The Influence of Architecture and Composition on the Evolution on Thin Films During Sliding Contact

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THE INFLUENCE OF ARCHITECTURE AND COMPOSITION ON THE EVOLUTION OF THIN FILMS DURING SLIDING CONTACT

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Materials Science and Engineering

by
Bradley Matthew Schultz
August 2016

Accepted by:
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ABSTRACT

As surfaces undergo sliding contact, their structure and mechanical properties can evolve or change relative to their as-fabricated state. These shifts can then influence the tribological performance of the system. To understand the extent and implications of these structural and property shifts, this dissertation examines the tribological performance of face centered cubic (f.c.c) metallic films and f.c.c. metallic/ceramic nanolaminates using nanoscale testing methods. Specifically, we sought to (1) understand the influence of deformation zone development to interpret nanowear testing results, (2) quantify the strain hardening exponent in metallic f.c.c. films with and without passivation layers, (3) quantify the impact of ceramic interlayers within f.c.c. metallic layers on the strain hardening relationship and the evolved structure during nano-sliding wear in metallic/ceramic nanolaminates, and (4) identify if (how) the wear mechanisms and wear rates of f.c.c. metallic/ceramic nanolaminates change primarily through altering interfacial density and ceramic composition.

In this work, we quantified changes in mechanical properties (strain hardening, hardness) with nanoindentation when f.c.c monolithic films (Cu and Au) underwent linear reciprocating wear using a range of maximum contact pressures (4.1-14.1 GPa for Cu and 3.3-11.4 GPa for Au) and controlling the separate or overlay between deformation zones (contact and plastic) around parallel pass center points. The hardness for the Cu thin films decreased until the 100 µN wear boxes and increased as the contact pressure increased. The Au thin film wear boxes did not have the same effect. The hardness of the Au thin film remained similar to the as-deposited Au. The morphology of the Cu films did not
have a significant change, but the Au film, with increased contact pressure during wear, there was an increase in wave-like texturing in the worn surface mirroring prior work on single crystal Ni films and gold thin films. Results highlighted the role of deformation zone interaction. As the spacing between parallel passes changed to transition from partial overlap of plastic zones to complete overlap of contact zones, there was also an increase in the worn film’s average hardness. There is a significant difference in the Cu film that is consistent with the empirical model, but there is no trend in the significant difference in the Au film. The percentage of overlap was estimated using empirical models, but not confirmed through structural characterization. This hardness difference between films undergoing sliding with the same contact pressure but different spacing between parallel passes could be due to the hardness test method sampling volumes of material. When the indentations were made within films containing heterogeneous deformation (passes separated by larger distances), the hardness would be lower since some of the volume could not have been modified during the sliding contact. Using only worn samples with the homogenous deformation along the surface (closely spaced passes), we calculated the strain hardening exponent ($n$) of the worn films to be 0.11 for the Cu.

In addition to f.c.c. monolithic coatings, this work focused on f.c.c metallic/ceramic nanolaminate wear. The ceramic interlayers allowed us to better understand the impact of interfacial density, composition of the ceramic layers (TiN), and further investigate the influence of the H/E ratio on wear rate. Nanoindentation results displayed that the as-deposited nanolaminates with increased interfacial density had a higher hardness. Instead of changing the line spacing, the cono-spherical tip diameter and load were changed to
create wear boxes with increasing contact pressures and either one or ten passes. To measure the volume lost due to wear in the nanolaminate systems, AFM was used. For the wear boxes that displayed a distinct height difference between the as-deposited material and the worn region, it was determined that there was no difference in volume loss between the 1 and 10 cycle wear boxes created with the same tip contact pressure. Most of the wear boxes also had a wear rate coefficient > 0.001, which signifies severe wear. The specific wear rates for these nanolaminate samples were higher than the wear rates found by J. Lackner and M. Kot. For the indentation results in the worn regions, there was no statistical difference between the 1 and 10 cycle wear boxes for the samples at each contact stress. In addition, most of the hardness values were not significantly different from the as-deposited material except in the 1 µm/100 nm/RT sample. The flow stress and plastic radial strain were estimated using calculated mechanical properties. From the Hollomon’s relation, it was found that the strain hardening exponent was most effected by the total thickness than any other parameter. The $n$ for the 1 µm coatings was 0.50 and the $n$ for the 3 µm coatings was 0.60 (RT) and 0.64 (500 °C). This signifies that the flow stress will increase higher and faster when more strain is applied to the 3 µm nanolaminates.

The macrowear of the coatings were performed using linear reciprocating dry sliding tribological tests and the post-wear characterized. For coefficient of friction (COF), the steady-state COF decreased as the layer thickness increased. The dominant wear mechanism that was observed for the four nanolaminate coatings varied based on interfacial density. The 20 nm layered coatings displayed dominant wear mechanisms of plowing and wedging, while the 100 nm layered coatings exhibited many asperities relating
to third-body abrasion. During post-wear characterization, it was determined using TEM and EELS that there was a formation of an amorphous titanium layer between the TiN layer below and the remnants of a recrystallized nanocrystalline titanium layer above in the worn region of the 100 nm layered nanolaminate. This effect had not been reported within published literature previously.
DEDICATION

I dedicate this work to my parents, Arthur and Joyce. They have offered me unconditional support and always encouraged me both to make my own decisions and utilize every opportunity to the fullest.
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I would like to first and foremost thank my advisor, Dr. M. Kennedy. Thank you for talking to me when I was a nervous undergraduate at MS&T and giving me the opportunity to be a part of your group here at Clemson. You have allowed me to meet wonderful people and experience great opportunities that I know I would never have had without your help. Thank you for putting up with me when I tested your limits and treating me like a human being. You have been the best advisor and I am a better researcher and person because of you.

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CHAPTER ONE

CONTEXT FOR, MOTIVATION OF, AND OPPORTUNITIES WITHIN TRIBOLOGY
RESEARCH OF METALLIC AND METALLIC/CERAMIC FILMS

1.1. Overview of Dissertation

Many devices have components whose design intentionally or unintentionally results in sliding contact between surfaces. As these surfaces come into contact and move relative to each other, friction and/or wear can occur impacting the device performance. Friction is the force that is resisting the motion of these contacting surfaces relative to each other [1], while wear is a system response to the interactions between multiple surfaces, which potentially results in the removal and deformation of those surfaces [2]. Depending on the desired application, a component or device may be designed for either high or low friction (i.e. high friction of automobile tires on roads to decrease stopping distance or the low friction between ice skate blades and ice to decrease effort by skaters), as well as with high or low wear (examples include the high wear of pencils to facilitate the transfer of writing). The study of friction, wear, and the lubrication within systems is known as tribology [3].

Devices and systems whose operation would involve tribology principles include drill bits, knives, hard drives, microelectromechanical systems, artificial implants. The lifetimes and efficiency depend on the wear and friction during operation. The economic impact of friction and wear stems from both the need for maintenance and the replacement of components [estimated ~$680 billion/year in 2013 (4% of U.S. gross domestic product)] [3, 4]. To lower the economic impact, research teams in industry, academia and, national
laboratories are focused on building foundational knowledge within tribology related to both mechanical loading and materials science.

1.1.1. Intended Contribution of Work to the Scientific Community

By understanding how the structures and mechanical properties affect the wear of protective films, newer and more well designed films can be produced with adequate long-term performance. By improving the lifespan and increasing the wear resistance, the manufacturing industry will have increased savings. The first step in this process it to understand how the strain evolves within monolithic and nanolaminate films. The research outlined in this dissertation will help accomplish this by:

(1) **Quantifying the strain hardening exponent in metallic f.c.c. films with and without passivation layers (Chapter 2)**

In order to elucidate if there is a way to find a more accessible and easy way of determining a change in strain by wear is possible, the calculated mechanical properties from the wear deformed regions were used to estimate the strain hardening exponents. Assessment of both copper and gold films, metallic films typically used within the microelectronics industry, were used to qualitatively access the influence of passivation layers on how strain evolves during wear. By better understanding how testing parameters influence the strain fields below the surface in monolithic metallic thin films, it will allow for researchers to design better films.
(2) To identify if (how) the wear mechanisms and wear rates of f.c.c. metallic/ceramic nanolaminates change primarily through altering interfacial density and ceramic composition (Chapter 3)

To examine how the interfacial density or contact pressure affects the wear and structure of metallic/ceramic nanolaminates, various layered films were produced with different layer thickness (20 nm and 100 nm), total film thickness (1 µm and 3 µm), and ceramic composition. These films had linear reciprocation sliding wear tests performed with various size counterfaces at different loads to produce maximum contact stresses ranging from the ≈ 220 MPa to 30 GPa. This wide range of maximum contact pressures will elucidate how increasing the maximum contact pressure changes the wear rate and wear mechanism in these novel films. By better understanding how metallic/ceramic nanolaminates wear, it will allow for the enhanced design of these films to improve the long-term performance and use these films for practical applications.

(3) To quantify the impact of ceramic interlayers within f.c.c. layers on the strain hardening relationship and the evolved structure during nano-sliding wear in metallic/ceramic nanolaminates (Chapter 4)

To further the work that was initiated in Chapter 2 and 3, the nanowear of f.c.c. metallic/ceramic films were investigated to determine if increasing the interfacial density can be sensed in the change of strain produced. Prior research on metallic/metallic nanolaminates has shown how the strain in these systems are altered by increasing the interfacial density due to the dislocation strengthening mechanisms [5]. Determining how the dislocation impediment in the ceramic layer is crucial in understanding how the interfacial density affects the strain fields produced in these structures. By determining if there is a difference in the strain hardening exponents of each worn coating, it can help
lead to the understanding of how deposition parameters can increase the long-term performance of metallic/ceramic nanolaminates. The wear of the metallic/ceramic films produced in this work will be compared to values in literature to determine if there is a relationship between the hardness to elastic modulus ratio and the wear rate of these systems [6].

1.1.2. Chapter Overview

The objective of this chapter is to summarize the key contributions to tribology and material deformation under normal and lateral loading. Section 1.2 summarizes concepts related to normal loading, while section 1.3 defines wear properties, wear mechanisms, tribological testing, the wear of titanium and its alloys, the tribology of thin films, and ends with the introduction to nanotribology. Finally, this chapter will discuss the applications for hard ceramic coatings (Section 1.4) and a brief summary of the results (Section 1.5).

1.2. Deformation during Normal Loading

Contact mechanics is the study of deformation in solids that are in contact with each other at one or more points [7, 8]. Basic contact mechanics involves the understanding of normal loading, or loading perpendicular to the surface, and the pressures that are associated with these loads and the system properties. The first set of established equations in the field were first postulated by Heinrich Hertz in 1882 [9]. Hertz outlined how the stresses form at the contact of two elastic bodies [9]. Hertz developed a series of
derivations for the contact stresses of various contact geometries during 1880 while studying the influence of elastic deformation on the surfaces of lenses [8].

In order for Hertzian contact to be applicable for a given system, four assumptions are needed: (1) the surfaces are continuous and non-conforming, (2) the strains are small and have similar elastic properties, where both surfaces deform, (3) each solid is considered an elastic half-space, and (4) the surfaces are smooth and frictionless [8]. One of the geometries Hertz calculated was point-on-point contact. The basic solutions to his work of point-on-point contacts can be seen in Equations 1.1-1.4. In order to determine the maximum contact pressure in contacting surfaces, the reduced modulus and system radius has to be calculated. The reduced modulus is estimated by:

\[
\frac{1}{E^*} = \frac{1-v_1^2}{E_1} + \frac{1-v_2^2}{E_2}
\]  

(1.1)

\(E^*\) is the reduced modulus, \(E_1\) and \(E_2\) are the elastic moduli for the two materials in contact, and \(v_1\) and \(v_2\) are Poisson’s ratio for the two materials in contact. In order to determine the system radius, Equation 1.2 can be used.

\[
\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2}
\]  

(1.2)

\(R\) is the system radius and \(R_1\) and \(R_2\) are the contact radii for the two materials in contact. After the system properties have been calculated, they can be used to determine the contact width of the spherical counterface at the surface of the substrate.

\[
a = \left(\frac{3PR}{4E^*}\right)^{\frac{1}{3}}
\]  

(1.3)
$a$ is the contact width of the counterface, $P$ is the normal load, $R$ is the system radius (Equation 1.2), and $E^*$ is the reduced modulus (Equation 1.1). Finally, the maximum contact pressure can be calculated by:

$$p_o = \left( \frac{3P}{2\pi a^2} \right) = \left( \frac{6PE^*}{\pi^3 R^2} \right)^{\frac{1}{3}}$$

(1.4)

where $p_o$ is the maximum contact pressure, $P$ is the load, $a$ is the contact width of the counterface (Equation 1.3), $R$ is the system radius (Equation 1.2), and $E^*$ is the reduced modulus (Equation 1.1).

