [5], high ductility [6], [7], morphological stability [8], radiation damage tolerance [9], and unusually high fatigue resistance [10], [11], making them uniquely multifunctional materials. These findings are significant and imply the special role the dislocations and their collective behavior inside the layers play on the strengthening of NMM, in unison with the chemistry and the composition of the interface. As a result, by controlling the motion of dislocations inside the layers, new and stronger structures can be designed. One approach to achieve that is by introducing inside the layers strengthening factors as second phase particles. This paper is a first attempt to examine this hypothesis.

The strengthening achieved by precipitates of a second phase is of great importance from a scientific as well as practical point of view. It occurs when the solute atoms are not dissolved but form separate particles that in turn are dispersed in the matrix. When a moving dislocation encounters precipitates, it will not, in general be able to cut through them if the precipitates are
generally stronger than the matrix. Consequently, it will have to bow between the precipitates and around them, leaving a dislocation loop around the particle. The stress required for this process is approximately $\tau_p = 2Gb/\ell$ where $\ell$ is the distance between the particles [12]. When $\ell \leq 50b$ then very large stresses must be applied before the dislocation motion can occur and the material exhibits high yield strength. Similarly, voids, formed by the agglomeration of vacancies at elevated temperatures, can also act as obstacles to the dislocation motion and result to substantial changes in the yield stress and the ductility of the material. Atomic-scale computer simulations have provided detailed information on how these effects are influenced by obstacle structure, applied stress, strain rate and temperature [13,14].

Although the effect of precipitation on nanomaterials have been studied by a number of researchers [15–17], limited research has been performed thus far on the role of second phase particles on the strengthening of NMM structures. In particular, recent work [18,19] has shown that for the case of 20 nm thick Pt/Mo, oxidation of the Mo within the structure leads to precipitates (most likely MoO$_3$) which can increase the hardness of the films by almost 20% while leaving the modulus effectively unchanged. However, this preliminary study was not able to control the precipitate spacing; in fact the precipitates continued aging during testing and as such were not controlled for size and spacing.

In this work, MD simulations on a Cu/Nb NMM system with individual layer thickness of 8 nm and 14 nm were contacted. In all cases the niobium layer thickness was kept constant and equal to 8 nm to reduce the size of the simulated structures since the niobium layer acts as a buffer region only. The particular system was chosen because it is exhibiting unique characteristics compared to bulk metals under irradiation, including several orders of magnitude higher He solid solubility, interface confined growth of He bubbles, much lower radiation
hardening and dramatic reduction of bubble density [20]. Since the fcc/bcc systems do not generate coherency stresses, an optimization technique was used to find the number of atomic columns in each layer that produces the minimum in-plane strains [21]. The molecular dynamics software LAMMPS [22] was used in our simulations. The EAM interatomic potentials [23] for Cu, Nb and their interactions were employed [24–26]. The produced structure is in accordance to Kurdjumov–Sachs (KS) crystallographic orientation [3,27,28] corresponding to (111)\(_{\text{Cu}}\) \parallel (110)\(_{\text{Nb}}\) and \langle 110 \rangle \(_{\text{Cu}}\) \parallel \langle 111 \rangle \(_{\text{Nb}}\) with periodic boundary conditions applied in the in-plane directions [28]. In order to avoid interactions between the dislocation and the free surface, the Cu layer was sandwiched between two Nb layers. Two Nb spherical particles were introduced inside the Cu layer and two threading dislocation of mixed character were formed by cutting a rhombic shape plate of atoms on the (110)\(_{\text{Cu}}\) plane that intersects with two (T T T)\(_{\text{Cu}}\) planes on the sides, thus forming a dislocation dipole. After relaxation the two dislocations reside on the corresponding (T T T)\(_{\text{Cu}}\) planes and are positioned right ahead the two precipitates. The resulting structure served as our initial configuration. In this point it should be noted that the choice of niobium as precipitate was made purely due to its comparatively higher strength than that of copper and because of the existence of good interatomic potentials for the interaction between Cu and Nb. It constitutes in no case an actual recommendation on what material should be used as second phase particle in real applications to harden the structure, and it is used in this work only as a hypothetical scenario to study how a relatively harder precipitate can affect the strength of an NMM.
5.2 Precipitate – single threading dislocation interaction

A constant shear strain rate of $6 \times 10^8 \text{ s}^{-1}$ was applied that caused the dislocations to slip on $(\overline{1} \overline{1} 1)$ planes and interact with the precipitates. The interaction steps between a dislocation and a precipitate are shown in Fig. 5-1 where only one precipitate and the interacting dislocation are shown. For clarity only one dislocation and its corresponding precipitate are shown in the figure. First, and at a stress of about 750 MPa the dislocation starts to propagate and come in contact with the precipitate (Fig. 5-1a). Then, and as the stress continues to increase, the dislocation starts to cut the precipitates in its first attempt to pass through (Fig. 5-1b). This result to an increase in stress that is more pronounced as the precipitate size increases as shown in Fig. 5-3a. Eventually, and at a stress of about 1.4 GPa for the 2 nm radius precipitate, the dislocations clear the particles (Fig. 5-1c) and the stress drops. Due to the applied periodic boundary conditions in the slip direction, the dislocations pass through the precipitates several more times during the loading. The condition is similar to the case that a dislocation passes through an array of particles. This will result to consecutive drops in stress as the dislocations pass through the precipitates for the second and third times (not shown in the Figure). However, since there are no dislocations inside the Nb layer, this layer continues to deform elastically [1,21], thus leading to a continuous hardening of the material shown in Fig. 5-2a. For comparison purposes only, in Fig. 5-2b the stress – strain curve of two threading dislocations with two 2 nm radius precipitates inside a copper strip of 8nm thickness is shown. Since there is no Nb layer to deform elastically, the hardening is not observed and the stress – strain curve looks more like the traditional elastic – perfectly plastic with peaks and valleys that correspond to the consecutive passes of the threading dislocations.
In Fig. 5-2a, the stress – strain curves for structures with precipitates of various sizes are also shown and compared to the stress – strain curves of the precipitate – free NMM. As expected, a small precipitate of 1 nm radius does not affect considerably the yield stress but, as the precipitate size increases, the yield stress increases accordingly. The reason is because a small precipitate allows more space to the threading dislocation to move and thus a smaller additional stress is required to overcome the obstacle. A larger particle would require higher additional stress in order for the dislocation to pass through, Fig 5-2b. Furthermore, and in an attempt to identify how the presence of a precipitate can improve the strength of a thicker NMM (compared to a thinner NMM without precipitates), a second structure was considered with about twice the layer thickness as the first one. The results reveal that, as expected, the presence of the precipitates can lead to an increase in strength of the thicker structure. Most important, the simulations show that after a certain precipitate size the strength of the thicker structure can be made similar to that of the thinner structures without precipitates. This outcome can be used to manufacture thicker NMM’s with the strength of thinner structures.

However, as the insert of Fig. 5-2a suggests, since the dislocation transmission strength is lower than the precipitate strength the material strength will be still dominated by the slip transmission. But, this do not cancel the importance of the present observation since it allow us to manufacture thicker structures that, with the correct choice of precipitate, will be as strong as the thinner ones.

The above observations are confirmed by Figs. 5-3a and 3b where two different structures, one with a 1 nm radius precipitate and one with a 2 nm radius precipitate inside, is shown at the same strain levels. Obviously, the 2 nm radius precipitate constitutes a stronger
obstacle for the dislocation to pass, and thus a higher stress level is required. In the extreme case of a particle of size equal to the layer thickness (in our case $r = 4 \text{ nm}$) the behavior is similar to that of a Cu/Nb thin film without precipitates. Our simulations show that in this case the dislocations are absorbed by the precipitate and never pass through (see Figs. 5-3c and 5-3d). This case corresponds to the interaction between a dislocation and the Cu/Nb interface and has been extensively discussed elsewhere [3,27,29,30]. The result is that the structure behaves like a Cu/Nb thin film without residual dislocations in it, and the stress shown in Fig. 5-2b saturates to the value corresponding to the nucleation of dislocations from the precipitate interface.

5.3 Analytical model

In an attempt to physically explain the strengthening behavior and to identify the thermodynamic driving forces for the atomic mechanisms inside the copper layer an energetic model was developed and is presented below. The model is based on the energy of straight dislocation segments as described in [31].