However, one drawback to the classical Hertzian contact is that adhesion is not taken into account. In the 1970’s, two sets of researchers altered Hertz’s equations to incorporate adhesion. K. Johnson, K. Kendall, and A. Roberts created what is known as the JKR model, which uses a balance between the stored elastic energy and the loss in surface energy [10]. The other adhesive model, the DMT model, was created by B. Derjaguin, V. Muller, and Y. Toporov, after they rejected the JKR model [11]. The DMT model assumes that the contact profile remains the same as with Hertzian contact, but with additional attractive force (van der Waals) interactions outside the area of contact. In 1977, David Tabor investigated the DMT and JKR model and determined that the two theories were the limits of a single theory parametrized by the Tabor coefficient [12]. D. Tabor determined that the JKR theory applies to compliant, large spheres where the Tabor coefficient is large and the DMT theory applies to stiff, small spheres where the Tabor coefficient is small. Similarly to the Tabor coefficient, the Maugis-Dugdale Model is used to clarify differences between the JKR and DMT models and help transition between the
two adhesive models [13]. The equations comparing the Hertz, DMT, and JKR model for pull-off force, contact radius, and deformation can be seen in Table 1.1.

**Table 1.1-** Equations relating the differences in tip pull-off force, contact radius, and deformation between the Hertz model and the two adhesive models- DMT and JKR [14].

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<th>$F_{\text{pull-off}} = F_{\text{ad}}$</th>
<th>Contact Radius <strong>,</strong>***</th>
<th>Deformation ***</th>
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<td>Hertz</td>
<td>0</td>
<td>$a_{\text{Hertz}} = \left(\frac{RF}{E^*}\right)^\frac{1}{3}$</td>
<td>$D_{\text{Hertz}} = \frac{a_{\text{Hertz}}^2}{R}$</td>
</tr>
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<td>DMT</td>
<td>$F_{\text{ad}}^{\text{DMT}} = 2\pi RW_{132}$</td>
<td>$a_{\text{DMT}} = \left(\frac{R[F + F_{\text{ad}}^{\text{DMT}}]}{E^*}\right)^\frac{1}{3}$</td>
<td>$D_{\text{DMT}} = \frac{a_{\text{DMT}}^2}{R}$</td>
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<tr>
<td>JKR</td>
<td>$F_{\text{ad}}^{\text{JKR}} = \frac{3\pi}{2} RW_{132}$</td>
<td>$a_{\text{JKR}} = \left(\frac{R}{E^*}\left[\sqrt{F_{\text{ad}}^{\text{JKR}}} + \sqrt{F + F_{\text{ad}}^{\text{JKR}}}</td>
<td></td>
</tr>
</tbody>
</table><p>ight]\right)^\frac{1}{3}$ | $D_{\text{JKR}} = \frac{a_{\text{JKR}}^2}{R} - \frac{4}{3} \left[\sqrt{F_{\text{ad}}^{\text{JKR}}} a_{\text{JKR}} \sqrt{RE^*}\right]$ |</p>

* - No surface forces $\rightarrow W_{132}=0$

** - Hard to define accurately when small contacts present

*** - Adhesive correction

$W_{132}=\Delta \gamma = \gamma_{13} + \gamma_{23} - \gamma_{12}$

$F_{\text{ad}}^{\text{DMT}}$ and $F_{\text{ad}}^{\text{JKR}}$ are the pull-off forces for the DMT and JKR, $R$ is the tip radius, $W_{132}$ is the surface energy, $a_{\text{Hertz}}, a_{\text{DMT}}, a_{\text{JKR}}$ are the contact radii, $E^*$ is the elastic modulus, and $D_{\text{Hertz}}, D_{\text{DMT}}, D_{\text{JKR}}$ are the deformation constants [14].

One aspect of contact mechanics that is often overlooked is the variation between real and apparent contact area. To the naked eye, the entire observable area that is in contact is perceived to be completely in contact, but most materials are not perfectly smooth and the surface roughness of both components results in only a percentage of the ‘apparent area’ to be in contact to create the ‘real area’ (Figure 1.1). F. Bowden and D. Tabor are credited with this discovery and examined the implications of surface roughness in the field of contact mechanics [15, 16]. Because of the complexity of the real area of
contact, researchers have been working on more multifaceted computational models to take the real area of contact to better determine the properties of the contact mechanics in the system [17].

![Figure 1.1 Schematic of the apparent vs. the real area of contact for two objects in contact. Figure inspired by [18].](image)

1.3. Introduction of Tribology

Wear is a system response to the interactions between multiple surfaces, which results in the potential removal of material and deformation on a surface as a result of the counterface and potential asperities [2]. Wear is a component of the field of tribology, which was defined by Peter Jost in 1966 [3]. Even before the term tribology was coined, researchers have been investigating ways to decrease wear due to the economic burdens that can accompany material loss in industry and manufacturing [3]. It was determined that one third of the world energy resources are spent on overcoming friction forces and wear [19].
Although the term tribology wasn’t created until 1966, the application of tribology has been around for centuries. Early evidence of tribology has been shown with members of the Stone Age crafting tools and creating fire through rubbing of sticks or stones [20] or the creation of the wheeled vehicle in the Middle East and China 5,000 years ago [20]. The first illustrated drawing of a tribologist stems back to the time of the Egyptians, where a laborer was shown pouring a lubricant down in front of a wooden sledge to pull heavy rocks (Figure 1.2) [21, 22].

![Figure 1.2- An Egyptian laborer pouring down lubricant in front of a wooden sledge in order to ease the pulling, circa. 2500 B.C. Reproduced without permission from [21].](image)

The first documented laws regarding tribology were the Laws of Friction. Although first thought to be penned by Amontons (1699), it was discovered much later that Leonardo da Vinci had created these two laws two hundred years prior [20–23]. The two main laws stated that (1) the frictional force is directly proportional to the applied load and (2) the frictional force is independent of the apparent area of contact (apparent vs. real area of contact) [20–23]. A third lesser used law is sometimes added that (3) the frictional force
is independent of the sliding velocity [23], which was created by Coulomb in 1785. The three laws have some exceptions to them depending on what materials are used in the tribological system, the velocity selected, if lubricants are involved, and the normal loads of the counterface on the tested material. For the first law of friction, an exception would be using a very hard material such as diamond or soft material such as Teflon. For the second law of friction, an exception would be an extremely clean and highly polished surface. This exception comes back to the argument of real versus apparent area of contact. The exception for the third law of friction is if a very low or very high speed is used. The friction will be influenced by the speed to gradually increase (slow speed) or gradually decrease (high speed).

A common misunderstanding about the field of tribology is that wear and friction are material properties, when in reality, the properties are a result of a tribosystem. A tribosystem is comprised of all the materials, testing conditions (e.g. velocity, load, and geometry), and environmental (e.g. lubrication, temperature, and humidity) contributions that create a response to change the wear and friction outcome [21, 23]. Every alteration to the tribosystem will have some sort of effect on the outcome of the wear test. As many test parameters as possible are needed to be held constant during testing and closely mimic the application at hand (i.e. loads, environment, etc.) to be able to have comparable results amongst the materials used in the tribological testing.
1.3.1. Wear Properties and Tribological Testing

The coefficient of friction (COF) ($\mu$) is the relationship of the friction force ($F_f$) and the normal force ($N$) applied to the surface [1] (Figure 1.3).

$$F_f = \mu N$$  \hspace{1cm} (1.5)

**Figure 1.3**- Illustration of the frictional force created during sliding.

As mentioned in Section 1.3, the coefficient is unique to the environment and testing parameters, such as material selection, forces, lubrication, surface roughness/finish, and temperature [24]. The COF was originally thought to have been a correlation between the bulk shear strength of the softer material over the hardness of the softer material [25], but due to the variance in friction, modifications were added to factor in surface energy [26] and distance [27]. The new proposed model for COF breaks down the summation of friction into three components: $\mu_d$, $\mu_p$, and $\mu_a$. $\mu_d$ is the component that is due to the deforming asperities, $\mu_p$ is the component that is due to the plowing by the wear particles that are trapped between the sliding surfaces, and $\mu_a$ is the component due to adhesion [27].
The other main wear property that is investigated is the wear coefficient or specific wear rate [2]. These are two different parameters, but can be used in a similar fashion if one wants a unitless parameter index (wear coefficient) or an actual measure of wear (specific wear rate). The wear coefficient can be found from Archard’s Law [28, 29]:

\[ K = \frac{V \times H}{W \times L} \]  

(1.6)

where \( K \) is the wear coefficient (unitless), \( V \) is the wear volume (m\(^3\)), \( W \) is the load (N), \( L \) is the sliding distance (m), and \( H \) is the hardness of the softer surface (Pa). \( K \) is normally used as an index of wear severity [30]. The value for \( K \) usually has a value below 0.001, except for the most severe types of wear. The wear factor, or specific wear rate can be found by [30]:

\[ k = \frac{V}{W \times L} \]  

(1.7)

where \( k \) is the specific wear rate (m\(^3\)/Nm), \( V \) is the wear volume (m\(^3\)), \( W \) is the normal load (N), and \( L \) is the sliding distance (m). Determining the COF and wear rate of a system can be found using various forms of wear testing.

The main question one should ask before selecting what form of testing set-up or what materials to use is “What is the application?” Tribological testing should revolve around this question so that researchers can perform the most optimal wear testing to improve that application for the research or industrial environment. The two main types of sliding and abrasive wear testing are pin/sphere-on-disk [31–34] and linear reciprocating wear testing [35, 36]. The major difference in the two types of testing is that the pin-on-disk method motion remains in one direction in a circular motion (but can reciprocate),
while the linear reciprocating wear testing method will have motion in two different directions over the same location. The tribological tests focus on finding out three properties of the materials being tested: the coefficient of friction (COF) [37–39], cycles until failure [33, 40], and the volume lost/wear rate [41–43]. Figure 1.4 displays diagrams of the two forms of testing. Typically, the opposing surfaces are referenced to by the geometry of the set-up. Depending on the test, the surfaces are often referred to as the ‘counterface’, ‘pin’, ‘ball’, ‘block’, ‘disk’, ‘flat’, ‘wheel’, or ‘sample’ [44], where either one or both surfaces are moving. The respective wear is generally not equivalent for these surfaces. These main types of testing can lead to different coefficient of frictions. One of the main causes behind these changes are the altered wear mechanisms.

Figure 1.4- Schematic of a (a) linear reciprocating wear test and (b) pin-on-disk wear test showing the motion of wear for the counterface on the sample.
1.3.2. *Observed Wear Mechanisms in Relation to Coefficient of Friction*

Wear mechanisms describe how the material is being deformed or removed from the surface. The four main types of wear mechanisms are adhesive wear, abrasive wear, fatigue wear, and corrosive wear [45]. Adhesive wear is due to a localized bonding between two contacting solid surfaces leading to a material transfer [2, 46]. Abrasive wear is the wear created by hard particles or protuberances that are forced against and moving along a solid surface [2, 47]. Abrasive wear is commonly broken up into sub-categories to further describe the type of abrasive wear that is taking place (Figure 1.5). First, the cutting mode is present when cracks propagate in front of the counterface pin and ribbon-like wear particles are formed [18, 48]. Second, wedging mode is present when wear particles are collected on the front of the counterface pin and are ‘wedged’ between the surface and the counterface pin [18, 48]. The last abrasive mechanism, plowing, is present when only plastic deformation occurs and no particles are created [18, 48].

![Figure 1.5](image.png)

*Figure 1.5* - Examples of the three types abrasive wear mechanisms: a) cutting- a steel pin on a brass plate, b) wedging- a steel pin on a stainless steel plate, and c) plowing- a steel pin on a brass plate. Taken without permission from [48].
Next, fatigue wear is the wear of a solid surface caused by fracture that occurs from cyclic stresses applied to a material [2, 49]. Finally, corrosive wear is the material removal as a result of chemical or electrochemical reactions with the environment [2]. These wear mechanisms are not dependent on the contact types between two surfaces [2], such as sliding, rolling, fretting, and slurry wear [45]. Schematics of the four main wear mechanisms can be seen in Figure 1.6.

Figure 1.6- Schematics of the four main types of wear mechanism. Taken without permission from [18].

Often, multiple wear mechanisms will occur simultaneously, but one mode will tend to dominate during different stages of the wear process [27, 50]. These wear mechanisms, along with the material properties, evolve to produce different values of coefficient of friction (Figure 1.7).
Figure 1.7- Schematic of COF ($\mu$) versus the total sliding distance. This figure shows an example of the COF evolution, which can have a total of six stages. The COF is broken into six stages due to how the wear mechanisms evolve during wear. Taken without permission from [27].

It has been postulated by N. Suh and H. Sin that there are six stages of evolution during the wear process (Figure 1.7) [27]. Stage I is controlled by the plowing of the surface by asperities (i.e. protuberances in the small-scale topography of a surface [18]), which is a type of abrasive wear. This is due to the natural contaminated state of the surface. Stage I is followed by a region (Stage II) that is dominated by an increase in adhesion, where the COF slowly starts to rise. Stage II may not exist if the system uses lubrication [27]. Stage III is recognized by a steep increase in slope of the COF. This stage is often referred to as the ‘run-in’. The increase in COF is a result of the rapid growth in the number of wear particles that becomes trapped between the counterface and the sample surface. Next, stage IV is reached when the amount of wear particles entrapped remains constant. If the two surfaces are like-materials or the mechanism for stage V does not influence the friction, then stage IV is the steady-state friction for the system [27]. If this is not the case, stage V occurs where there is a decrease in plowing and deformation, which leads to a decrease in the COF. This can be a result if a hard stationary counterface is slid...
against a soft specimen. The final stage, stage VI, only occurs in the second scenario when the frictional forces level off into a steady-state [27].

1.3.3. Introduction to the Tribology of Titanium and Titanium Alloys

Due to the Kroll process in 1940, industrial production of titanium has increased due to the lower costs and decreased energy for processing [51]. Since the increased availability of titanium alloys in the past 75 years, many product designs have included these alloys due to their high specific strength, relatively light weight (41-45% weight reduction compared to stainless steel components of same dimensions [52]), high corrosion resistance, and biocompatibility [53–57]. Applications for these alloys have included biomedical implants (orthopaedic devices and dental inserts) [53, 58, 59], aircraft and aerospace components (bolted interfaces, pinned joints, and couplings in structural and engine assemblies) [60, 61], automotive components (brake pads) [62], and in chemical process industry (valves) [55].

Although titanium and its alloys (most commonly Ti-6Al-4V [53, 55, 56]) would be ideal candidates for many applications based on their low density, high strength, and corrosion resistance, many studies have also shown that these materials have poor wear resistance [53–57, 62–65]. Titanium alloys poor tribological properties can be accredited to two main factors. The first factor is the low resistance to plastic shearing and low strain hardenability [57]. The second is the low protection of the underlying metal by the surface oxide, which forms due to high flash temperatures induced by friction during dry sliding [56, 57]. During dry sliding, the native oxide layer (usually TiO₂) is easily worn away by
spalling or micro-fragmentation. This native oxide is slow to reform, resulting in a surface vulnerable to more severe wear. Not only does the removal of the oxide layer allow for more wear, but the dissolved oxygen coming from the atmosphere tends to embrittle the matrix, which reduces the mechanical resistance of the material [66]. Understanding the dominant wear mechanisms and wear modes for certain tribosystems will allow researchers to design enhanced alloys and surface treatments to improve the wear or friction response for optimization for the desired application.

The main wear mechanism that takes place with titanium and its alloys is often reported to be galling [56]. Galling is a severe form of adhesive wear between coupling solids, where material from the worn area flow up from one or both surfaces and adherence occurs [67, 68]. With high loads and poor lubrication, when the wear system galls, seizure often takes place. Galling usually occurs in face centered cubic (f.c.c.) metals due to the increased cross-slip than in other standard crystal structures [68]. Hexagonal closed packed (h.c.p.) metals with a high c/a ratio (crystal structure height-to-hexagon base edge) have a low dislocation cross-slip rate and are less prone to galling, but titanium’s ratio is lower, which allows for an increased chance to gall. A visual schematic of galling versus other wear events are shown in Figure 1.8. It should be noted that not all researchers agree that galling is an issue for titanium alloys. When K. Budinski et al. studied a galling-resistant substitute for a silicon nickel alloy, they found that materials mated with Ti-6Al-4V and commercially pure (CP) Ti showed the best resistance to galling (or highest threshold galling stress) [69]. They also showed that Ti-6Al-4V is more galling resistance that CP-Ti.
Figure 1.8- This schematic shows the types of damage on surfaces when a counterface slides along the surface. a) Burnishing: a rubbed area is visible, but only a surface texture change is present, b) Wear: the removal of material can be measured, c) Galling: the material flows up from the surface and macroscopic excrescences are formed, and d) Transfer: the platelets of materials A are adhered to material B. This image is taken without permission from [69].

Literature has shown studies of researchers attempting to alter the material or tribosystem to prevent galling. The amount of galling can potentially be prevented by the following six techniques: (1) allowing for sufficient space between the two components in the wear system (tightly packed components are prone to galling) [70], (2) using adequate lubrication to separate the components [71, 72], (3) coating the components [72], (4) increasing the hardness of the tribosystem component [68, 73], (5) controlling the surface roughness (highly rough finishes increase tendency to gall) [70, 71], and (6) altering the composition of the opposing surfaces [55, 73]. It is common to use ASTM Standard G-98 to compare the relative galling between tribosystems [74]. The research proposed will focus on coating the components and increasing the hardness of the tribosystem component, which will be accomplished by using nanolaminate films.
1.4. Applications of Hard Protective Films

The four most commonly utilized alloys by volume are iron, aluminum, copper, and titanium [75]. Depending on the application, the wear resistance of these alloys used in machinery can be improved by adding hard ceramic films, such as titanium nitride (TiN) [76], titanium aluminum nitride (TiAlN) [77], and silicon carbide (SiC) [78]. While the wear resistance of these films have shown to be superior to their uncoated counterparts, the comparatively low toughness (ability to absorb energy and plastically deform without fractioning [52]) and adhesion energy of the system (i.e. coating and substrate) can result in susceptibility to both cracking and delamination [79].

To increase the reliability of ceramic films, researchers have tended to use three primary methods to improve coating performance: (1) modifying the structure by altering the deposition processing parameters to decrease the number of defects (e.g. pinholes) in the ceramic coating [80], (2) adding a metallic interlayer between the substrate and ceramic coating to block defect (e.g. pinholes, cracks) pathways though the coating to the underlying substrate [81], and (3) producing a lamellar structure within the coating by alternating thin ceramic and metallic layers (i.e. nanolaminates) [82]. An example of a metallic/ceramic nanolaminate deposited at Clemson University is shown in Figure 1.9. The figure displays that a metallic layer is deposited first and is adhered to the native SiO$_2$ layer on the substrate, and the ceramic layer is deposited last and is exposed to the environment.

Nanolaminates are one type of system that has gained attention for preventing pinholes from running throughout the coating [81]. These novel films can be referred to by
multiple different names: multilayers [83, 84], layered composite [85], lamellar structure [86]; but the films will be referred to as nanolaminates for the entire body of work. Nanolaminates are films of alternating sub-100 nm layers, that are comprised solely [87–89] of, or combinations [90, 91] of, metals, ceramics, or polymers. They are being investigated for their improved mechanical properties when compared to monolithic films, such as increased toughness [92]. Their increase in the mechanical properties, specifically the enhanced strength, is due to their high density of interfaces that restrict dislocation motion [82].

![Figure 1.9-](image)

Figure 1.9- Cross section of a Ti/TiN nanolaminate on a silicon substrate that displays uniform 100 nm individual layers separated by distinct interfaces. This image has been marked to show the distinction between three common thickness designations- layer, bilayer, and total film thickness. [93] Layers indicate the thickness of a individual layer, in this instance either Ti or TiN. Bilayer thickness is the thickness of a repeat layers, such as the thickness of both a Ti and TiN layer combined. Total film thickness refers to all the layers deposited within the film.
1.4.1. Tribology of Thin Film Systems

As sliding bodies move across each other, equipment with moving parts can lose their durability and reliability due to wear; thus, researchers have looked to extend the service life by adding films or films to provide wear resistance. These films, or protective coatings, can be a metal, ceramic, or polymer, and generally have a thickness ranging from 1-100 µm. Films that are less than one micron are known as a thin film (or microfilm) and films that are thicker than 100 microns are known as a cladding. Tribological films are developed to improve the performance, reliability, and integrity of aerospace drive systems [94, 95], biomedical applications [37, 96, 97], cutting tools [98], and marine and offshore sites [95]. Since the original use of natural occurring materials for protective coatings (i.e. beeswax, clay) [21, 99], researchers have produced advances in the field by developing better suited materials for different applications and corresponding techniques to coat components at various size scales [18, 21, 22, 99].

As stated earlier, one way that researchers have attempted to increase the reliability of thin films is to deposit an interlayer between the film and the substrate. By adding this interlayer to the coating system, not only does it inhibit pinholes from creating a pathway through the coating to the substrate [81], but depending on the material, it can increase the adhesion between the film and substrate [100]. Certain films have a thickness limit due to the large internal stresses that are created during deposition. Titanium nitride (TiN) has a thickness limit of 6-7 µm due to these large internal stresses, as well as a low adhesion energy to the substrate. By adding a titanium interlayer to the system, the titanium layer allows better adhesion between the ceramic layer and the substrate by adhering to the native
SiO$_2$ layer, as well as decrease some residual stress in the system [100]. Researchers have taken the layering a step further and have found that by increasing the amount of layers, and therefore, increasing the amount of interfacial volume, the residual stress of the film decreases further and allows for a harder and thicker film if desired [101]. One type of layered film that researchers are investigating are nanolaminates (briefly described in Section 1.4.), which are films with alternating sub-100 nm layer. For a portion of the research in this dissertation, there is a strong focus on the tribology of metallic/ceramic nanolaminates.

Primary studies on metallic/ceramic nanolaminates and multilayers (> 100 nm layers) show similar trends for different material systems. For Ti/TiN systems, it was found that as the layer thickness is decreased or the amount of interfacial density is increased, the hardness and the resistance to friction and wear increases [34, 40, 42, 43, 90, 102–105]. It was also shown that increasing the ceramic-to-metallic ratio of layer volume (i.e., 20 nm/20 nm vs. 20 nm/10 nm) increases the hardness and resistance to wear further [102]. Another study found that decreasing the ceramic-to-metallic ratio of layer volume displayed that the erosion rate of the coating decreases, while the abrasion wear rate increases [105]. Adhesion testing, performed by applying a scratch test to an Al/SiC nanolaminate showed that there is a higher critical load in nanolaminate films than in monolithic films [106]. A scratch test is when a single linear line is produced with a constant increasing loading rate [107]. It was stated that the reason the metallic/ceramic nanolaminate showed a higher critical load was because the composite coating provides a compromise of metallic and ceramic properties by having a strong interface and providing
both increased strength and toughness [106]. M. Gomez et al. showed similar results as the Al/SiC with the group’s work on Cr/CrC [108]. Research by Y. Kim et al. [109] and H. Holleck [101] showed opposite trends from each other’s work. While H. Holleck showed there is an optimum interfacial density that displays the best tribological properties, Y. Kim showed that there is a least optimal interfacial density and by increasing or decreasing the amount of layers will decrease the wear volume [109]. Being able to fully understand how increasing the interfacial density of these films influence the wear properties in different applications, will help nanolaminates become a viable option as a protective coating.

1.5. Summary

This multifaceted research project investigates the tribological properties of metallic and metallic/ceramic thin films at the macroscopic and microscopic levels. Being able to understand the amount of strain that is produced by altered sliding wear testing parameters at the microscale is crucial in understanding how the deformation field underneath a worn area evolves at all size scales of wear. Although advanced techniques, such as the neutron source (BL-7 VULCAN) at Oak Ridge National Laboratory or a synchrotron can be used to analyze the stress/strain that is produced under the surface, these techniques are expensive and difficult to access. Being able to sense if there is a change in the strain field in an easy, cheap, and timely fashion would greatly serve to the benefits of the field of tribology and contact mechanics.

Furthermore, not only will understanding the strain produced in monolithic films
be important, but advancing the understanding with more complex systems, such as nanolaminates. Being able to understand how defects, such as layered interfaces, influence the properties of these systems is important to furthering the knowledge of these newer studied systems. Although metallic/metallic nanolaminates have been more thoroughly investigated, metallic/ceramic systems have been gaining interest due to their unique capabilities of having both aspects of the metal and ceramic of which they are comprised.

In addition to understanding the how the monolithic and layered films mechanical properties are altered by a normal load, understanding how the addition of a lateral motion affects the wear properties of these systems. These issues will be investigated by examining the sensitivity of deformation estimated by nanoindentation in nano-worn f.c.c. materials (Chapter 2), characterizing the wear mechanisms as a function of composition and layer thickness in metallic/ceramic nanolaminates (Chapter 3), and understanding the nanowear of metallic/ceramic nanolaminates as compared to literature (Chapter 4). Finally, it will be concluded with the overarching themes and larger implications and the future work that will further the knowledge of this work will be presented (Chapter 5).

1.6. References Cited in Chapter One


106. Singh, D.R.P., Chawla, N.: Scratch resistance of Al/SiC metal/ceramic


CHAPTER TWO
TRIBOLOGICAL PERFORMANCE OF MONOLITHIC FACE CENTERED CUBIC THIN FILMS

2.1. Metal Structures within Electronic Devices and Their Response to Sliding Contact

As the requirements for devices, their subsequent designs, and incorporated materials change, so has the field of tribology. A recent subfield is nanotribology, which explores wear at the nanoscale [1, 2] and is applicable to both microelectromechanical systems (MEMS) and other small scale electronics [3, 4]. Since the dominant wear mechanisms and the magnitude of wear can change significantly with the contact pressure, this work focuses on the nanotribology of materials used within the narrow device subclass - electronics. Some electronic components are designed with the intent that their surfaces will be in contact during use: such as the insertion of electrical connectors onto pads (pins), the arm on the platter (disk) in a hard drive during severe vibration, and certain gears and mirrors in microelectromechanical systems (MEMS) devices.