A schematic of the dislocation behavior close to a precipitate is shown in Figure 5-4a, while the assumed configuration for the model is outlined in Figure 5-4b. The initial configuration includes an infinite dislocation line made of segments A through E. The total length of segments B, C and D represents the thickness of the copper layer and the semi-infinite segments A and E are necessary in order to maintain the dislocation continuity. A shear stress $\tau$ is applied to the layer in the slip plane along the Burgers vector causing the dislocation to move around the precipitate.
As the dislocation bows out, four new dislocation segments (f, g, h and i) of length $\eta$ (the precipitate diameter) are formed. The change of the system free energy is $\Delta G = W_{II} - W_I - \tau b \Delta A$ where $W_{I,II}$ represent the system’s energy at the initial and final configurations respectively, $\tau$ the applied shear stress, $b$ is the magnitude of the Burgers vector, and $\Delta A$ the swept area by the dislocation. Here $\Delta A = \eta(H - D)$, where $H$ is the thickness of the layer, $D$ the diameter of the precipitate and $\eta$ the height of the dislocation segment as explained in Figure 5-4b. The system’s energy at each configuration can be found by adding the interactions between the various dislocation segments and the dislocation self-energy of each dislocation segment (the method is explained in more details in [7]). The change of the system free energy is:

$$\Delta G = 2[W_{ab} - W_{AB}] + 2[W_{cd} - W_{CD}] + 2[W_{ad} - W_{AD}] + 2W_{fg} + 2W_{fh} + W_{fi} + W_{gh} + 4W_{self} - \tau b \eta(H - D)$$

(1)

where, $W$ with capital subscripts represents the interaction energy between segments of the initial configuration and $W$ with low case subscripts is the interaction energy between segments of the final configuration. The factor two in front of the interaction terms is explained by the symmetry between segments $AB - DE$, $CD - BC$ and $AD - BE$ of the initial configuration and segments $ab - de$, $cd - bc$ and $ad - be$ of the final configuration. The same holds for segments $fg - hi$ and $fh - gi$ of the final configuration. Finally, the factor four in front of the self energy includes only segments $f$, $g$, $h$ and $i$ of the final configuration, since the self energy of segments $A$, $B$, $C$, $D$ and $E$ of the $a$, $b$, $c$, $d$ and $e$ is the same and cancel out.

Equation (1) is evaluated using the software Mathematica® and the final result for the $\Delta G$ expression is an explicit function of $H$, $D$ and $\eta$. Equilibrium is then determined by the condition $\partial G/\partial \eta = 0$, which yields a function for $\tau(H,D,\eta)$. It turns out that for all values of
\(H\) and \(D\) \(\tau\) approaches asymptotically a constant value as illustrated in Figure 5-4c. Thus the critical stress \(\tau_{cr}\) is then determined by the condition \(\partial \tau / \partial \eta \to 0\) as \(\eta \to \infty\), yielding

\[
\tau_{crit} = \frac{b\mu}{4\pi} \ln \left[ \frac{H D (H - D + b \sqrt{H + D}) / b^2}{H - D} \right] \frac{1}{H - D}
\]

(2)

where \(\mu\) is the shear modulus and \(\nu\) the Poisson ratio. Physically, this stress corresponds to the stress needed by the threading dislocation to bow out around the precipitate to the point where the configuration becomes unstable and the dislocation will clear the obstacle and propagate indefinitely. The critical stress as a function of precipitate diameter for various layer thicknesses inside a copper layer is shown in Figure 5-4d for an edge and a screw dislocation. The thickness of the layer is measured in terms of Burgers vectors and corresponds to actual values in the range 6 – 15 nm for the copper \((b_{Cu} \approx 2.56 \text{ nm})\). The trend is similar to the one shown in Figure 5-2b. In the limit as \(D / H \to 0\), and \(D \to b\), equation (2) reduces to the confined layer plasticity model [32–34]. The upper limit based on equation (2), \(D / H \to 1\), e.g. \(D = H\) corresponds to the complete blockage of the channel by the precipitate and the stress becomes singular, corresponding to the breakdown of the elastic solution. However, the upper threshold is determined by the shear strength of the interface and or the precipitate as shown by the MD results. Equation (2) shows that both the channel width and the precipitate size control strength with inverse dependence on the mean fee path “\(H-D\)” and logarithmic dependence on both the channel width \(H\) and precipitate size \(D\). In passing we note that the strengthening effect may be approximated by the theory of the sum of harmonic mean of individual barrier free path [35,36] which yields a dependence of the form \(1/H + 1/(H-D)\), but does not capture the logarithmic term as predicted by the exact solution.
However, although this model can explain the interaction between a dislocation and a precipitate, real applications will comprise of many dislocations interacting at the same time with precipitates and may include complex geometries and interactions that this simple model presented herein cannot predict. In order to understand we performed MD simulations with many dislocations inside the structure and the results are discussed in the next section.

5.4 Collective behavior of dislocations

In this section a Cu/Nb bilayer was considered with spherical precipitates of different sizes inside the Cu layer. The thickness of each layer was again constant and equal to 8 nm and the precipitates radii ranged from 1.0 to 3.5 nm. Using full periodic boundary conditions, the resulted structure corresponded to a thin film with alternating Cu and Nb layers [1], containing arrays of Nb precipitates inside the Cu layer. All the structures were loaded uniaxially with a constant strain rate of $10^8$ s$^{-1}$. The loading continued until a final strain of 15% was achieved. The high strain level was necessary in order to assure that dislocations will nucleate inside both the Nb and Cu layers. Then, and in order to produce a structure similar to the experimentally found, the bilayer was relaxed by removing the load, leaving a structure with residual dislocation distribution (more on this can be found in Refs. 1 and 2). The relaxed structures containing dislocations were loaded again using the same method of loading described above. The loading continued until the total strain became higher than 20%. The stress-strain curves and the yield stress vs. the precipitate radius were obtained and are shown in Figs. 5-5a and 5-5d respectively.
The resulting stress – strain curves have similar trends: a first diversion from the linearity when the dislocations start to move inside the copper layer following by a drop in stress that demonstrates the dislocation propagation inside the Nb interface and corresponds to the actual strength of the material. Since in all cases the thickness of the layers remains constant, the observed difference corresponds to the presence of the precipitates of different size. Again the findings show that the bigger precipitate results in the higher strength. This was expected since the strength depends on the free space available to the dislocations to move, which is reduced as the precipitate size increases. The drop in strength for the 3.5 nm case (very close to the actual thickness of the layer) is attributed to the small free distance inside the Cu layer that favors the dislocation transmission inside the Nb layer to the passing through the precipitate, showing the limits of the precipitate strengthening in NMMs.

5.5 Conclusion

In conclusion, the atomistic simulations showed that the addition of bcc precipitates in the fcc layer of an incoherent nanolayered thin film improved the strength of the film by reducing the free space of the threading dislocations, thus making their motion more difficult. The effect is more pronounced as the precipitate size increases. This observation was verified by an analytical model that gives the critical stress required by a dislocation to clear a precipitate of various sizes. Therefore, the present work proves that it can be possible to increase the strength of an NMM by adding second phase particles. However, this strengthening has an upper limit that depends on the relative thickness of the precipitate with respect to the layer inside which the threading dislocations are moving. Practically that means that the strength – layer thickness
curve as is shown in [6] can move up only in the hardening region and that the addition of precipitates cannot improve the strength of very thin structures where the stress required by a dislocation to cross the interface is lower than that to go through the precipitate.

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5.6 Appendix

The change of the system free energy (Fig. 5-4b) is:

\[
\Delta G = 2[W_{ab} - W_{AB}] + 2[W_{cd} - W_{CD}] + 2[W_{ad} - W_{AD}] + 2W_{fr} + 2W_{fh} + W_{fi} + W_{gh} + 4W_{self} - \tau b \eta (H - D)
\]

Explicit expressions for the interaction energy between any two dislocation segments (W_{ab}, W_{AB}, etc.) and self energy are given in [31], which when substituted in the above expression and after taking into account that segments A and E are semi-infinite, the following expression for the activation energy is derived.

\[
\Delta G = 2A \left\{ 2\sqrt{M^2 + \eta^2} - 2M - 2\eta + \sqrt{\eta^2 + D^2} - 2\sqrt{\eta^2 + (D + M)^2} + \sqrt{\eta^2 + (D + 2M)^2} + 2M \ln \left[ \frac{2M}{\sqrt{\eta^2 + M^2} + M} \right] + D \ln \left[ \frac{2D}{\sqrt{\eta^2 + D^2} + D} \right] - 2(D + M) \ln \left[ \frac{2(D + M)}{\sqrt{\eta^2 + (M + D)^2} + M + D} \right] + (D + 2M) \ln \left[ \frac{2(D + 2M)}{\sqrt{\eta^2 + (2M + D)^2} + 2M + D} \right] \right\} \left\{ \begin{array}{c} -4M + 4\sqrt{\eta^2 + M^2} - 4\sqrt{\eta^2 + (M + D)^2} + 2\sqrt{\eta^2 + (2M + D)^2} + 2\sqrt{\eta^2 + D^2} \\ -2\eta \ln \left[ \frac{\eta + \sqrt{\eta^2 + D^2}}{D} \right] - 4\eta \ln \left[ \frac{\eta + \sqrt{\eta^2 + M^2}}{M} \right] \end{array} \right\} + 4A \eta \left\{ \begin{array}{c} \eta + \sqrt{\eta^2 + (M + D)^2} \\ M + D \end{array} \right\} - 2\eta \ln \left[ \frac{\eta + \sqrt{\eta^2 + (2M + D)^2}}{2M + D} \right] \}
\]

\[+ 4B \eta \left( \frac{2\eta}{be} - 2\tau b \eta M \right) \]

where
\[
A = \frac{b^2 \mu}{4\pi} \left[ \cos^2 \theta + \frac{1}{1 - \nu} \sin^2 \theta \right], \quad B = \frac{b^2 \mu}{4\pi} \left[ \sin^2 \theta + \frac{1}{1 - \nu} \cos^2 \theta \right]
\]

\[
M = \frac{H - D}{2}
\]
References


Figure 5-1. The interaction between the dislocation and the precipitate. Only the copper layer and the one interacting precipitate-dislocation pair are shown. The thickness of the copper layer is 8 nm and the radius of the precipitate is 2 nm.