Since parts of these electrical components can be in sliding contact, their materials may potentially experience wear and eventual failure. The types of wear conditions vary between each electronic component types (connectors, disk drives and MEMS). Electrical connectors often undergo either linear reciprocating wear by the repeated insertion and removal of the plug-in or fretting wear if the system had vibrations during operation (such as Part # 30785, Waytek Inc.). Fretting wear is a type of wear where surface deformation and damage occurs from the contact of solids undergoing small scale reciprocating wear, normally due to vibrations [5–7]. Additionally, hard disk drives have the potential to have
debris interfere with the rapid movements of the read/write arm on the platen (disk), which can result in catastrophic failure in severe conditions (such as Part # 9312067, Best Buy™). A hard drive disk (HDD) is different from a solid state drive (SSD), which can also be used in electronics. Although as SSD does not have moving parts, making it more ideal, the HDD can often have a significantly less cost for the same amount of storage, which is why they are often utilized. Finally, MEMS devices1 to 100 µm, usually consist of a microprocessor attached to actuators or sensors. These devices are often classified into one of four classes [8]: Class I - no moving parts, Class II – there are moving parts, but there is no rubbing or impacting surfaces, Class III – there are moving parts with impacting surfaces, and Class IV – there are moving parts with rubbing and impacting surfaces. Tribological issues with electrical components have been pushing researchers to improve the current technologies.

All electronic devices include a range of material types, often integrating ceramics, metals, and polymers. Material selection for each component is made to maximize performance. Often designers must weight a specific material property higher in their decision-making criteria relative to than other properties. The ranking of properties can be done based on application or the ability of the materials engineer to modify the material property through structure changes (such as grain size or alloying). So, while both copper (Cu) and gold (Au) might have low hardness values (≈ 3.0 GPa and 1.5 GPa, respectively and poor tribological properties, they are often selected for electronic devices due to their relatively high electrical conductivity [9, 10]. For this research, monolithic Cu and Au films underwent tribological testing at the nanoscale to replicate conditions that might be
experienced in connectors or MEMS. However, once the decision is made to include a material, the secondary properties can be optimized. In the case of Cu and Au films, the hardness can be increased through alloying, annealing, and surface treatment.

Since tribology testing should replicate the precise parameters as the material would experience during the product lifetime, new methods and test rigs have been developed. Recent additions have included the utilization of existing instruments like \textit{in situ} atomic force microscopes (AFM) within transmission electron microscopes (TEM) [11, 12] and the use of nanoindenters [13–19]. Researchers have been attempting to replicate the sliding conditions of Class III and IV devices to accurately predict failures and lifetimes [8]. They first predicted and then applied similar contact stresses that are experienced within the actual MEMS to model systems (often thin films). Prior analysis of Class III and IV MEMS devices estimated the contact stresses to range from 10s to 100s MPa [20, 21]. However, these estimates assumed the surfaces were perfectly smooth. Had asperities been on the surfaces, the real contact pressures may be 10 to 100 times larger. One way groups have experimentally simulated the asperity contact within MEMS devices has been to raster atomic force microscope (AFM) tips across surfaces with a high set point (i.e., a measure of force applied by the tip to the sample) [1]. Commercial AFM tips can be purchased with highly uniform radii in a range of sizes for pyramidal or conical geometries (2-100s of nm [22]), which can produce a wide range of contact pressures.

Another characterization system that is now used for small scale tribological studies are nanoindenters [13, 16, 17, 23, 24]. Nanoindenters were originally designed to measure local mechanical properties [25]. Similar to the AFMs, most nanoindenters use a
piezoelectric actuator directly above the probe to control either the load or displacement of the tip, while monitoring the other. These tips are larger than those in AFMs (1-100s of µm) and low load transducers can apply loads from 10-1,000 µN during wear. The small loads and tip geometries can lead to high contact pressures.

The high contact pressures (GPa) of the AFM and nanoindenter overlap more closely with the pressures that are found in individual small contacts in small scale electronics and mimics the fretting wear that takes place during the small vibrations (µm to mm). Increasing the tribological performance of microelectronics has been the driving force into the research of material selection and properties in interconnects [26].

This chapter will investigate the effect of contact pressure and wear overlap on the deformation and mechanical properties of tribological systems involving gold and copper thin films. Empirical models indicate that the strain across these wear boxes can be either uniform or heterogeneous, depending on the contact pressure and wear overlap. This experiment will determine if the strain changes are distinctive enough to vary the calculated hardness from the load-displacement curves of the worn films. The wear boxes produced with altered test parameters are indented with multi-step quasi-static indents to determine the changes in hardness.

2.1.1. Nanowear Testing

One of the most common ways an AFM or nanoindenter are being used for tribological test methods are for wear box formation and analysis. These wear boxes are produced by reciprocating parallel lines of the sliding tips. By altering the film material,
tip load, spacing between reciprocating lines, or the counterface radius, researchers can predict the size of the wear track, the size of the plastic deformation zone, and the overlap of these features during testing. By understanding the overlap of the plastic zone and wear track, researchers can create various amounts of homogeneous or heterogeneous deformation.

2.1.1.1. Types of Nanowear Testing

During nanowear experiments, there are two main types of tests that have been reported previously—scratch testing and wear boxes [27]. During wear box experiments, a hemispherical tip is rastered back and forth, and the tip is in contact with the specimen surface with a known applied load. Once this single line has been traced and retraced, the tip is shifted vertically in the test plane and the process is continued until 256 parallel lines are created, resulting in the shape of a square. By altering the edge length of the wear box (e.g. edge length of 20 µm to 80 µm), the spacing between the 256 lines in the wear box will either increase or decrease. Prior studies have investigated how altering the contact pressure changes the amount of homogeneous or heterogeneous wear that is being created during the formation of the wear box [24], but this work will further the initial investigations by introducing the effect of wear overlap.

2.1.1.2. Prior Nanowear Studies on Metallic Films

Wear boxes produced in Al/Ti nanolaminates by S. Izadi et al. demonstrated the effect of altering the dimensions (or the line spacing) of the box produced. The results
showed that by increasing the edge length of the wear box from 2 µm to 35 µm, the depth of the wear track is increased, therefore the wear rate increases as well [16]. The conclusion was that the smaller wear box had similar dimensions (box width) to the 2 µm diameter cono-spherical tip used during wear. The smaller wear box was formed more from severe plastic deformation due to the extreme high degree of overlap in wear tracks, while the larger wear box volume loss was more attributed to abrasive wear [16]. Based on S. Izadi’s study, the wear box edge length in this chapter’s experiments are all greater than 35 µm, so abrasive wear will be investigated for the dominate wear mechanism for this nanosliding wear application.

In addition to line spacing, the normal loads used during wear and the diameter of the counterface can determine if the wear zones and/or deformation zones will overlap (Figure 2.1). The field of contact mechanics describes deformation within surfaces [28–30]. Researchers within this field focus on understanding the deformation zone/strain that is formed during normal loading [31–38] and how the strain field is altered for directional loading during wear (scratch test) [39–43]. Research by M. M. Chaudhri experimentally demonstrated the strain hardening of bulk Cu. He first deformed the specimen with a large spherical indent and then made small Vickers indents inside and outside the spherical indent [44]. With the small indents, he was measuring the hardness as a function of distance from the apex of the large spherical indent to determine the strain hardening. It was found that the largest strain hardening is located at the base of the indent and that the strain hardening increases as the ratio of contact area to the indenter diameter increases.
The normal load and contact depth at which the plastic zone and contact zone overlap can be determined using an altered Hertz contact stress model. The model is “altered” to include plastic deformation in Equation 2.2 to calculate the contact depth for a more accurate representation of the cono-spherical probe indenting into the surface during wear [28]. The wear track overlap can be determined by solving for the contact radius (Equation 2.1). The different contact pressure and wear overlap combinations were used to vary the deformation between homogeneous and heterogeneous wear in the x and y direction. The contact area (wear track) and plastic zone width were estimated by an empirical model for normal loading. It was assumed that similar strain fields are produced near the surface and the major changes in strain are in front of the moving counterface [39].
Based on the line spacing, once the contact radius is larger than half the line spacing, there is wear track overlap. The contact radius at the surface can be found using [29]:

\[
a = \sqrt{3 \frac{F}{8} \left( \frac{1}{E_1} + \frac{1}{E_2} \right)^{\frac{1}{3}} \left( \frac{1 - \nu_1^2}{d_1} + \frac{1 - \nu_2^2}{d_2} \right)^{\frac{1}{3}}} \tag{2.1}
\]

where \(a\) is the radius of contact, \(F\) is the load, \(\nu_1\) and \(E_1\) are the Poisson’s ratio (0.07) and elastic modulus (1140 GPa) for the counterface (diamond), \(\nu_2\) and \(E_2\) are the Poisson’s ratio (Au - 0.4, Cu – 0.34) and elastic modulus (Au - 79 GPa, Cu – 119 GPa) for the sample, \(d_1\) is the diameter for the counterface (2 µm), and \(d_2\) is the diameter for the sample (due to flat surface, \(d_2 = \infty\)). The depth of the spherical indenter was found using [28]:

\[
h = \frac{1}{2} \left( \frac{P}{\pi R_i H} + \frac{3 \sqrt{P \pi H}}{4 E} \right) \tag{2.2}
\]

where \(h\) is contact depth, \(P\) is normal load, \(R_i\) is the initial tip radius (1 µm), \(H\) is the sample hardness (Au - 1.7 GPa, Cu – 3.5 GPa), and \(E\) is the sample elastic modulus. The overlap in the plastic zone was found similarly to the wear track overlap. To determine the plastic zone overlap, once the sum of the plastic deformation zone and the contact radius was larger than the line spacing, there is plastic zone overlap. In Equation 2.3, the size of the deformation zone can be estimated using Johnson’s cavity model [19]:

\[
c = \sqrt{\frac{3P}{2\pi \sigma_{ys}}} \tag{2.3}
\]

\[
\sigma_{ys} \approx \frac{H}{3} \tag{2.4}
\]

where \(P\) is the wear load, \(\sigma_{ys}\) is the yield strength (approximated by the Tabor relation [30, 45]), and \(H\) is the hardness.
2.1.2. Strain Hardening of f.c.c. Metals

Strain hardening, or work hardening, is the strengthening of a material by the increasing the barriers to dislocation movement through the increased dislocation-dislocation interaction [46–48]. Fundamental studies of strain hardening were performed on single crystal materials. For single crystal f.c.c. metals, there are three main regimes in the stress-strain behavior of the material (Figure 2.2) [47].

![Stress-strain behavior](image)

**Figure 2.2-** The stress-strain behavior for single crystal f.c.c. materials. Figure inspired by [47, 48].

These three regions include easy glide (stage I), linear hardening (stage II), and parabolic hardening (stage III). Before stage I, there is an elastic response where the resolved shear stress is less than the critical resolved shear stress. Stage I occurs when there is a heterogeneous distribution of low energy dislocations. During this stage, the dislocations are only on a single slip-plane, which results in a low strain hardening rate [47, 48]. As the dislocation density increases, there is a transition from stage I to stage II. Stage II has a severe increased slope due to the existence of a uniform dislocation array across the slip systems, which begins to interact with other slip systems [48]. Additionally, there
are clusters of dislocations surrounding cells of low dislocation density, which represents the minimum energy and preferred dislocation configuration. Finally, stage III displays a material with a high dislocation density. In low temperature situations, stacking faults propagate through dense dislocation networks [48]. In materials exposed to high temperature environments, there can also be thermally activated cross-slip that is associated with a decreased in the work hardening slope [48]. Stage I and III are influenced by temperature, composition, and crystal dimension, while Stage II is not and has a value between shear modulus (G)/200 and G/400 [47].

Polycrystalline f.c.c. materials do not display a Stage I and deform similarly to Stage III [47]. The main reason that polycrystalline materials do not behave in a similar fashion as a single crystal is due to the introduction of grain boundaries. By decreasing the grain size diameter, the material is strengthened [46], which prevents the material from experiencing stage I. The grain boundaries act as dislocations which hinder the motion of newly created dislocations or moving dislocations. When discussing polycrystalline thin films, it is important to understand that thin films behave differently than bulk material. It has been shown that thin films can support higher stresses than bulk materials [49] and shown higher strain hardening rates [50, 51] due to microstructure and interface interactions. Additionally, by either decreasing the film thickness or adding a passivation layer, the stress or strain of the film will increase due to the interactions with the dislocations bowing at the restriction of the substrate and passivation layer [50].
2.1.3. Metallic Coatings Used on Electrical Components

The design of electronic devices has been evolving quickly, resulting in the incorporation of new designs and materials. For the very-large-scale integration (VLSI) process, researchers increased the efficiency of integrated circuits by selecting a new material in the mid-1990’s that was more conductive than the currently used aluminum (Al) to minimize the resistance-capacitance (RC) delay [26]. The only three pure metals that have a lower resistivity than Al (2.82*10^{-8} \ \Omega m [9]) are Au (2.44*10^{-8} \ \Omega m [9]), silver (Ag) (1.59*10^{-8} \ \Omega m [9]), and Cu (1.68*10^{-8} \ \Omega m [10]). Of these, Cu was preferred due to its relatively low cost compared to Au and Ag [26]. Before 1997, Cu was not an option for electronics due to the then current deposition techniques. That year, IBM developed an advanced electrodeposition technique called ‘damascene plating’ [52]. This technique is the process of first patterning a dielectric film and then filling patterned pores within the dielectric with Cu [26, 52].

2.1.4. Prior Studies Characterizing Wear of Electronic Metals

Due to the increase in performance of the microprocessors, other types of Cu deposition have been developed to improve the overall properties of the system [26]. One issue with Cu is that it is a soft metal (hardness ≈ 2.9 GPa), so as the thickness of the Cu films decreases, small volume loss due to wear can result in device failure [26]. This issue is not only for microprocessors, but most microelectronics using Cu. With small electronics, small movements and vibrations of the system create the potential for sliding or fretting wear in the Cu [5, 53, 54].
A thorough investigation of the performance of Cu thin films under fretting wear against Cu, glass, and steel was performed by D. Godfrey and J. Bailey [5]. Their findings showed that when fretting wear (scratch length ≈ 150 µm) is occurring between Cu and either Cu, glass, or steel, there is initially either both adhesion and metal transfer or galling that occurs. When galling occurred, there generally was a higher COF (> 1.0) [5]. After the initial run-in during the first 100 cycles, the COF decreases to a steady-state value between 0.5-0.6. The reduction in COF is due to decreased plowing and an increasing concentration of Cu oxide debris around the wear scar [5].

Although Cu is predominantly used in electronics due to its reduced costs, another metal that is often used as a conductive via in electronics is Au. Au is a precious metal that is predominately used in the jewelry, commodities, aerospace, dental and electronics market [55, 56]. According to the World Gold Council in 2015, electronics used around 9% of the annual mined Au [56]. Au is normally used as a coating or a plating over current carrying components, such as electronic connectors, slip rings, and switches [55, 57, 58]. Au is often used in the field of electronics due to its resistance to tarnish and oxidation at room and elevated temperatures, its ability to act as a conductor of heat and electricity, and its capability to form solid solutions with most common metallic elements [17, 55, 57–63].

From a tribological perspective, Au is a relatively soft metal (lower hardness than Cu) (∼ 1.4 GPa) and has a low shear strength [58]. These aspects of Au will normally lead to cold welding (joining by force with no heat [64]) or adhesive wear [58] in both thin films and bulk material. The most common wear mechanism that occurs in Au, especially in electrical contacts, is prow formation [58, 59, 62, 65].
Prow formation is a type of severe adhesive wear that is characteristic of ductile metals that are soft and unlubricated [57–59]. This wear mechanism occurs when unsymmetrical components come into contact and the material of the surface from the sample is transferred to the counterface. The work-hardened metal that is transferred continually grows in volume, while the sample continues to wear by plastic shearing. The counterface itself does not wear during the formation of a prow. Once the prow (material build-up on the surface) is no longer stable, the material is detached from the counterface and is transferred back to the sample as loose or attached debris [58, 59, 65]. Typically, if Au is worn under reciprocating loading, the prow formation will eventually discontinue and rider wear will dominate (a form of abrasive wear) [57, 59]. This is the process of the counterface losing volume due to the accumulation of the work hardened back transferred material on the larger surface during the original pass. An example of prow formation and rider wear is displayed in Figure 2.3.
Researchers have created methods to improve the wear properties of Au by altering the deposition parameters and techniques, improving the adhesion of the Au film to the substrate, and investigating different sliding metal combinations [58]. The most common way that researchers have been trying to decrease the wear rate and friction of Au is to increase the hardness [17, 63, 66] by electrodepositing Au with small amounts of cobalt (Co) or nickel (Ni) for solid solution strengthening or oxide dispersion strengthening [66, 67] or introducing oxide particles [17]. R. Schoepner et al. added various concentrations of ZnO (0.1%-2.0%) was added to gold to see how the wear was affected at the nanoscale (wear boxes with Hysitron TriboIndenter). Their work showed that the adding the ZnO increased the hardness with increases ZnO concentration (∼1.6 to 2.7 GPa). When worn, the COF remained constant with increased ZnO concentration, but the wear volume was
decreased by half from 0.1% to 2.0% concentration [17]. J. Mogonye et al. implanted He ions into Au films to determine how the wear properties changed. The COF and specific wear rates decreased in the implanted Au compared to the as-deposited Au. Due to this result, it was assumed the hardness increased [63].

C. Lo et al. alloyed Au with 3.3 at.% Co and annealed the material from 400-800 °C for 2 hours. The hardness followed a sinusoidal curve where the hardness increased and peaked at 450 °C, then decreased to 700 °C, where it increased again after. C. Lo et al. also attempted to increase the strength by decreasing the grain size of the as-deposited Au from 10 µm to 20 nm [66], which is attributed to Hall-Petch strengthening [68, 69]. Their group found that the Vickers hardness increases from ≈ 50 to 200 [66].

2.2. Experimental Methods

2.2.1. Fabrication of f.c.c. Thin Films

The films produced in this study, Cu and Au, have a f.c.c. structure. For the Cu, a 1 µm film was deposited by magnetron sputtering onto (100) Si wafers (n-type, < 2 Å roughness, Wafer World Inc.) using a 99.999% pure Cu target. There was a native surface oxide layer and a 5 nm niobium (99.99% pure) layer for adhesion. The film was deposited at Clemson University using a Kurt J. Lesker sputter deposition system under a base pressure of 1.0 x 10^{-6} torr and a working pressure of 9.5 x 10^{-3} torr, with 100 W DC for Cu and 200 W RF for Nb yielding rates of 4.0 nm/min (Cu) and 2.8 nm/min (Nb) [70].

A 3 µm Au film was fabricated by magnetron sputter deposition onto (100) Si wafers (n-type, < 2 Å roughness) using a 99.99% pure Au target. There was a native
surface oxide layer and a 10 nm titanium layer for adhesion. The Au film was deposited at the Center of Integrated Nanotechnologies (CINT) at Los Alamos National Laboratory (LANL) by Mr. J. K. Baldwin with an AJA International Inc. electron beam evaporator. The film was deposited at room temperature with a base pressure of $5.0 \times 10^{-9}$ torr, a working pressure of $7.0 \times 10^{-7}$ torr, and a deposition rate of $10 \text{Å/sec}$. The deposition rate and thickness was monitored by a Sigma quartz crystal monitor.

2.2.2. Pre- and Post-Wear Characterization

The average surface roughness and average grain size of the as-deposited Cu and Au thin films were characterized using an AFM (Veeco Dimension). Five AFM height scans (2 µm x 2 µm for Cu and 1 µm x 1 µm for Au) were collected for each sample with seven lines used for calculating the grain size of each image, which were then used to calculate the average and standard deviation of grain size. Electron microscopy micrographs were taken using the Hitachi S-4800 Field Emission Scanning Electron Microscope (FE-SEM). Out-of-plane X-ray diffraction (XRD) was performed on the Au and Cu films using a Scintag XDS2000 powder diffractometer. To obtain a higher resolution image of the wear box and to measure their surface roughness, the Olympus OLS4000 Laser Scanning Microscope was used. To investigate the wear boxes surface feature and edges, a Veeco (Digital Instruments) Enviroscope AFM was used.
2.2.3. Nanowear Testing

A cono-spherical diamond counterface was rastered across the thin films surfaces to replicate unlubricated sliding wear. Nanowear boxes were produced using the Hysitron Triboindenter 950, using a 2 µm diameter cono-spherical diamond tip at 40 µm/sec and 256 lines (512 due to trace and re-trace). Different loads and line spacing combinations were used to vary the deformation between homogeneous and heterogeneous wear in the x and y direction. The single pass wear boxes were made with three different center-to-center line spacings with 156 nm, 234 nm, and 313 nm. These line spacings were created by producing wear boxes with edge lengths of 40 µm, 60 µm, and 80 µm. Different loads were applied (25, 50, 100, 200, 400, 600, 800, and 1,000 µN) to simulate a range of contact pressures. Between each wear box created, the 2 µm cono-spherical tip was cleaned (removal of debris) by performing three 10,000 µN quasi-static indentations into single crystal Al. The contact area (wear track) and plastic zone width were estimated by an empirical model for normal loading that is outlined in Section 2.1.1.2. Although the magnitude and vectors of the strain field are altered in the direction of the moving counterface, this model assumes that the strain field produced is symmetrical [39].

2.2.4. Cleaning of Cono-Spherical Probe

As stated in Section 2.2.3., the cono-spherical probe was cleaned with three 10,000 µN indents into the Al standard. The cleaning was performed due to the creation of third body particles and/or adhesion of the film to the cono-spherical diamond probe during wear. Figure 2.4 demonstrates the build-up of debris on the wear tip. These results show
that the first indent always has a statistically lower hardness than the following two indents in the set. This is due to the adhered materials during the creation of the wear box being transferred from the tip to the sample during the first indent. Hardness is the relation of the load to the contact area. As the contact area increases due to the particles on the counterface, the hardness will decrease. Similar results can be seen with the cleaning between the Cu wear boxes as well. In Figure 2.4, the indent set reference number refers to the three indents performed after each sequential fabricated wear box (30).

**Figure 2.4**- The figure illustrates the hardness of the cono-spherical nanoindentation probe used for nanowear in the Al standard during the cleaning of the tip between wear boxes. The first indent of each indent set (reference number is for the 30 wear boxes) has a statistically lower hardness due to the Au asperity build up that is on the probe. As the area of contact increases, the hardness will decrease, which can be observed in the first indent in each cleaning set. The material is removed from the tip in the first indentation and presents a higher hardness for the remaining two indents.

The material is not removed from the tip, but instead, it is displaced higher ≈ 2 µm from the tip (Figure 2.5). The adhered material is raised high enough to where it should not interfere with the next wear box, but no *in situ* imaging was performed to verify this.
The wear boxes are being created with a max normal load of 1,000 µN, while the cleaning indents are being performed with 10,000 µN, so the contact depth for the cleaning is larger than for the wear boxes. In Figure 2.5b, the probe has been cleaned with a cotton swab and acetone.

Figure 2.5- a) Micrograph of the probe after the wear boxes were created with adhered wear debris. b) Micrograph after of the probe after being cleaned with a cotton swab with acetone. c) Micrograph of the cleaned probe at higher magnification.

2.2.5. Indentation of Monolithic Films

To monitor mechanical properties changes due to the sliding contact, a nanoindenter was used to measure the load-displacement response at set depths (Berkovich tip) and these results were used to calculate the hardness and elastic modulus [25]. All of the indents had a 10 µm spacing between each other to avoid any interaction between the adjacent deformation created by the previous indent. The number of load-displacement measurements was maximized for the three different edge length wear boxes. For the wear box with an edge length of 40 µm, there was a three by three indentation grid, for an edge length of 60 µm, there was five by five indentation grid, and for an edge length of 80 µm, there was a seven by seven indentation grid.
2.2.5.1. Nanoindentation Testing Parameters for the Gold Film

For the indents in the Au thin film, there was a 15-step load controlled indent where the max loads for each step went from 200 to 3,000 µN with a 200 µN step increase and a 50% unload after each three second hold. The indents loaded and unloaded at a rate of 1,000 µN/sec. The use of the 15-step indent was to obtain multiple hardness values as a function of depth.

2.2.5.2. Nanoindentation Testing Parameters for the Copper Film

Due to the 1 µm thickness of the Cu film, there was only a 10-step load controlled indent where the max loads for each step went from 200 to 2,000 µN with a 200 µN step increase and a 50% unload after each 3 sec hold [71]. An example of the 10-step indent is shown in Figure 2.6. The maximum load used for the Cu Film indents was decreased compared to the Au Film is because the indentation depths should normally not exceed greater than 10% of the total film thickness due to a potential influence of the substrate on the measured load-displacement of the tip [72, 73]. Indents that were observed by optical microscopy after to not be within the wear box region were removed from analysis.
Figure 2.6- All experiments were performed with a load-controlled 10-step indentation sequence used to characterize the Cu thin film. The loads increased by 200 µN for each step, have a 3 second hold at each load, and a 50% unload after each hold. This pattern was the same for the Au thin film with an addition five steps that followed the same trend.

2.2.6. Statistical Analysis of the Nanoindentation Steps

To determine if there is a significant difference between the hardness values for each step during nanoindentation (Figure 2.6), statistical analysis was performed to compare the step values. Based on if there is an influence of the prior step on the mechanical properties of the following step, the different cycles of loading and unloading can be deemed either dependent or independent. If the steps are dependent, it would represent that the deformation created by step 1 influences the mechanical properties of step 2, and so on. If this were the case, a block t-test analysis would be used to compare the steps, which analyzes the difference between the steps (i.e., analysis of step 2 minus step 1 for all of the indents). An independent effect results in no influence of the steps on each other and each step can be treated as an independent static indent. For independent steps, a student t-test would be used to compare the individual steps (i.e., step 1 vs step 2).
Based on the results, we have determined that the steps are independent of each other. After each step, there is a 50% unload before the next loading segment of the 10 or 15-step indent process. During the unload-load, there is complete overlap (Figure 2.7), representing that there is a completely elastic response. This elastic response represents that the next loading will occur at the same location of the prior unload. If there was more of a loop, it would display a viscoelastic rebound and would result in a different amount of dislocations being produced, effectively changing how the next loading period would indent into the material [74, 75]. Since the overlap is independent, the step with the maximum indent depth (final step), should have the same contact depth as a quasi-static single indent with the same contact depth, which was confirmed with experimental testing.