Figure 5-2. (a) Stress – strain curves for the interaction between the threading dislocation and precipitates of different sizes for the case of 8 nm individual layer thickness structure. The first drop corresponds to the critical stress at which the threading dislocation inside copper clears the precipitate. In the case of 4 nm radius precipitate, the drop corresponds to the nucleation of new dislocations from the precipitate interface. In the inset the stress – strain curves of a single Cu layer and Cu/Nb thin film with the same thickness are compared. In both cases two threading
dislocations are introduced inside the Cu layer together with two precipitates blocking their way. The stress – strain curve of the first case exhibits an elastic – perfectly plastic behavior while the second hardens due to the presence of the Nb layer that continues to deform elastically. (b) Critical stress as function of the precipitate size for two different structures, one with 8 nm and one with 14 nm copper layer thickness respectively. In all cases the niobium layer thickness was kept constant and equal to 8 nm. The arrow depicts the ability of the precipitates to strengthen the thicker structure to the point that it exhibits the same strength with a thinner structure without precipitates.
Figure 5-3. Dislocation – precipitate interaction for three different particle sizes. (a) 1 nm radius and (b) 2 nm radius at the same strain. The dislocation loops around the 1 nm precipitate thus requiring lower stress. (c) and (d) 4 nm radius. The dislocation is now absorbed by the precipitate in (c) and as the stress increases new dislocations start nucleating from the interface in (d) (shown with the white arrows). In all cases the thickness of the copper layer is 8 nm.

Figure 5-4. (a) Dislocation – precipitate interaction inside the copper layer. The dislocation initially is at position 1 and when the interaction started the dislocation is at position 2. (b) Dislocation configuration used to model the bow out around a precipitate. The arrow represents
the direction of Burgers vector. (c) Analytical model: length of bow out for a given stress. (d) Analytical model: critical stress vs. precipitate diameter for an edge dislocation inside copper. The curves correspond to layer thicknesses varying from 6 nm (the top curve) to 15 nm (the bottom curve).

Figure 5-5. (a) Stress – strain curves of the 8nm layer thickness bilayers. The structure with the 3 nm radius precipitate exhibits the higher strength. (b) The structure with the 2 nm radius precipitates during loading. The copper layer is at the bottom and the niobium on the top. The
dislocations can pass through the precipitate (the blue colored atoms correspond to the two partials). (c) The structure with the 3.5 nm radius precipitates during loading. A dislocation transmission through the interface (blue colored atoms) is observed due to the very small free space left by the precipitate inside the Cu layer. Again, like in 5b, the copper layer is at the bottom and the niobium on the top. (d) The critical stress as a function of the precipitate radius. The drop in stress exhibits the limits of precipitate strengthening in NMMs. In all cases shown here the thickness of both copper and niobium layers is 8 nm.
CHAPTER SIX: MULTISCALE MODELLING AND SIMULATION OF DEFORMATION IN NANOSCALE METALLIC MULTILAYER SYSTEMS

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Abstract

Nanoscale metallic multilayers (NMM) have very high strength approaching a fraction of the theoretical limit. Their increased strength is attributed to the high interface density and is limited by the interfacial strength. As the density of interfaces increases (due to smaller layer thicknesses) the strength of NMM structures becomes increasingly determined by the specific nature and properties of the interfaces and is most likely controlled by the nucleation of dislocations from the interfaces. With focus on material systems with incoherent interfaces, we performed MD simulations to determine the controlling deformation mechanisms at different length scales for Cu-Nb multilayers under biaxial tensile deformation conditions. The results of the simulations show that there is a transition in the operative deformation mechanism in NMMs from Hall-Petch strengthening for the length scales of sub microns to microns, to individual dislocations confined to glide in individual layers for few nm to few tens of nm, and dislocation-nucleation-controlled models for less than few nanometers. Based on these results, we develop a
Molecular Dynamics-based rate-sensitive model for viscoplastic flow which describes the anisotropic deformation behavior of NMMs at different length scales.

**Keywords:** Nanoscale metallic multilayers, deformation mechanisms, molecular dynamics, multiscale modelling

**Background**

Experimental observations show that fundamentally different deformation mechanisms control the mechanical behavior of nanoscale materials from that of conventional materials at bulk scales. Recent studies on nanoscale materials such as nanowires, nanotubes, thin films and nanoparticles have reported the “ultra-strength” phenomena, where yield stresses approach a significant fraction of the ideal strength: the highest strength that a defect free crystal can attain at zero temperature. Among these nanoscale materials a large portion of both theoretical studies, including molecular dynamics (MD), dislocation dynamics (DD), continuum based models and experimental techniques such as nanoindentation and bulge testing, are dedicated to investigate the behavior of nanoscale metallic multilayers (NMMs). NMMs exhibit very high strength, a relatively high ductility, morphological stability, radiation damage tolerance, and unusually high fatigue resistance, making them uniquely multifunctional materials. Understanding the deformation mechanisms of such structures and their dependency on the interface structure, chemical composition and morphology, as well as to the underlying dislocation mechanisms at different length scales, is critical in designing such nanocomposites with desired properties for various applications.
Two types of interfaces can be classified for NMMs: coherent and incoherent. Coherent interfaces can be fundamentally defined as interfaces between two layers of materials with the same crystallographic structure, but in which there exists a small lattice mismatch that leads to a very strong interface with high coherent stresses. The slip systems are nearly continuous in coherent interfaces, and there is no discontinuity between slip directions of two layers; therefore, dislocations can pass from one layer to another through the coherent or so-called transparent interfaces. High coherency stresses are the barriers that dislocations need to overcome to transmit to the other layers. Incoherent interfaces are defined as the interfaces between layers of different lattice structures or with high lattice mismatch. There is no continuity between the slip systems of the adjacent layers through incoherent or opaque interfaces. These interfaces act as a barrier for slip transmission and entrap approaching dislocations. During loading, an incoherent interface may shear easily and attract gliding dislocations because of its low shear strength relative to the layers. Interacting with interface, dislocations dissociate and create disconnections at the interface. Disconnections are composed of two parts: an in-plane dislocation that shears the interface locally and an out of plane step or ledge that cannot transmit to the other layer due to discontinuous slip systems. Disconnections expedite the process of the initiation of the plasticity slightly due to additional stress concentration they add at the interface. On the other hand, they add extra barriers to slip transmission due to extra interface-dislocations interactions. As a result, disconnections increase the strain hardening effect of the interface and strengthen the structure.

Alternatively, NMMs with various layer thicknesses exhibit different deformation mechanisms. At higher scales, when the thicknesses of layers of NMMs are varied from microns to hundreds of nanometers, the density of dislocations increases rapidly once deformation starts,
due to double cross slip and other Frank-Read type multiplication processes. However, in smaller volumes, and as the thickness of layers decreases to less than several nanometers, dislocations annihilate at free surfaces or interfaces, which could lead to dislocation starvation in the bulk. It is also possible that in small-volume materials, the initial configuration does not contain a single dislocation in it. Under these dislocation-starved scenarios, dislocation nucleation is expected to be an important factor in controlling plastic deformation of small-volume materials at low temperature.

There are many potential applications for NMMs in a wide variety of future technologies such as surface coatings of exceptional wear or fatigue resistance, MEMS devices with high performance and reliability, and lightweight metal panels for automotive and aerospace industries. Towards this end, there is a critical need to develop reliable models to be able to analyze and design systems consisting of such materials. Most of the current models are based on phenomenological constitutive equations, assuming certain deformation mechanisms that are derived from limited empirical data. The empiricism of these models stipulates the need of developing new models that are associated with the fundamental physics of the deformation mechanisms of NMMs.

There has been significant interest in investigating the deformation mechanisms of the NMMs. Hoagland et al. 53 explored the slip behaviors in coherent and semicoherent metallic bilayer composites by using atomistic simulations. They reported several interesting phenomena in these kind of materials such as nonlinear elastic lattice strains and different core structures of misfit dislocations with different materials. They showed that Cu-Ni interfaces with narrow misfit dislocations are more stable than Cu-Ag interfaces with wide and mobile misfit dislocations. Rao et al. 89 and Misra et al. 48 showed that coherency stress of the interface is the
main strengthening mechanism in NMMs with coherent interfaces. Dislocations in one layer need to overcome to the coherency stress of the interface in order to pass to other layer. They showed that the strength of the NMM is not dependent on the layer thickness in the coherent systems. Abdolrahim et al studied the effect of coherent interfaces in the core-shell ligaments of nanoporous Au-Ni foams. Their simulations demonstrated two different strengthening mechanisms with the increased activity of the twins in plated Au-Ni ligaments, leading to more ductile behavior, as opposing to the monolithic Au ligaments where nucleation of dislocations govern the plasticity during loading. Henager et al explored the effect of disconnections on slip transmission in fcc NMMs. They showed that disconnections add extra barrier to slip transmission because of residual dislocations, cause work hardening, and prevent shear band formation during deformation that helps the shear process to be more homogenous. Wang et al studied the interactions of dislocations with incoherent interfaces using atomistic simulations. They showed that incoherent interfaces are very weak in shear, and act as dislocations sinks, resulting in the shearing of the interface. The results from their simulations indicate that the shear resistance of the Cu-Nb interfaces is: 1) lower than the theoretical estimations for shear strength for perfect crystals, 2) strongly anisotropic, 3) spatially non-uniform, and 4) strongly dependent on the atomic structures of interfaces. Dislocations nucleate in the weakest regions of the interfaces. In another work, Wang et al investigated the effect of the temperature on the interaction of the dislocations and incoherent interface and showed that dislocations could climb in metallic interfaces at higher temperatures. Dislocation climbs aid the slip transmission from the interface. Reactions between interfacial dislocations assisted by climb could lead to annihilation of dislocation content (recovery) and the absorption of discrete pileups in to the interface plane thus reducing the stress concentration of the pileup. This implies that unless a
long pileup can form, the slip transmission across the incoherent interfaces will not be assisted by the mechanical advantage of the pileup. A more recent work by Abdolrahim et al showed that the addition of second phase particles significantly improves the strengthening behavior of Cu-Nb NMMs, and developed an analytical model that explained the effect of precipitates on the strengthening behavior of such NMMs.