![Load-Displacement Curve](image)

**Figure 2.7**- The load-displacement curve of a 15-step indent into the gold film. The complete overlap in the load/unload portion represents that each step can be treated as an independent indent.
2.2.7. *Empirical Determination of Wear Overlap*

The normal load and contact depth at which the plastic zone and contact zone overlap were determined using an altered Hertz contact stress model (Table 2.1). The overlap of the plastic zone and contact zone can be determined using Equations 2.1-2.3. The model displays that the plastic zone overlap occurs at shallow depths. For this model to be effective, it is assumed that the surface is perfectly smooth, but due to the surface roughness of the films, these depths may be slightly different.

**Table 2.1** - This table displays at what load is required for wear track and plastic zone overlap for various wear box size. The associated depth at the load is listed on the right. Assumptions: 2 µm conical diamond tip against Cu [E=119 GPa, H=3.5 GPa, v=0.34] or Au [E=79 GPa, H=1.7 GPa, v=0.4].

<table>
<thead>
<tr>
<th>Material</th>
<th>Predicted Edge Length (µm)</th>
<th>Line Spacing (nm)</th>
<th>Plastic Zone Overlap</th>
<th>Contact Zone Overlap</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Load (µN)</td>
<td>Depth (nm)</td>
</tr>
<tr>
<td>Cu</td>
<td>40</td>
<td>156</td>
<td>5.3</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>234</td>
<td>13.0</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>313</td>
<td>27.1</td>
<td>3.0</td>
</tr>
<tr>
<td>Au</td>
<td>40</td>
<td>156</td>
<td>2.8</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>234</td>
<td>7.2</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>313</td>
<td>13.6</td>
<td>2.6</td>
</tr>
</tbody>
</table>
The model used to determine the plastic zone and contact zone overlap can be further used to determine if there will be no interaction between the parallel passes, only a plastic zone interaction, or both a plastic and contact zone interaction. The interactions between the parallel wear passes are shown in Table 2.2. Using a 2 µm diameter cono-spherical, the contact pressures are slightly lower in the Au thin film due to the lower hardness of Au compared to Cu. A visual presentation of the wear track and contact zone interaction is Cu is shown in Figure 2.8.

**Table 2.2**- Matrix of selected loads and used line spacing combinations for the nanowear of Cu and Au. White box shading indicates there was neither wear track or plastic zone interaction. The light gray shading indicates that there was a plastic zone interaction between parallel passes but no wear track interaction. The dark gray shading indicates both a plastic zone and wear track interaction. '*' indicates that indents were performed inside wear box.
2.3. Results and Discussions

2.3.1. Analysis of Copper Results

2.3.1.1. As-deposited Structure and Properties of f.c.c. Monolithic Copper Films

The as-deposited mechanical properties for the Cu thin films are similar to properties that are found in literature and the hardness is significantly lower than the hardness of the silicon (Si) substrate they are deposited on (H - 9.0 GPa). The mechanical properties of the films are shown in Table 2.3.
Table 2.3- The mechanical properties determined by static nanoindentation and surface properties determined by AFM are shown in the table below for the as-deposited films.

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface Roughness (nm)</th>
<th>Average Grain Size (nm)</th>
<th>Elastic Modulus (GPa)</th>
<th>Hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>24.1 ± 2.2(^a)</td>
<td>122.2 ± 7.9(^a)</td>
<td>122.3 ± 14.4(^b)</td>
<td>2.9 ± 0.1(^b)</td>
</tr>
</tbody>
</table>

\(^a\)Taken from five 2 µm x 2 µm AFM scans
\(^b\)Taken from as-deposited steps 2 through 7

The Cu thin film has a dominant orientation of (111), but also displayed CuO and Cu\(_2\)O oxide layers (Figure 2.9). Literature has shown that there are a ≈ 1.3 nm thick CuO layer and a ≈ 2.0 nm thick Cu\(_2\)O layer that are formed in ambient air on top of Cu [76], which XRD confirms the presence of both.

Figure 2.9- Diffraction pattern of the Cu thin film. There was an oxide layer observed on the surface.

2.3.1.2. Characterization of Copper Wear Boxes

All of the wear boxes that had nanoindentation performed in the deformed region are shown in Figure 2.10 for the Cu thin film. The profilometry results of the wear boxes investigating the surface roughness of the wear boxes are shown in Table 2.4. Only the as-
deposited Cu, a middle load wear box (400 µN), and the max load (1000 µN) are displayed to show how the surface roughness evolves as the load during wear is increased.

**Figure 2.10** - Optical micrographs of the wear boxes produced in the Cu thin films. The top row has a line spacing of 156 nm, the middle row has a line spacing of 234 nm, and the bottom row has a line spacing of 313 nm.

**Table 2.4** - Roughness and surface feature measurements calculated by a laser profilometer. ‘ASD’ stands for as-deposited, ‘LS’ stands for line spacing, ‘Sa’ represents the arithmetic average roughness, ‘Sq’ represents the root mean squared roughness, ‘Sp’ represents the maximum peak height, ‘Sv’ represents the maximum valley depth, and ‘Sz’ represents the average distance between the max peak and max valley.

<table>
<thead>
<tr>
<th>Cu</th>
<th>ASD</th>
<th>156 nm LS</th>
<th>234 nm LS</th>
<th>313 nm LS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Load (µN)</td>
<td>0</td>
<td>400</td>
<td>1,000</td>
<td>400</td>
</tr>
<tr>
<td>Sa [nm]</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Sq [nm]</td>
<td>3</td>
<td>2</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Sp [nm]</td>
<td>200</td>
<td>20</td>
<td>49</td>
<td>52</td>
</tr>
<tr>
<td>Sv [nm]</td>
<td>88</td>
<td>11</td>
<td>25</td>
<td>101</td>
</tr>
<tr>
<td>Sz [nm]</td>
<td>287</td>
<td>30</td>
<td>74</td>
<td>153</td>
</tr>
</tbody>
</table>

The profilometry results for the Cu indicate that the roughness and the root mean square are not changed compared to the as-deposited material. The maximum peaks decrease when a load is applied, but the maximum valleys increases as the load is increased, signifying that there potentially is texturing in the Cu wear boxes, but not verified.
2.3.1.3. Mechanical Properties of Nano-Worn Copper Thin Films

The average hardness vs. the average contact depth is shown in the collage of graphs (Figure 2.11). The graphs display two different ways of analyzing the data. Figures 2.11a, 2.11b, and 2.11c can be used to investigate the hardness changes in the line spacing and wear overlap as a function of contact pressure. All three loads show multiple similar trends: (1) the hardness decreases as the line spacing increases, (2) there is a softening effect for the lower loads compared to the as-deposited specimen, and (3) there is a significantly different decrease in hardness in the initial and an increase in hardness in the final steps.
Figures ‘a’, ‘b’, and ‘c’ are comparing the hardness for the different line spacings at each load, while Figures ‘d’, ‘e’, and ‘f’ are comparing the hardness for the different loads at each line spacing. ‘a’, ‘b’, and ‘c’ show that by decreasing the line spacing, the hardness increases and ‘d’, ‘e’, and ‘f’ show that increasing the normal load during wear increases the hardness. ‘WT’ and ‘P-zone’ represent wear track and plastic zone overlap, respectively.
The hardness decreasing as the line spacing increasing should be due to the change in heterogeneous deformation that is taking place during the wear. For the decreased line spacing, there is more overlap between the wear tracks, compared to the increased line spacing where only the plastic zones may be overlapping.

The softening effect for the lower loads compared to the as-deposited materials was a surprise to the researchers, but is potentially due to an alleviation in residual stress that was built up during deposition. This reduction in residual stress may have allowed for a decrease in hardness compared to the as-deposited material. For the third trend, the decrease in hardness in the initial steps may be a result of two things—either the surface effects or an induced strain during wear. The increase in hardness in the final steps is due to the depth of the indent being below the 10% thickness mark and creating substrate effects in the hardness. In addition to the hardness, the average modulus for these data sets was compared to the average contact depth (Figure 2.12). Apart from the initial step (contact depth < 40 nm), which has surface effects altering the modulus, there is a linear trend in the elastic modulus where it increases with increasing depth.
Figure 2.12- The average modulus of the 25 µN, 200 µN, and 400 µN wear boxes for the three line spacings. Apart from the shallow indents, the elastic modulus increases with contact depth. The trend is similar for all of the Cu wear boxes. The modulus at the first step (contact depth < 40 nm) are inaccurate due to surface effects.

Figures 2.11d, 2.11e, and 2.11f can be used to investigate the average hardness for all of the created wear boxes at each line spacing. All of the figures show similar trends to Figures 2.11a, 2.11b, and 2.11c, with the addition that ≈ 400 µN, the hardness of the wear box exceeds the hardness of the as-deposited material.

Due to the decreasing hardness in the initial steps and the increasing hardness in the final steps, statistical analysis was performed to determine if there was a difference between the hardness at each step. As determined in section 2.2.6, the steps are intendent of each other. As a result, student t-tests were used to calculate if there was a significant difference between each step. JMP Pro was used for the analysis of the hardness values with a level of significance of 0.01. The results are shown in Table 2.5.
Table 2.5- Determination of a statistical significant difference between each step for each of the loads and line spacing for the Cu wear boxes. At each step, the probe indents further into the surface. An ‘*’ indicates that there is a significant difference (p < 0.01). The differences were determined using a t-test.

<table>
<thead>
<tr>
<th>Line Spacing</th>
<th>Load during Wear (µN)</th>
<th>1v2</th>
<th>2v3</th>
<th>3v4</th>
<th>4v5</th>
<th>5v6</th>
<th>6v7</th>
<th>7v8</th>
<th>8v9</th>
<th>9v10</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited</td>
<td>25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>156 nm</td>
<td>25</td>
<td>*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td></td>
<td></td>
<td>*</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>*</td>
<td></td>
<td></td>
<td>*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>200</td>
<td></td>
<td>*</td>
<td></td>
<td></td>
<td>*</td>
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The purpose of the statistical analysis was to determine if there was a step-like trend in the significant different for the increasing contact pressure during load. The statistical analysis results display that as the load during wear is increased and the wear overlap is decreased, then there is more significant difference in the hardness as a function of contact depth.

Based on the as-deposited material changes in hardness due to the surface effects and the substrate effects (indents > 100 nm), steps 1 and 8-10 were removed from further analysis. The averages of the remaining steps were grouped together and averaged compared to the other wear boxes. In Figure 2.13, the averages of the hardness of the non-
influenced indents were compared to the as-deposited material by line spacing. The solid black line in Figure 2.13 represents the average hardness of the as-deposited material with a dashed black line above and below representing one standard deviation. If there is a star underneath an average hardness for a wear box, it indicates that the hardness is significantly different than the as-deposited material.

**Figure 2.13** - After removal of indents influenced by the substrate and surface effects, the average hardness of all of the indents are displayed. The solid black line is the average for the as-deposited Cu and the dotted line is one standard deviation. The star represents that the average is significantly different than the as-deposited hardness.

These results more clearly display the trends that were observed in Figure 2.11. The first trend displays that the hardness is higher for a decreased line spacing. The second is after these is a decrease in the hardness in the initial wear boxes, the hardness increases as the load during wear increases. At lower loads, there is softening of hardness compared to the as-deposited material. As the residual stress built up during deposition is being relieved, there is the possibility that the hardness will decrease until an optimal point in relaxation is achieved. Once the optimal load is used, in this case 100 µN, the hardness
will increase where it can exceed the as-deposited material, which is approximately 400 µN for the Cu thin film.

Additionally, it was statistically found that there is a difference in hardness between the spacings as empirically determined in Table 2.2. The 313 nm line spacing sample was different than the 156 nm and 234 nm in the wear boxes produced with 25 µN and 400 µN. Also, the 156 nm line spacing sample was different than the 234 nm and 313 nm in the wear boxes produced with 200 µN. These differences show that the spacing creates a difference in overlapping wear track and plastic zone created during wear.