Experiments and atomistic simulations, although may be expensive and time consuming, can provide important insight on the deformation behavior of nanoscale materials. However, a general physics based analytical framework is desired to make predictions of NMM mechanical performance. A number of investigators have developed several predictive models for NMMs with different length scales. The Hall-Petch relation, which is based on dislocation pile ups, is able to address the deformation behavior of multilayers at layer thicknesses of microns to submicrons. In the Hall-Petch model, the dependence of the yield strength defined on the film thickness is given by a function of the form:

$$\sigma_{ys} = \sigma_0 + \frac{k}{\sqrt{h}}$$  \hspace{1cm} (1)

where $\sigma_{ys}$ is the yield strength, $h$ is the layer thickness, $k$ is the Hall-Petch slope and $\sigma_0$ is the lattice friction to slip. By decreasing the layer thicknesses to the scale of tens of nanometers, there is no possibility for dislocations to pile up at the interface due to the restrictive thickness of the nanoscale layers. Then the flow strength of the nanomaterials deviates from the Hall-Petch relation. That is when other slip mechanisms begin to operate. Misra et al showed that at these length scales plastic flow of NMMs with incoherent interface features glide of single Orowan-type loops in one layer bounded by two interfaces. This process is followed by the deposition of misfit type dislocations at the interface and transfer of load to the other elastically deforming
layer. The composite begins to yield when slip is eventually transmitted across the interface after overcoming the resistance from the dislocation arrays. Misra et al.\textsuperscript{13} and later Akasheh et al.\textsuperscript{14,15} suggested the following model for the confined layer slip (CLS) regime:

\[
\sigma_{\text{cls}} = M \frac{\mu b}{8\pi h} \left( \frac{4 - \nu}{1 - \nu} \right) \ln \left( \frac{ch}{b} \right) - \frac{f}{h} + \frac{C}{\lambda}, \quad \text{with } C = \frac{\mu b}{(1 - \nu)}
\]

where, \(b\) is the burgers vector, \(h\) the layer thickness, \(\alpha\) is a constant representing the core cutoff parameter and \(f\) is a term accounting for the interface stress and is given as the gradient of the interfacial energy \((E_i)\) with respect to strain \((\varepsilon)\), i.e. \(f = E_i + \frac{dE_i}{d\varepsilon}\), and \(\lambda\) is the spacing between the interfacial dislocations. The CLS model can only predict the mechanical behavior of the NMMs from few nanometers to few tens of nanometer. However, the results of simulations\textsuperscript{13,72} show that there is a transition in the operative deformation mechanism in NMMs from confined layer slip to interface mediated plasticity mechanisms as the layer thickness is reduced to less than a few nm. The interface slip barrier strength decreases with decreasing layer thickness to the scale of the dislocation core, leading to dislocation-nucleation-controlled deformation and thus softening behavior of the NMMs with decreasing the thickness of the layers. The underlying mechanism involves the nucleation, absorption, and desorption of dislocations to and from interfaces and free surfaces. It seems that only a limited number of investigations have studied the behavior of NMMs at these tiny length scales compared to larger length scales. However, a number of researchers have proposed dislocation nucleation based deformation mechanisms for other kind of nanocrystalline metals at decreased length scales. For example, Li et al.\textsuperscript{94} identified a dislocation-nucleation-controlled softening mechanism in nanotwinned Cu\textsuperscript{95,96} in which dislocation nucleation and storage are highly organized by existing twins. Their simulation results indicate a critical twin-boundary spacing below which the
nucleation and motion of partial dislocations parallel to twin-boundaries leads to the softening behavior of the nano-twinned metals. Beyond the critical thickness, dislocations cut across twin planes and cause strain hardening. In their proposed model, the strength of the material depends on both twin-boundary spacing $\lambda$ and grain size $d$ as:

$$\tau = \frac{\Delta U}{SV^*} - \frac{k_B T}{SV^*} \ln \left( \frac{d \nu_D}{\lambda \dot{\varepsilon}} \right)$$  \hspace{1cm} (3)

where $\Delta U$ is the activation energy, $S$ is a factor representing local stress concentration and geometry, $V^*$ is the activation volume, $k_B$ is the Boltzman constant, $T$ is temperature, $\nu_D$ the Debye frequency, and $\dot{\varepsilon}$ is the macroscopic strain rate. More details about the activation parameters will be discussed later in Section 3.1. In another work Zhu et al. 97 developed an atomistic modeling framework to address the probabilistic nature of surface dislocation nucleation in nanopillars. They suggested a model for nucleation stress in nanopillars as:

$$\sigma = \frac{Q^*}{\Omega} - \frac{k_B T}{\Omega} \ln \frac{k_B T N \nu_0}{E \dot{\varepsilon} \Omega(\sigma, T)}$$  \hspace{1cm} (4)

where $Q^*$ is the activation energy in the absence of applied stress, $\Omega$ is the activation volume, $E$ is the Young’s modulus of the nanopillar, $N$ is the total number of nucleation sites that they considered to be all the atoms at the surface as potential nucleation sites, $\nu_0$ is the attempt frequency and $\dot{\varepsilon}$ is the strain rate. Equation (4) reflects the softening size effect of the nanowires on the nucleation stress as it appears directly in the total number of surface nucleation sites, $N$. A similar model is needed to describe the controlling deformation mechanism in metallic thin films at lower length scales of less than few nanometers. It is yet to be established how the macroscale elastic-plastic response of “bulk” NMMs is linked to their deformation mechanism modes at the nanoscales.
In this paper, we investigate the controlling deformation mechanisms of NMMs at different length scales and develop predictive models for general applications that would facilitate the design and analysis of bulk NMMs. The paper is organized as follows. In Section 2 we study the deformation behaviors of NMMs in physical details using MD simulations and discover the controlling deformation mechanisms of NMMs at different length scales. We consider Cu-Nb thin films as a model system which has incoherent interfaces, and perform a series of MD simulations. These deformation mechanisms are either relevant to previously proposed mechanisms or completely new deformation mechanisms not yet suggested in the literature. MD results elucidate how the nucleation of dislocations is critical in defining the governing plastic deformation of such materials at smaller length scales. Building on the fundamental physics of deformation as exposed by these simulations, we propose models that explain the dependence of strength on layer thickness and identify the regions where the deformation is controlled by either dislocation propagation mechanism or dislocation nucleation mechanism. In Section 3, we develop analytical models based on the fundamental physical deformation behavior observed at the atomistic level during molecular dynamics (MD) simulations.

6.1 Molecular Dynamics simulations

6.1.1 Simulation set-up

Atomistic simulations of Cu-Nb multilayers are carried out within LAMMPS \(^44\). The structure is made up of two layers of Cu and Nb with Kurdjumov–Sachs (KS\(_1\)) \(^1\) crystallographic
orientation such that \((111)_{\text{Cu}}\||(110)_{\text{Nb}}\) and \((110)_{\text{Cu}}\||(111)_{\text{Nb}}\), Figure 6-1a and 6-1b. There are five \((110)\) type planes in Nb and three \((111)\) type planes in Cu layer that are non-parallel to the interface. Among them one set of planes has the common trace of intersection at the interface plane, \((11\overline{1})/(01\overline{1})\), Figure 6-1b. Despite the difference of about 11 degrees, this set has the highest probability for dislocations residing on a glide plane in one layer to transmit to another glide plane in the other layer. Periodic boundary conditions are applied on all directions to simulate the configuration of the multilayers in bulk. The lateral dimensions are 49.6×9.7 nm in \(x\) and \(z\) directions. These dimensions are specifically selected to assure periodic boundary conditions with minimum stresses at equilibrium. The thickness \(h\) of each of the layers along \(y\) direction varies between 1nm to 14nm in different simulations. The structure is then brought to minimal energy by allowing all atoms to adjust their coordinates until the maximum force applying on any atom does not exceed \(1\times10^{-10}\) N. Figure 6-2a shows \(\text{KS}_1\) crystallographic orientation of interfacial atoms after relaxation according to the centro symmetry parameter \(^{62}\). Atoms near interface rearrange to equilibrium positions forming periodic patterns as it is typical for \(\text{KS}_1\) crystallographic configuration shown in Figure 6-2a. Figures 6-2b and 6-2c show the atomistic configurations of interfacial atoms of Cu and Nb separately. The fact that the interfacial atoms of Cu and Nb layers have the same patterns on top and bottom, confirms that the periodic boundary conditions are applied appropriately meaning that each Cu layer is sandwiched properly by two Nb layers reproducing bulk multilayers. The simulations were first carried out at the equilibrium temperature of 0K to avoid thermally activated processes. Temperature effects are studied at elevated temperatures of 300K.
6.1.2 Simulation results

The structure is subjected to uniaxial loading with the strain rate of $3 \times 10^{-8} \text{s}^{-1}$.

Stress-strain curves of the corresponding loading for different layer thicknesses are shown in Figure 6-3. Apparently, there are two peak points in the related stress-strain curves. Here we call regions (b) and (e) in Figure 6-3 the first and second yield point respectively. The first yield point corresponds to the nucleation of dislocations from the interface and in the fcc layer, that is Cu in this case, followed by a drop in the stress-strain curve. With continuing loading, more slip systems are activated in the fcc layer and more dislocations nucleate from the interface and propagate in the Cu layer. Dislocations nucleating in different slip systems in the Cu layer entangle and strain harden the structure. Due to the weak properties of the incoherent interface dislocations are absorbed by the interface and they cannot pass through the Nb layer, leaving the Nb to deform elastically up to the second yield point (region (e)). Plasticity initiates in the Nb layer when dislocations start to nucleate in that layer at the second yield point. Therefore, the plastic yielding in the whole NMM composite corresponds to the second yield point when both fcc and bcc layers deform plastically. The dislocation configurations of the Cu and Nb layer at different stages of loading in Figure 6-3 are shown in Figure 6-4. The layers are defect free initially, deforming elastically, Figure 6-4a. Dislocations start to nucleate in Cu as shown in Figure 4b at the corresponding stress state b indicated in Figure 6-3. The amount of dislocation nucleation and propagation inside the Cu layer increases between the states b to e, Figures 6-3 and 6-4b-e. The incoherent interface shears easily, absorbs coming dislocations and act as a barrier to transition of dislocations from Cu layer to Nb, leaving the Nb to deform elastically without any dislocations inside up to state e, Figure 6-3. Eventually dislocations start to nucleate inside the Nb layer and from the interface at state e, Figure 6-4e. No additional hardening
behavior is observed after this point, dislocations propagate all over the layers, and the multilayer starts to soften around state f, Figure 4f.

Figure 6-5 shows the comparison of the first and second yield points for temperatures of 0K and 300K. The first yield point corresponds to the nucleation of dislocations in the fcc layer while the second yield point relates to the nucleation of dislocations in the bcc layer. At T=0K the first yield point slightly changes with varying layer thicknesses and the yield value becomes constant with increasing thickness. This is not surprising since the first yield stress corresponds to the nucleation of the first dislocation from a defect free structure that is dependent on just material properties and not on the layer thickness. The second yield point, however, shows very different behavior. Here the yield values increase with decreasing layer thickness up to a critical thickness of 4nm, and then drop for layer thicknesses less than this size. The trends are identical at 300K with the critical thickness of 5nm, indicating similar deformation mechanisms being active in the two regimes at both temperatures. This raises the following question: What are the different deformation mechanisms that lead to hardening (or softening) beyond (or below) this critical thickness? MD simulation results shown in Figures 6-6 and 6-7 clarify the distinctions between the different governing deformation mechanisms.

Comparing the active slip systems and dislocation contents of the fcc layer at the instant of the dislocation nucleation (2nd yield point) in the bcc layer reveals that, at increased layer thicknesses, fewer slip systems are activated and dislocations can propagate easily on the activated slip systems confined in the fcc layer with fewer interactions. Movements of the dislocations shear the interface, making it easier for the dislocations in Nb layer to nucleate.
Hence, less strain hardening happens and the onset of the second yield point decreases, as shown in Figure 6-6a and 6-6b. At smaller layer thicknesses the interface density grows, more dislocations are nucleated from the weak incoherent interface, and more slip systems are activated. Dislocations cannot move easily due to the restrictive thickness of the layers, they interact more with each other, making it harder for the interface to shear. This, in turn, delays the nucleation event in the Nb layer, enhances the hardening effect, and increases the yield properties, Figure 6-6c. Decreasing the layer thickness to less than 4nm leads to the nucleation and formation of a network of partials on parallel slip planes with less interaction of the dislocations, Figure 6-6d. This, in turn, leads to the softening behavior, Figure 6-5. Closer examination of the top and front view of the 2nm and 6nm multilayers at few loading steps after 2nd yield point (close to point f in figure6-3) are shown in Figure 6-7. Different slip systems are activated below (2nm) and above (6nm) the critical thickness. Nucleation of dislocations on parallel (111) planes with fewer dislocation interactions governs plastic behavior of the multilayers with layer thicknesses of less than the critical thickness and in the softening region. Due to the confinement imposed by the small size of the layers, there is limited room for the dislocations to move along the slip planes, leading to more nucleation of dislocations on parallel slip planes, Figures 6-6d, 6-7a-b. However, in the multilayers with layer thicknesses larger than the critical value (~5nm), activation of different slip systems with more dislocation interactions are being observed, as marked in Figures 6-6b, 6-6c, 6-7c, 6-7d. In passing, we point out that the MD simulation trends are consistent with experimental results reported Misra et al. They plotted the strength of Cu–Nb multilayers versus inverse square-root of the layer thickness. The strength is estimated using the Tabor relationship in which the measured hardness is divided by 2.7 to estimate the flow strength. The deformation behaviors reported under the experiments,
above and below the critical thickness are very similar to our MD simulation results, with a
critical layer thickness of 2.5nm, whereas form the MD simulations the critical thickness is about
4nm.

6.2 Development of a MD-based continuum model

6.2.1 Anisotropic viscoplastic constitutive model for NMM

Here we utilize the knowledge gained from the MD simulations for the behavior of
nanolaminate systems at the nanometer length scale, and develop a model for the behavior of
nanolaminate-based structures at the microscale where the structure would be composed of a
large numbers of nanolayers. We consider the material to be anisotropic and can be described
within the framework of viscoplasticity theory. We start by decomposing the overall strain rate
tensor \( \dot{\varepsilon}_{ij} \) into elastic \( \dot{\varepsilon}^e_{ij} \) and plastic \( \dot{\varepsilon}^p_{ij} \) parts such that

\[
\dot{\varepsilon}_{ij} = \dot{\varepsilon}^e_{ij} + \dot{\varepsilon}^p_{ij}
\]

The elastic strain rate tensor is related to the Cauchy stress rate, \( \dot{\sigma}_{ij} \), through Hook’s Law, i.e.

\[
\dot{\varepsilon}^e_{ij} = S_{ijkl} \dot{\sigma}_{kl}
\]

where \( S_{ijkl} \) is the elastic stiffness tensor. Normally, the plastic strain rate tensor is determined
from an associated flow rule that is based on the assumption that a plastic flow potential function
exists and whose gradient gives the direction of plastic flow \(^{98}\), leading to the following equation.

\[
\dot{\varepsilon}^p_{ij} = \lambda \frac{\partial \phi}{\partial S_{ij}}
\]

where \( \phi = \phi(S_{ij}) \) is the plastic flow potential and will be determined via in-plane loading of the
NMM through MD simulations later on. Upon defining the effective strain rate as:

\[
\dot{\gamma}^p = \sqrt{2\dot{\varepsilon}^p_{ij}\dot{\varepsilon}^p_{ij}}
\]
equation (6) can be re-written in the following form.

\[
\dot{\varepsilon}_{ij} = \dot{\gamma}^p M_{ij} , \quad M_{ij} = \frac{\partial \phi}{\partial S_{ij}} \frac{\sqrt{2 \frac{\partial \phi}{\partial S_{pq}} \frac{\partial \phi}{\partial S_{pq}}}}{\tau_{ij}} \]

where \( M_{ij} \) defines the direction of plastic flow and has the property \( M_{ij} M_{ij} = 1/2 \)

Next we develop constitutive equations for \( \dot{\gamma}^p \) for various NMM size regimes with different operative deformation mechanisms. As discussed earlier in Section 1, for NMMs there are three distinct regimes each corresponds to a specific deformation mechanism: I) dislocation pile-up mechanism for large layer thickness (sub microns to microns) where the Hall-Petch relation applies II) confined layer slip (CLS) mechanism for intermediate layer thickness (Few nanometers to few tens of nanometers) and III) dislocation nucleation mechanism for small layer thickness below the critical dimension (a few nm), Figure 6-8. We propose the following power law relations for effective strain rate for the first and second regions with Hall-Petch and CLS operative deformation mechanisms:

\[
\dot{\gamma}^p = \dot{\gamma}_0 \left( \frac{\tau}{\tau^*} \right)^{\nu^*} \]

\( \tau = \sigma_j M_{ij} \) is the effective shear stress, and \( \tau^* = \frac{\sigma^*}{M} \) is the resistance to plastic flow where \( \sigma^* \) is the yield strength and \( M \) is the Taylor factor.