2.3.1.4. Estimated Strain Hardening Relationship in Copper Thin Films

In order to further investigate the deformation that was produced during nanowear, the stress and plastic strain were estimated using material constants and calculated properties from the nanoindentation results. Since the statistical analysis from the nanoindentation did not reveal any significant trends to display that the deformation during wear was altering the strain field underneath the wear box, the strain hardening exponent for each of the wear boxes was calculated to determine if the estimated strain can show how the as-deposited material is being affected by wear. The stress and strain were estimated using Equations 2.4 and 2.5. The plastic strain can be estimated by [15, 77]:

\[
\varepsilon_r^p = -2(1 - \nu) \frac{\sigma_{ys}}{E} \left[ \frac{c^3}{r^3} - 1 \right]
\]

(2.5)

where \( \varepsilon_r^p \) is the plastic radial strain, \( \nu \) is the Poisson’s ratio, \( E \) is the elastic modulus, \( c \) is the deformation zone that is calculated in Equation 2.3, and \( r \) is the indentation depth. These two estimated material properties determined from Equations 2.4 and 2.5 can be
plotted to represent the Hollomon strain hardening relation to allow for the extrapolation of the strain hardening exponent of each wear box [46]. This power law relationship can be seen in Equation 2.6:

\[ \sigma = K \varepsilon^n \]  \hspace{1cm} (2.6)

where \( \sigma \) is the yield stress (Equation 2.4), \( K \) is the strength coefficient, \( \varepsilon \) is the plastic strain (Equation 2.5), and \( n \) is the strain hardening exponent. \( K \) and \( n \) are constants that are modeled from a power law relationship. The strength coefficient is numerically equal to the extrapolated value of the true stress of a true strain at 1. The strain hardening coefficient shows the ability of a metal to strain harden, where the larger the value, the greater the amount of strain hardening for the determined plastic strain [46]. The strain hardening coefficient will not only change from alloy to alloy, but also due to microstructural effects of the material (grain size, bulk vs. thin films, etc.). Most \( n \) values range from 0.2-0.4 for bulk metals, where annealed Cu has a strain hardening coefficient of 0.44 [46].

The results calculated from nanoindentation were used to determine the estimated strain that was induced on the material from the nanowear boxes to better understand the effects of wear deformation. Using Equations 2.3, 2.4, and 2.5, the yield stress and plastic strain were calculated to estimate the strain hardening exponent and strength coefficient. The indent values that were used are steps 2-7, which were calculated not to have surface or substrate effects altering the values. The strain hardening exponent and strength coefficient values are displayed in Figure 2.14.
The strain hardening exponent was found to be greater in the wear boxes than in the as-deposited material. This finding is understandable due to the generated dislocations due to the deformation. The as-deposited material has a strain hardening exponent of 0.05, while the strain hardening exponents of the wear boxes ranged between 0.06-0.12. These values are all lower than the standard metallic stain hardening exponent of 0.2-0.4 and for bulk annealed Cu (0.44) [46].

In addition to investigating the strain hardening exponent, the strength coefficient increases with increasing load during wear (Figure 2.13b). The strength coefficient increases with increasing load because the hardness increases with increasing load during wear. $K$ is an extrapolated value of the true stress of a true strain at 1. Based on a re-arranged Hollomon relation, if:

$$K = \frac{\sigma}{e^n} \tag{2.7}$$
where $\epsilon^n$ is equal to 1, then $K$ would be proportion to the stress, which is correlated to $H/3$ (Equation 2.4). Also, all of the stress vs. strain points for each indent were plotted and compared for each overall line spacing and all the collective indents. Figure 2.15 shows that the 234 nm line spacing and the 313 nm line spacing stress-strain overlap, while the 156 nm line spacing has a different slope. The strain hardening exponent is the slope of these lines, where $K$ is the intercept of a plastic strain of 1. Since the as-deposited material had a $n$ value of 0.045, the line would be almost horizontal, which represents that the worn material has a greater plastic strain.

![Graph showing stress-strain curves for different line spacings](image)

**Figure 2.15-** Comparison of strain hardening relationships for the three different line spacings. The 234 nm line spacing and 313 nm line spacing are overlapped. The change in $n$ is the result of the change in slope for the 156 nm line spacing wear box.

2.3.2. **Analysis of Gold Results**

2.3.2.1. **As-deposited Structure and Properties of f.c.c. Monolithic Gold Films**

The as-deposited mechanical properties for the Au thin film are similar to properties that are found in literature and the hardness is significantly lower than the hardness of the
silicon (Si) substrate they are deposited on (H - 9.0 GPa). The as-deposited structural (AFM) and mechanical properties (nanoindentation) of the Au film are shown in Table 2.6. Although the Au thin film displayed a low surface roughness ($R_a$), the Au film had abnormal grain growth that produced elevated asperities that interfered with wear and indentation. These abnormal grains are shown in Figure 2.16. The growths were found to be up to $\approx 2.5 \, \mu m$ in height and $\approx 2.0 \, \mu m$ in width.

**Table 2.6**- The mechanical properties determined by static nanoindentation and surface properties determined by AFM are shown in the table below for the as-deposited films.

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface Roughness (nm)</th>
<th>Average Grain Size (nm)</th>
<th>Elastic Modulus (GPa)</th>
<th>Hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>$8.7 \pm 2.1^a$</td>
<td>$89.0 \pm 13.0^a$</td>
<td>$99.3 \pm 13.3^b$</td>
<td>$1.4 \pm 0.3^b$</td>
</tr>
</tbody>
</table>

$^a$Taken from five 1 µm x 1 µm AFM scans

$^b$Taken from as-deposited steps 2 through 15

**Figure 2.16**- Micrographs of the as-deposited Au. The ‘asperity-like’ growths are abnormally grown grains during deposition. The grains were measured to be up to $\approx 2.5 \, \mu m$ tall.

To determine the crystallinity and orientation of the Au film, XRD was performed. Figure 2.17 displays that the Au film had two dominant orientations. Both the (111) and (200) have similar intensities, displaying that the Au is potentially more textured due to the lack of one dominant orientation.
2.3.2.2. Characterization of Gold Wear Boxes

The effect of load during wear can be more predominantly seen in the Au thin film in Figure 2.18. As the load is increased from left-to-right, the wear box becomes more visually defined and the abnormal grains are worn away to appear to have more of a flattened surface. Although the surface roughness is lower in the Au thin film, according to the AFM scan results in Table 2.6, when a larger area is sampled, the Au has a higher roughness. This is due to the larger area of analysis. For the AFM, the Au was only analyzed with a 1 µm by 1 µm scan size, where no asperities were scanned. For the profilometry, a larger area was scanned with many asperities being imaged. In Table 2.7, laser profilometry scans were performed on the as-deposited material, as well as the wear boxes made at 400 µN and 1,000 µN for each wear box line spacing, are shown. Although only the as-deposited, 400 µN, and 1,000 µN results are shown, there is a similar trend for all of the wear boxes at each load and line spacing. 400 µN is the closest to the median load, so it is displayed as a comparison between the no deformation and the highest load.
Figure 2.18- Optical micrographs of the wear boxes produced in the Au thin films. These micrographs illustrate that as the load is increased, the wear box becomes more pronounced and the surface appears smoother. Scale bar is 40 µm.

Table 2.7- Roughness and surface feature measurements calculated by a laser profilometer. ‘ASD’ stands for as-deposited, ‘LS’ stands for line spacing, ‘$S_a$’ represents the arithmetic average roughness, ‘$S_q$’ represents the root mean squared roughness, ‘$S_p$’ represents the maximum peak height, ‘$S_v$’ represents the maximum valley depth, and ‘$S_z$’ represents the average distance between the max peak and max valley.

<table>
<thead>
<tr>
<th>Au</th>
<th>Load (µN)</th>
<th>ASD</th>
<th>156 nm LS</th>
<th>234 nm LS</th>
<th>313 nm LS</th>
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<tbody>
<tr>
<td></td>
<td>0</td>
<td>400</td>
<td>1,000</td>
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<td>$S_a$ [nm]</td>
<td>10</td>
<td>12</td>
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<td>$S_q$ [nm]</td>
<td>40</td>
<td>28</td>
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<td>$S_p$ [nm]</td>
<td>916</td>
<td>678</td>
<td>113</td>
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<td>$S_v$ [nm]</td>
<td>501</td>
<td>294</td>
<td>302</td>
<td>290</td>
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<td></td>
<td>$S_z$ [nm]</td>
<td>1,417</td>
<td>972</td>
<td>415</td>
<td>565</td>
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</table>

For the Au films, the surface roughness remains relatively the same for all of the wear boxes, but the $S_q$, $S_p$, and $S_v$ are all decreasing. This is most likely due to the abnormal growths (Figure 2.16) being displaced to the edge of the wear boxes during wear. Although the average $S_z$ roughness decreases compared to the Au as-deposited, it is still higher than the Cu thin film except for the 313 nm line spacing wear boxes in the Cu. The higher $S_z$ values are due to the textured wear box that is created during wear. This has been seen with other Au wear boxes [13], as well as with other materials [15, 19, 78].
Cross-sectional profiles of the three different line spacing wear boxes created with 1,000 µN in the Au film are shown in Figure 2.19. These profiles are parallel to the reciprocating wear passes. All three wear boxes show that the surface profile is above and below the as-deposited Au outside the wear box. It can be seen that the lowest valley inside the wear box is directly next to the two wear box edges. These regions are the start and finish of the reciprocating wear passes.

![Cross-sectional profiles of the three different sized wear boxes formed with 1,000 µN. The profiles show that the area inside the wear box is textured. The bottom line (green line- 313 nm, 1,000 µN) show the indentation into the wear box. The profiles are parallel to the reciprocating wear passes.](image)

**Figure 2.19-** Cross-sectional profiles of the three different sized wear boxes formed with 1,000 µN. The profiles show that the area inside the wear box is textured. The bottom line (green line- 313 nm, 1,000 µN) show the indentation into the wear box. The profiles are parallel to the reciprocating wear passes.

For the nanowear of Au, this wavy-like texture is similar to the texture when slick-slip is occurring [13]. The diamond probe most likely induces pile-up in front of the counterface during the wear until a point of instability is reached to where the sliding occurs at a lower original friction value, which is known as spragging [79]. If there are ripples present, which can be observed in the cross-sectional profiles in Figure 2.19, then the probe is plastically deforming the Au film to create a ripple and then yield, or spragging [79].
This process is repeated to create the wavy-like structure. The wavy-like texturing can affect the load-displacement measurements due to the change of strain hardened material. The wavy-like material has the potential to have more strain hardened material in the piled-up regions, causing the hardness calculated from the load-displacement to be higher. A closer look of the surface texturing in the wear boxes is shown with the height image AFM scans (Figure 2.20), which are also associated with the cross-sectional profiles in Figure 2.19.

![AFM scans of the 1,000 µN wear box for the a) 156 nm, b) 234 nm, and c) 313 nm line spacing. The AFM shows that wear boxes are larger than the dimensions selected within the Triboscan software, resulting in a larger center-to-center line spacing.](image)

**Figure 2.20**

2.3.2.3. Mechanical Properties of Nano-Worn Gold Thin Films

Due to the thicker total thickness in the Au film (3 µm), the depth of the indentation can be deeper than in the Cu film. The hardness as a function of contact depth is shown in Figure 2.21.
Figure 2.21 - a) The comparison of the average hardness as a function of contact depth in the Au thin film. The loads used at 25 µN and 1,000 µN, which are the lowest and highest normal load used during the creating of the wear boxes. b) is a magnified plot of the last seven ‘steps’ to show that the higher load wear boxes, as well as the decreased line spacing, have a slightly higher hardness, which is similar to the Cu.

Due to the large amount of data, only the lowest (25 µN) and highest (1,000 µN) load wear box properties are displayed in Figure 2.21. The hardness decreased as a function of contact depth. Even the as-deposited Au followed a similar trend, which is unexpected. The as-deposited hardness and elastic modulus of a thin film should be fairly horizontal, with the exceptions of surface and substrate effects.

A closer look at the results are shown in Figure 2.21b. The hardness displayed similar trends to the Cu. As the load during wear is increased, the hardness is increased. This is similar for decreasing the line spacing. By decreasing the line spacing and increasing the load during wear, there is more of an overlap in the wear track and plastic deformation. As a result, a more homogeneous region of deformation with more dislocations was produces, increasing the hardness. All twenty-four wear boxes showed a
similar trend to the as-deposited Au, where the hardness decreased as a function of contact depth. There was also not a large difference in hardness for all of the samples.

Due to the decreasing hardness as a function of contact depth, there is speculation that there may be an issue with the quality of the gold thin film. A Au sample was tested at three different locations to determine if the same negative power log trend would be observed using three different nanoindenters. The Au sample was tested at CINT (Hysitron TribolIndenter 950), Clemson University (Hysitron Triboscope), and Purdue University (Hysitron TribolIndenter 950). The hardness as a function of contact depth for the three indenters is shown in Figure 2.22.
Figure 2.22: The hardness as a function of depth for the 15-steps indents into the as-deposited Au. Each plot is associated with a location of indentation: a) CINT, b) Clemson University, and c) Purdue University. The results show there are two different trends in data, either a decreasing hardness as a function of depth (a & c) or a non-decreasing trend in hardness as a function of depth (b & c).
The hardness as a function of depth changes for the three different nanoindenters. For the indenter at CINT (Figure 2.22a), there is a decreasing hardness as a function of contact depth (negative power log). For the Clemson indenter (Figure 2.22b), apart from the hardness of the first few indents increasing, the hardness is relatively constant throughout the entire 15-step test. But for the indents at Purdue (Figure 2.22c), the results display both trends shown at CINT and Clemson. This result is most likely the result of a heterogeneous film that was produced during deposition. The three samples came from three sample locations from the 3 in. diameter Si wafer. Although the sample at Purdue did not display an increasing hardness for the first initial steps, the hardness was completely level throughout the multicycle indent.