\textit{Region I}

For region I the strengthening mechanism is of the Hall-Petch type as given by Equation (1), but here we modify it to account for strain hardening arising from the storage of dislocations.
The underlying concept is that the material hardening is controlled by the total density of dislocations. Generally, the strength in crystalline materials can be related to two families of dislocations: those stored during uniform deformation, related to the plastic shear strain rate and called statistically stored (SS) dislocations $\rho_{ss}$, and those necessitated by the spatial gradients of plastic shear strain, called geometrically necessary (GN) dislocations $\rho_{GD}$. Statistically stored dislocations accumulate by trapping each other in a random way while gradients of plastic shear result in the storage of geometrically necessary dislocations. That being said, Equation (1) is modified as following:

\[
\sigma^* = \sigma_0 + \frac{k}{\sqrt{h}} + \frac{\alpha^*}{\lambda}
\]  

(11)

where $\sigma_0$ is the lattice friction to slip, $k$ is the Hall-Petch parameter, $h$ is the layer thickness, $\alpha^*$ is a material parameter, and $\lambda$ the dislocation mean free path which is related to the dislocation content through the following relation.

\[
\lambda = \frac{1}{\sqrt{\rho_{ss} + \rho_{GD}}}
\]

(12)

where $\rho_{ss}$ and $\rho_{GD}$ are the densities of the statistically stored dislocation and geometrically stored dislocation respectively.

**Region II**

For region II, we adopt the flow stress given by Equation (2) but we modify it to account for storage of geometrically necessary dislocations within the laminate structure, such that
\[
\sigma^* = M \frac{\mu b}{8\pi h} \left( \frac{4-v}{1-v} \right) \left[ \ln \frac{\alpha h}{b} \right] - \frac{f}{h} + \frac{C^*}{\lambda}
\]

where as before, \( \alpha \) is the dislocation core cutoff parameter, \( f \) is as before the interface stress that arises from the elastic deformation of the interfacial region. The average value of \( f \) can be calculated from atomistic simulations.

The dislocation densities appearing in Equation (12) evolve with deformation, resulting in strain hardening as can be deduced from both Equations (11) and (13) for regions I and II respectively. The evolution of the statistically stored dislocation can have the following form\(^{101}\).

\[
\dot{\rho}_{ss} = \alpha_2 \frac{\dot{\gamma}}{b\lambda}
\]

where \( \alpha_2 \) is a numerical constant of order of unity. Generally, the net content of geometrically necessary dislocations can be related to the spatial gradient of the plastic strain\(^ {102}\). Here we adopt the simplified version derived by Ohashi et al\(^ {100} \text{ 103} \text{ 104} \), such that

\[
\rho_{GD} = \frac{1}{\ell} \| \nabla \dot{\gamma} \|
\]

where \( \ell \) is a material length scale that can be related to the size of the evolving dislocation microstructure.

**Region III**

For small layer thicknesses (region III ) where there exist no or very few initial dislocations in the layers, our MD simulations showed that, dislocation-nucleation mechanisms govern the deformation behavior of the NMMs, see Figures 6-6 and 6-7. In this paper we propose a model based on dislocation nucleation mechanisms for this specific regime.

As stated in\(^ {97}\) the dislocation nucleation mechanisms are controlled by two kinds of quantitative parameters. : the athermal (ideal) strength and activation parameters. The athermal
strength is the elastic limit at the zero temperature where no thermal fluctuations exist the corresponding activation energy is zero. The activation parameters, including the activation energy and activation volume, account for the effect of the thermal fluctuations that lead to lower strengths below the athermal critical strength. At a given temperature \( T \) and stress \( \sigma \), the nucleation rate for any nucleation event can be defined as follows:

\[
v = N \nu_D \exp\left(-\frac{Q(\bar{\sigma}, T)}{k_B T}\right) \tag{16}
\]

where \( N \) is the number of possible nucleation sites, \( \nu_D \) is Debye frequency, \( k_B \) is Boltzmann constant, \( T \) is the absolute temperature, and \( Q \) is the activation free energy which is a function of temperature and stress. The activation volume \( \Omega \) is defined as the derivative of the activation energy with respect to flow stress at constant temperature, i.e.

\[
\Omega(\bar{\sigma}, T) = -\frac{\partial Q}{\partial \bar{\sigma}} \bigg|_T = k_B T \frac{\partial \ln(\nu)}{\partial \bar{\sigma}} \Omega(\bar{\sigma}, T) = -\frac{\partial Q}{\partial \bar{\sigma}} \bigg|_T = k_B T \frac{\partial \ln(\nu)}{\partial \bar{\sigma}} \tag{17}
\]

For competing processes with the same activation energy, the activation volume is a good measure for determining the operative deformation mechanism since it includes both thermodynamic activation and mechanical stress-assistant effects\textsuperscript{105}. Physically, the activation volume is proportional to the number of atoms involved in a thermally activated process, such that it measures the individualistic and collective nature of transition \textsuperscript{72}. During thermal activation, the applied stress does work on the activation volume. The activation volume can be used as an effective kinetic signature of deformation mechanisms. Generally, one can say that for small volume materials i.e. nanocrystalline materials, the activation volume varies between \( \hat{\Omega} \approx 1 - 10b^3 \) and for large scale materials \( \hat{\Omega} \approx 100 - 1000b^3 \textsuperscript{72} \), where \( b \) is the magnitude of the Burgers vector.
In NMMs with small layer thickness, the nucleation event corresponds to the nucleation of the plastic strain increment via emission of an individual dislocation as depicted in Figure 6-9 and can be defined as \( \varepsilon_p = \beta \frac{b}{h} \), where \( \beta \) can be considered as a geometric factor that accounts for Taylor factor and the contribution from all possible active slip systems. The number of nucleation sites specifically for the case of thin films can be assumed to depend on the atomic sites available along the interface, and thus \( N = \alpha l/b \) where \( l \) is the specimen’s length (or the size of the grain boundary) and \( \alpha \) is a constant that accounts for the possible emission sites. For instance in the Cu-Nb thin film with KS1 interfacial orientation those atoms that form the repetitive patterns on both sides of the interface are the most probable sites for dislocation nucleation. This leads us to the following relation for the macroscopic strain rate in region III, where the plastic strain rate is defined as the plastic strain per one nucleation event times the rate of the nucleation.

\[
\dot{\varepsilon}^p = \varepsilon \nu = \varepsilon N \nu_D \exp\left(-\frac{Q(\sigma, T)}{k_B T}\right) = \alpha \beta \frac{l}{b} \nu_D \exp\left(-\frac{Q(\sigma, T)}{k_B T}\right)
\]

(18)

Considering a simple case where the activation energy is linearly dependent on stress\(^9^7\) and assuming that the activation volume at a given stress \( \tilde{\sigma} \) is \( \tilde{\Omega} \), then the activation energy \( Q \) can be written as:

\[
Q(\sigma) = Q(\tilde{\sigma}) - \tilde{\Omega} (\sigma - S \tilde{\sigma}) \text{ or } Q(\sigma) = Q^* - \sigma \tilde{\Omega}
\]

(19)

where \( Q^* \equiv Q(\tilde{\sigma}) + S \tilde{\sigma} \tilde{\Omega} \) and is defined as the nucleation barrier in the absence of applied stress that is calculated by assuming the activation energy to be linear in stress, and \( S \) is a local stress concentration factor. Then equation (18) can be rewritten as:
The effective strain rate, $\dot{\varepsilon}^p = \frac{1}{h} \frac{\alpha \beta}{v_D} \exp\left( -\frac{Q^* - \Omega}{k_B T} \right)$ (20)

The effective strain rate, $\dot{\varepsilon}^p = \sqrt{\frac{2}{3} \dot{\varepsilon}^p_{ij} \dot{\varepsilon}^p_{ij}}$, can be related to effective shear strain rate $\dot{\gamma}^p = \sqrt{2\dot{\varepsilon}^p_{ij} \dot{\varepsilon}^p_{ij}}$ in equation (8) as $\dot{\varepsilon}^p = \frac{1}{\sqrt{3}} \dot{\gamma}^p$. Rearranging equation (20), we obtain the following relation for the nucleation or flow stress in region III.

$$\sigma = \frac{Q^*}{S\Omega} - \frac{k_B T}{S\Omega} \ln \frac{\alpha \beta v_D}{\dot{\varepsilon}^p h}$$ (21)

where $\frac{Q^*}{S\Omega} = \sigma_{\text{thermal}}$ is the athermal limit for the dislocations to nucleate. The prefactor $\frac{k_B T}{\Omega}$ has a stress unit and incorporates the effect of thermal fluctuations on the nucleation stress reduction.

Calculating the Debye frequency from $v_D = \left( \frac{3N}{4\pi V} \right)^{\frac{1}{3}} v_s$, where $\frac{N}{V}$ is the number density and $v_s$ is the sound speed gives a value of $v_D = 1.3 \times 10^{13}$.

The activation energy and activation volume can be determined from MD simulations. Here we first assume a case of uniaxial extension with constant strain rate $\dot{\varepsilon} = 3 \times 10^8 / s$. We also assume a rough upper bound of $\alpha \beta = 1$ since both $\alpha$ and $\beta$ are of order of unity. Then, upon implementing the values for these parameters in equation (21) and fitting the function of equation (21) to the MD results shown in Figure 6-10 in the softening region at temperature of 300K we obtain the following values for athermal stress and thermal prefactor:

$$\sigma_{\text{thermal}} = \frac{Q^*}{S\Omega} = 2.61 \text{ GPa}$$

$$\frac{k_B T}{S\Omega} \bigg|_{T=300K} = 0.265 \text{ GPa}$$ (22)
The activation parameters can then be calculated as:

$$\hat{Q}_{T=300^\circ K} = 0.8b^3$$

$$Q_{T=300^\circ K} = 0.25 \text{ ev}$$

(23)

These values are on the order of those computed for nucleation from surfaces in nanopillars and single crystal Cu, signifying that the presented calculated activation parameters are approximated reasonably within a valid range for small volume materials and supports the suggested dislocation nucleation deformation mechanisms.

6.2.2 Plastic flow potential

Next, and in order to establish a fully defined generalized viscoplastic flow rule in NMMs, we establish based on MD simulations a generalize form for the plastic flow potential. To do so, we use the concept of yield surface, which is the boundary between the elastic and plastic domains. It is a continuous surface in the stress space and corresponds to all stress states $\sigma_{ij}$ that cause yielding. During plastic deformation, the updated yield locus is expected to expand or contract, translate and distort. An isotropic surface expands without any distortion. Any other form of yield surface evolution, such as kinematic hardening, which is defined by the translation of the yield surface, is anisotropic. Drucker showed that, based on a stability postulate, the flow surface must be convex. In the present investigation we performed a series of MD simulations of Cu-Nb NMM under biaxial tensile deformation conditions to determine the corresponding in-plane plastic potential function.

The loading path imposed on the structure is illustrated in Figure 6-11a. A loading path is attained by first applying a constant strain rate in one direction, say the x-direction, up to a certain stress $\sigma_{xx}$ below the yield stress in that direction. Then while that stress is kept constant.
the structure is loaded in the z-direction at a constant strain rate and the stress-strain curve is obtained, from which the stress $\sigma_{zz}$ at the first-yield and second yield can be determined; a typical result is shown in Figure 6-11b. Then each pair of $(\sigma_{xx}, \sigma_{zz})$ corresponds to a point on the yield surface. Comparisons of yield surfaces for first and second yield properties of NMMs with two different layer thicknesses of 4nm and 14nm are shown in Figure 6-12. The results show that the plastic flow potential $\phi$ for this system is highly anisotropic i.e., the yielding behavior is dependent on the loading direction. The results for the first yield surface does not vary considerably for different layer thicknesses as can be deduced from Figure 6-12a. This is due to the fact that this yield surface corresponds to first dislocation nucleation in the defect free fcc layer and is not a function of layer thickness. The properties of the second yield properties, however, vary more significantly with decreasing the thickness. Figure 6-12b shows how yield surface expands with decreasing the layer thickness from 14nm to 4nm. Yet, the expansion is mainly along one loading direction while the yield points hardly vary in other directions. The explanation for this behavior could be due the arrangement of the slip planes related to the corresponding loading direction meaning that there exists no difference in the strain hardening mechanisms of NMMs with varying the layer thicknesses on those specific points with no expansion. The evolution of the yield surface from the first yield to the second yield can also be constructed from the MD stress-strain results. Figure 6-13 shows the evolution of the yield surface for the NMM with 4nm layer thickness during deformation. The anisotropic behavior of the multilayer is well pronounced during several steps of plastic strain as the form of the yield surface changes differently on different loading directions.
An appropriate functional form for the yield surface is now established based on the MD results. There are a number of functional forms that have been proposed to in-plane anisotropic yield surfaces, among them are the most well-known function by Hill \cite{112,113}, Barlat \cite{114,115,116} and Montheillet \cite{117}. The main features, advantages, and drawbacks of these models are discussed in details elsewhere \cite{108,118}. Montheillet’s model \cite{117} best describes the so-called “anomalous behavior” \cite{117} that is also observed within the current MD results of the Cu-Nb NMMs. This model is as follows.

\[
\phi = C[\alpha_1 \sigma_1 + \alpha_2 \sigma_2]^m + \alpha_3[\sigma_1 - \sigma_2]^m + 2n|\sigma_{12}|^m - \sigma_0^m
\]  

(24)

where \(\sigma_1\) and \(\sigma_2\) are the stress components in the material orthotropic axes. \(\alpha_1\) and \(\alpha_2\) are constants that take planar anisotropy in to account, and the presence of planar shear stress \(\sigma_{12}\) allows any in plane shear stress to be applied to the multilayer. The model is always convex \cite{117}. The scaling factor \(\sigma_0\) is assumed to be equal to \(\sigma_{y1}\), the uniaxial tensile yield stress along the x direction such that equation (24) involves five independent parameters: \(C, \alpha_1, \alpha_2, \alpha_3, m\). The five independent parameters of Equation (24) can be found by fitting the equation to the MD data points of the yield surface for multilayers with layer thickness of 4nm and 14nm. It should be mentioned that in these simulations the shear stress values are negligible comparing to normal stress components. Therefore, the prefactor of the shear component \(\sigma_{12}\), is assumed to be zero; \(n = 0\). In addition, a few modifications are applied to the general Montheillet model to best fit the MD results and the pronounced asymmetry of the observed flow surfaces. These modifications include adding constant values to \(\sigma_{xx}\) and \(\sigma_{zz}\) stress components which bring into account the effect of internal stresses and/or kinematic hardening. With these modifications we obtain the following form for the plastic flow surface for in-plane deformation of NMMs.
\[
\phi = C\alpha_1(\sigma_1 - \sigma_1^*) + \alpha_2(\sigma_2 - \sigma_2^*)^m + \alpha_3(\sigma_1 - \sigma_1^*)^m - \sigma_0^m
\]  
(25)

The parameters appearing in Equation (25) are determined by fitting the surface to the MD results using the software Mathematica, and the results are given in Table 1 below. The fitted surface together with the MD results for the cases of NMMs with 4nm and 4nm layer thickness are shown in Figures 6-14a and 6-14b, respectively. It can be deduced from the figure that the analytical model can accurately describe the MD. The parameters are dependent on the multilayer thickness, since the yield values are dependent on the layer thicknesses. Also, \( \sigma_0 \) is scale dependent as it is expected both from MD simulations and the models defined earlier for the flow stresses.

<table>
<thead>
<tr>
<th>( h )</th>
<th>( C )</th>
<th>( \alpha_1 )</th>
<th>( \alpha_2 )</th>
<th>( \alpha_3 )</th>
<th>( m )</th>
<th>( \sigma_1^* )</th>
<th>( \sigma_2^* )</th>
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<td>1.085</td>
<td>0.029</td>
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</table>

### 6.3 Conclusion

The deformation behavior of nanoscale metallic multilayers with different layer thicknesses, and with fcc-bcc incoherent interfaces, and at different length scales are studied using MD simulations. The results of the simulations were able to capture the underlying deformation mechanisms of NMMs at different length scales. The results elucidate that the
nucleation of dislocations from interfaces on parallel slip planes with less interactions are responsible for softening behavior of such NMMs at tiny layer thicknesses of less than 5nm, while dislocation propagation mechanisms and dislocation accumulation mechanisms at the interfaces and internal grain boundaries are more responsible for the strengthening behavior of NMMs at higher length scales. Activation parameters were calculated to verify the proposed deformation mechanisms specifically at lower length scales where dislocation nucleation mechanisms are proposed to be responsible for the observed deformation behaviors. Building on the fundamental physics of deformation as exposed by these simulations, we established a unique viscoplastic continuum model, able to address the macroscale plastic behavior of bulk NMMs with layer thickness from few nanometers to hundreds of micrometers. Plastic flow potential of the NMMs was acquired by performing MD simulations, applying biaxial in-plane loadings with varying loading ratios. Finally, the yield surface data points well fitted to the known anisotropic Montheillet yield criterion.

The present model is based on the stated results that correspond to a case of NMMs with a specific interfacial orientation and without any interfacial imperfections. Future modeling work will be needed to refine the model for broader cases of NMMs with different interface configurations, which may include the effect of interfacial imperfections or impurities that may be introduced on purpose during deposition or during exposure to harsh environments. The model can be calibrated via micro scale experiments such as micro bulge experiments.\textsuperscript{119, 120}

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Appendix A

\[
M_{ij} = \frac{\partial \phi}{\partial S_{ij}} \sqrt{\frac{2 \phi \partial \phi}{\partial S_{pq} \partial S_{pq}}} \quad (A.1)
\]

Where \( \phi \) is just a function of \( \sigma_{11} \) and \( \sigma_{22} \)

\[
\phi = C \left| \alpha_1 (\sigma_{11} - \sigma_{11}^*) + \alpha_2 (\sigma_{22} - \sigma_{22}^*) \right|^m + \alpha_3 \left| (\sigma_{11} - \sigma_{11}^*) - (\sigma_{22} - \sigma_{22}^*) \right|^m - \sigma_0^m \quad (A.2)
\]

Therefore

\[
M_{11} = \frac{\max_1 \left| (\alpha_{11} - \alpha_1^*) - (\sigma_{22} - \sigma_{22}^*) \right|^m \left| (\alpha_{11} - \alpha_1^*) - (\sigma_{11} - \sigma_{11}^*) \right|}{\sqrt{\left( \max_1 \left| (\alpha_{11} - \alpha_1^*) - (\sigma_{22} - \sigma_{22}^*) \right|^m \right)^2 \left| (\alpha_{11} - \alpha_1^*) - (\sigma_{11} - \sigma_{11}^*) \right|}} \frac{\partial \phi}{\partial S_{11}} \quad (A.3)
\]

\[
M_{22} = \frac{\max_1 \left| (\alpha_{11} - \alpha_1^*) - (\sigma_{22} - \sigma_{22}^*) \right|^m \left| (\alpha_{11} - \alpha_1^*) - (\sigma_{11} - \sigma_{11}^*) \right|}{\sqrt{\left( \max_1 \left| (\alpha_{11} - \alpha_1^*) - (\sigma_{22} - \sigma_{22}^*) \right|^m \right)^2 \left| (\alpha_{11} - \alpha_1^*) - (\sigma_{11} - \sigma_{11}^*) \right|}} \frac{\partial \phi}{\partial S_{22}} \quad (A.4)
\]
References


S. Shao and S. N. Medyanik, Modelling and Simulation in Materials Science and Engineering 18 (2010).


A. Nazari and S. Riahi, Nano 5, 301 (2010).

T. Zhu and J. Li, Progress in Materials Science 55, 710 (2010).


Figure 6-1. a) Nb-Cu bilayer with the lateral dimensions of 49.6×9.7 nm and layer thickness of 4 nm. b) Side view of Cu and nb layers, KS1 crystallographic orientation is shown with (11T)/(01T) slip planes that have most common trace of intersection at the interface plane.
Figure 6-2. a) Atomistic configuration of interfacial atoms, shown according to centrosymmetry parameter. b) Cyclic patterns at the interfacial planes in Nb and c) in Cu layer.
Figure 6-3. Stress-strain curves of the Cu-Nb thin films under uniaxial tensile loading and with different layer thicknesses.
Figure 6-4.a) both layers deform elastically. b) Nucleation of dislocations in Cu layer. c and d) Nucleation and propagation of dislocations in Cu layer while Nb deforms elastically. e) Nucleation of dislocations in Nb layer f) Dislocation activity and plastic deformation in both Cu and Nb layers.

Figure 6-5. Comparison of First and second yield properties, for different layer thicknesses of Cu-Nb multilayers from uniaxial tensile loading and at two temperatures of 0k and 300k.
Figure 6-6. Dislocations in Cu layer at the moment of dislocation nucleation in Nb (2nd yield point) a) h=10nm. b) h=6nm. c) h=4nm. d) h=2nm. Arrows show the interaction of dislocations on different slip planes, indicating the increase of the interactions by decreasing the layer thickness up to the critical thickness of 4nm and then decrease of the interactions below the critical thickness due to the activation of the dislocations on parallel slip planes.
Figure 6-7. a) front b) top view of the 2nm multilayer after initiation of plasticity in both layers. c) front d) top view of the 6nm multilayer after initiation of plasticity in both layers. Different slip systems are being activated below (2nm) and beyond (6nm) the critical thickness. Nucleation of parallel dislocations with less interactions controls plasticity in the softening region.
Figure 6-8. Different deformation mechanisms are being active at different length scales: 

1) Dislocation pile-up where the Hall-Petch relation applies  
2) Confined layer slip (CLS) mechanism  
3) Dislocation nucleation mechanism for small layer thickness.

Figure 6-9. Schematic of the nucleation of parallel dislocations in a Cu-Nb thin film in regime III
Figure 6-10. Second yield properties versus $\ln\frac{\sigma\beta\nu_D}{\dot{\varepsilon}^p h}$ as $h$ varies for different layer thicknesses

Figure 6-11. a) Schematic of the method of applying load to get the plastic potential function. Load first applies on x-direction and then keeping the x-component constant while applying load
on z-direction up to the yielding of the structure b) Typical stress-strain curve, stress on x
 direction is kept constant, $\sigma_{xx} = 3.7\text{GPa}$ while it increases on z direction.

![Graph a) First yield point](image1)

![Graph b) Second yield point](image2)

**Figure 6-12.** Comparison of a) first and b) second yield properties for thin films with layer
 thicknesses of 4 nm and 14nm.
Figure 6-13. The evolution of the yield surface for the NMM with 4nm layer thickness at different strains during deformation and under bi-axial tensile deformation.

Figure 6-14. Flow surfaces as predicted by MD and fitted to the in-plane model for a) layer thickness= 4nm. b) layer thickness= 14nm (the blue line is from MD results and the dashed line is fitted to eq. 25).
CHAPTER SEVEN: SUMMARY AND FUTURE WORK

Deformation mechanisms of nanoscale metallic multilayers (NMMs) are studied in physical details using molecular dynamics simulations. One-dimentional nanowires and nanofoam ligaments as well as two-dimensional thin films with different kinds of interfaces are examined under varying loading conditions. The effect of different parameters such as types of interfaces, temperature, and layer thicknesses are investigated for both kinds of NMMs. The simulation results show fundamentally different deformation mechanisms governing plasticity of NMMs at different length scales and with varying interfaces. In addition, the effects of some types of interfacial disconnections and chemical impurities are explored on the yielding properties of the NMMs.

The results of simulation for nanowires show that below a critical size composite trilayer nanowires deform via twinning and exhibit pseudoelastic behavior. Due to the coupled effects of coherent interface and rectangular geometry of layers, we were able to increase the critical size of showing pseudoelastic behavior to much larger values than single crystalline Cu nanowires. Ni-Au nano ligament of nanoporous foam structures with similar type of interfaces exhibited similar pseudoelastic behaviors analogues to that of Cu-Ni nanowires. The results of our simulations show that the addition of Ni plating layers on Au nanofoams increases the twinning ability of the components of the structure and leads to better ductile behavior of nanofoams. The predicted strength of foams is within 15% of the experimental data for relatively low-density foams.

Next the deformation behavior of thin films with different layer thicknesses, fcc-bcc incoherent interfaces, and at different length scales are studied using MD simulations. The results of the simulations were able to capture the underlying deformation mechanisms of NMMs at different
length scales. The results elucidate that the nucleation of dislocations from interfaces on parallel
slip planes with less interactions are responsible for softening behavior of such NMMs at tiny
layer thicknesses of less than 5nm, while dislocation propagation mechanisms and dislocation
accumulation mechanisms at the interfaces and internal grain boundaries are more responsible
for the strengthening behavior of NMMs at higher length scales.

The effects of disconnections are explored via calculation of interfacial energy maps during
loading. The resultant energy maps show that layer disconnections increase the total energy of
the system due to the extra interface and dislocation strain field contributions. Disconnections
add extra barriers to slip transmission and increase the strength of the interface. Corresponding
stress-strain curves reveal that the barrier strength of the disconnections enhances with increasing
disconnection height up to a certain limit. In another survey the effect of the second phase
particles inside the layers of thin films with incoherent interfaces are explored. The atomistic
simulations showed that addition of precipitates improves the strength of the film by reducing the
free space of the threading dislocations, thus making their motion more difficult. The effect is
more pronounced as the precipitate size increases. An analytical model is developed to verify the
strengthening effect of precipitates based on the energy minimization of a dislocation passing
through a precipitates. The results of the analytical model are in good agreement with both
simulation and experimental results. Similar model with few modifications is used to look at the
effect of the interfacial disconnections.
Based on the fundamental physics of deformation as exposed by MD simulations, we established a unique viscoplastic continuum model, able to address the macroscale plastic behavior of bulk NMMs with layer thickness from few nanometers to hundreds of micrometers. Activation parameters are calculated to verify the proposed deformation mechanisms. Plastic flow potential of the NMMs is acquired by performing MD simulations via applying biaxial in-plane loadings with varying loading ratios. The acquired yield surface from MD simulations well fits to the known anisotropic Montheillet yield criterion with few alterations verifying the high ability of the developed analytical model to address the deformation behaviors of the NMMs with incoherent interfaces.

These kinds of fundamental studies are useful in designing NMMs with desired properties for various applications. Yet the effects of other aspects of interfacial imperfections such as geometry (obtuse or acute) of the ledges or chemical impurities are issues that are needed being examined in more details. The predictive analytical model is built upon the atomistic results of NMMs with specific interfacial orientation and without any interfacial imperfections. Future modeling work are needed to refine the model for broader cases of NMMs with different interface configurations, which may include the effect of interfacial imperfections or impurities that may be introduced on purpose during deposition or during exposure to harsh environments.

Validation and verification of the obtained yield surfaces for Cu-Nb NMMs from MD simulations are yet needed to be carried out by comparing to micro-bulge experiments of Cu-Nb micro-films. The bulge test has the advantage of testing under a relatively homogenous stress states, as opposed to the commonly used non-homogenous loading conditions. A general benefit of the bulge test is the ability to test various film thicknesses while maintaining other
microstructural features constant. Size effects can be investigated as a function of this length parameter, rather than using lateral dimensions. Another feature of the bulge test is that, by simply varying the geometry of specimens we can control the loading conditions such as uniaxial or biaxial with different in plane loading ratios, which is necessary for building up the yield surface. The Stated bulge test is developed at WSU and has been extensively used to test freestanding thin layers and membranes under different loading conditions.

The final goal of this research is to expand the current material model capabilities and implement the proposed model in continuum-based finite element softwares such as ABAQUS. As a result, we can first calibrate the model by comparing the bulge test experiment results to the finite element results. Next, we will be able to investigate complex boundary value problems of structures made of these materials.