The indents that were performed into the asperities (Figure 2.16) were not shown in the analysis in Figure 2.23. When the indent went directly into or into the side of one of these growths, the hardness dropped significantly to be almost zero. These indents were removed from analysis.

Statistical analysis was performed on the Au hardness values to determine if there is a significant difference in the average in difference between the steps. Similar to the statistical analysis of the Cu, the Au steps will be analyzed using a student t-test, due to the intendent nature of each step. JMP Pro was used for the analysis of the hardness values with level of significance of 0.01. The results are shown in Table 2.8.
Table 2.8- The statistical analysis of the hardness values for each independent step. The results display up to step 7, since all of the comparisons past are not significantly different. An "**" indicates that there is a significant difference (p < 0.01).

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</table>

The statistical analysis of the Au displays a step-like trend in the significant different for the Au film. As the load or contact pressure is increased during wear, there is an increase in the amount of steps that are significantly different. This is potentially a result of the surface material becoming more deformed during wear. Additionally, as the overlap in wear is decreased, the amount of significantly different steps increases. This is most likely result of the increased texturing in surface morphology, which changes the amount.
of overlap in plastic deformation zone. By statistically showing the differences, it elucidates that there is a more homogenous hardness for the decreased line spacing. Table 2.8 displays that there is only a significant difference between steps 1 and 2, which is an accurate depth in how the surface would influence the hardness. Because of this, only step 1 was removed from further analysis.

All of the calculated hardness values for the indents performed for steps 2 through 15 for each wear box were averaged and compared to the as-deposited Au, which is presented in Figure 2.23. Unlike the Cu hardness values that showed a softening, followed by a hardening, all of the Au average hardness values are somewhat similar for all of the wear boxes compared to the as-deposited Au. All of the averages fall within one standard deviation above or below the as-deposited Au hardness. However, there are a few wear boxes that exhibited a significant difference from the as-deposited Au (black stars).

![Figure 2.23](image)

**Figure 2.23**- After removal of indents influenced by the surface effects, the average hardness of all of the indents are displayed. The solid black line is the average for the as-deposited Au and the dashed line is one standard deviation. The star represents that the average is significantly different than the as-deposited hardness.
2.4. Conclusions

In this study, Cu and Au thin films were plastically deformed with a cono-spherical nanoindentation probe to form wear boxes with various line spacings and loads. The probe was then replaced with a Berkovich probe to perform either nine, twenty-five, or forty-nine 10- to 15-step static indentations to obtain hardness values as a function of depth. The Au wear boxes formed a textured surface as the load was increased during wear. This wavy-like texture is due to stick-slip between the probe and the surface.

Once the indentation was performed into the worn regions, it was found that both the Au and Cu had distinct trends in the hardness as a function of depth, which were supported with statistical analysis. The Cu film was only 1 µm thick, so substrate effects influenced the hardness values in the final few steps (contact depth > \approx 110 \text{ nm})

resulting in an increase in hardness. The Cu also had a slight decrease in hardness in the first step due to surface effects. These affected regions were removed from further analysis. Similarly, with the Au, there was a decreasing hardness as a function of depth for all of the steps. This was an unexpected trend, but additional testing at a separate facility confirmed that the hardness decreases as a function of depth.

The effects of the load and line spacing was similar for both the Cu and Au films. As the load was increased, the hardness increased. This is most likely due to the increased amount of dislocations that are generated during wear. In addition to load, by decreasing the line spacing, the hardness increases. As the line spacing during wear decreases, the amount of homogeneity in wear track overlap increases and the deformed area is more
condensed, resulting in a more localized deformed region to the wear box, increasing the hardness.

Once the mechanical properties of the films were calculated, the values were used to estimate the strain hardening exponent and strength coefficient of the worn regions, as well as the as-deposited material. The strain hardening exponent for the Cu film ranged from 0.06-0.12, which was higher than the as-deposited material (0.045). This high $n$ represents that when strain hardened, the flow stress of the worn material will increase faster than the as-deposited material. The $K$ increased as the load during wear increased, which is correlated to the increasing hardness as a function of increased wear load.

2.5. Reference Cited in Chapter Two


21. Romig, A.D., Dugger, M.T., McWhorter, P.J.: Materials issues in


CHAPTER THREE

IDENTIFYING THE WEAR MECHANISMS AND THE FORMATION OF AN AMORPHOUS METALLIC LAYER DURING THE SLIDING WEAR OF METALLIC/CERAMIC NANOLAMINATES

Before one can investigate the effects of wear at the nanoscale in nanolaminate (multilayer) systems, the wear of these systems are needed to be understood at the macroscale. Although there have been studies on the wear of metallic/ceramic nanolaminates, there is not an abundance of literature compared to the monolithic films studied in Chapter 2. This work in Chapter 3 will explain basic ideas of these novel systems found in literature, as well as further the understanding of the dry sliding wear of metallic/ceramic nanolaminates to allow for the better understanding of the deformation produced during sliding nanowear in Chapter 4.

3.1. The Enhancement of Metallic Surfaces for Improved Tribological Performance

Improving the wear performance of metallic components has been an important task in industry. Depending on the intended application of the component, hard ceramic coatings have been traditionally deposited to enhance the wear resistance. Despite the fact that these ceramic coatings have been shown to have a higher wear resistance than the metallic substrates, the coatings exhibit a lower fracture toughness and a low adhesion energy with their substrates that can result in the vulnerability to third body abrasion, cracking, and delamination during sliding wear [1].
Researchers have made attempts to increase the reliability of ceramic coatings by:

1. altering the deposition parameters to modify the structure of the ceramic coatings [2] and decrease the number of defects [3],
2. depositing an additional metallic interlayer to inhibit pinholes pathways for diffusion through the coating to their substrate and for increasing the adhesion between the substrate and coating [4], and
3. depositing a lamellar structure within the coating by alternating thin ceramic and metallic layers (i.e. nanolaminates) [5].

3.1.1. Current Understanding of Metallic/Ceramic Nanolaminate Systems

J. D. Embury and R. Fisher were the first to study the effect of layer thickness in pearlitic metallic structures on the metal’s mechanical properties [6]. Pearlite is a two-phased layered (lamellar) structure that is composed of alternating ferrite (α) and cementite (Fe₃C) in steel structures [7]. By decreasing the layer thickness between these two phases, the hardness of the region increased. Later, groups have leveraged the idea of their work to create complex film systems that mimic the pearlitic structure with a hard layer (ceramic) similar to cementite and a soft layer (metal) similar to ferrite.

Metallic/ceramic nanolaminates have the potential for use in applications such as wear resistant coatings [8, 9], micro-electromechanical systems (MEMS) [10], and protective coatings in corrosive environments [11]. In an effort to understand the structure-property relationships within metallic/ceramic nanolaminates, groups have attempted to identify how interlayer thickness [12, 13], the ratio of ceramic-to-metallic layer thickness...
and normal loading \([16, 17]\) affect their mechanical properties. This work has built off of earlier studies performed on metallic/metallic nanolaminates.

Experimental studies on metallic/metallic nanolaminates indicate that there are three distinct regimes of dislocation strengthening mechanisms: the dislocation pile-up, the confined layer slip, and the interfacial crossing (Figure 3.1) \([18]\). When the individual layer thickness is large, the dominant mechanism of deformation is dislocation-pile up. The layers are wide enough that the dislocations can pile-up at the interfaces, resulting in the material following a Hall-Petch relationship, where the flow stress is inversely proportional to the layer thickness \([19]\). When the individual layer thickness decreases below \(\approx 75\) nm (nanolaminate system), there is no longer enough room for dislocation pile-up in an individual layer and the deformation is a result of the confinement of single dislocations to individual layers, which is part of the confined layer slip model. If the individual layer thickness is reduced to below \(\approx 5\) nm, there is a drop-off in the strength of the layered structure, which is accounted to the dislocation cores already overlapping the layer interfaces \([18]\)
Figure 3.1- Illustration of the dominant strengthening mechanisms for the different regimes in nanolaminates. Although these strengthening mechanisms are normally used to describe the mechanisms controlling plastic deformation in metallic/metallic nanolaminates, it has been determined that metallic/ceramic nanolaminates follow similar mechanisms. Taken without permission from [5].
The same relationships between hardness and individual layer thickness are also observed in metallic/ceramic nanolaminates, but the exact mechanisms controlling the hardness have not been identified due to the ceramic layer [14]. Further investigations are needed to fully understand the mechanisms that control the properties of these metallic/ceramic nanolaminates. For ceramic/ceramic nanolaminates, by increasing the interfacial density, the optimum volume that results in the highest hardness is not obtained by many fine layers, like with metallic/metallic or metallic/ceramic, but is more accurate with the toughness of the composite coating (Figure 3.2) [20, 21].

**Figure 3.2**- Schematic of how interfacial volume changes specific mechanical properties for nanolaminates. Taken without permission from [20].
3.1.1. Previous Studies on the Wear of Metallic/Ceramic Nanolaminates

In the more recent years, there has been an increased amount of studies investigating the normal and lateral loading of these composite films due to the metallic and ceramic layers complimenting each other to have a compromised mechanical property system. Various nitride, carbide, and oxide containing ceramics have been integrated into nanolaminate systems and are being studied for various applications, such as wear resistant coatings [8, 9], micro-electromechanical systems (MEMS) [10], and protective coatings in corrosive environments [11]. A list comprising of various metallic/ceramic nanolaminate systems that have been examined in literature is shown in Table 3.1. Films are deposited by using various physical and chemical vapor deposition techniques (PVD and CVD, respectively). There are many different types of deposition techniques (sputter deposition, electron beam, pulsed laser, radio frequency, sublimation, atomic layer, plasma processing [22]) that result in more optimized mechanical properties for different materials used in these metallic/ceramic nanolaminate systems.
Table 3.1- A list of prior studies performed on various metallic/ceramic nanolamine systems.

<table>
<thead>
<tr>
<th>Layered System</th>
<th>Ceramic</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiN/W</td>
<td></td>
<td>G. Abadias et al. [23], Y. Lu et al. [24]</td>
</tr>
<tr>
<td>TiN/Al</td>
<td></td>
<td>D. Bhattacharyya et al. [12, 14, 17, 25], N. Li et al. [26], W. Mook et al. [27], S. Yadav et al. [28], J. Wang et al. [29], S. Pathak et al. [30]</td>
</tr>
<tr>
<td>TiN/Ni</td>
<td></td>
<td>M. Kumar et al. [31]</td>
</tr>
<tr>
<td>TiN/Ti</td>
<td>Nitride</td>
<td>M. Kot et al. [15, 32, 33], J. Lackner et al. [34–37], M. Flores et al. [38–40], E. Andrade et al. [41], A. Duck et al. [42], M. Ben Daia et al. [43], C. Sant et al. [8], T. Li et al. [44], Z. Farhat et al. [45–47], B. Subramanian et al. [48], L. Ries et al. [49], C. Le Paven-Thivet et al. [50], X. Bai et al. [51], K. Shih et al. [52], Q. Zhang et al. [11], S. Labdi et al. [53], B. Schultz et al. [54]</td>
</tr>
<tr>
<td>TiN/Pt</td>
<td></td>
<td>J. He et al. [55]</td>
</tr>
<tr>
<td>TiN/Cu</td>
<td>Nitride</td>
<td>S. Yadav et al. [28], Z. Farhat et al. [47], G. Abadias et al. [56], S. Pathak et al. [30], R. Raghavan et al. [57]</td>
</tr>
<tr>
<td>NbN/Mo</td>
<td></td>
<td>A. Madan et al. [58]</td>
</tr>
<tr>
<td>NbN/W</td>
<td></td>
<td>A. Madan et al. [58]</td>
</tr>
<tr>
<td>ZrN/Zr</td>
<td></td>
<td>N. Verma et al. [59]</td>
</tr>
<tr>
<td>ZrN/W</td>
<td></td>
<td>G. Abadias et al. [56, 60]</td>
</tr>
<tr>
<td>AlN/W</td>
<td></td>
<td>I. Kim et al. [61]</td>
</tr>
<tr>
<td>AlN/Al</td>
<td></td>
<td>X. Wang et al. [62], G. Zhang et al. [63]</td>
</tr>
<tr>
<td>WN/W</td>
<td></td>
<td>K. Shih et al. [52]</td>
</tr>
<tr>
<td>HfN/Hf</td>
<td></td>
<td>K. Shih et al. [52]</td>
</tr>
<tr>
<td>CrN/Cu</td>
<td></td>
<td>Y. Kim et al. [13]</td>
</tr>
<tr>
<td>CrN/Cr</td>
<td></td>
<td>E. Martinez et al. [64]</td>
</tr>
<tr>
<td>Si3N4/Al</td>
<td></td>
<td>M. Wang et al. [65]</td>
</tr>
<tr>
<td>CrC/Cr</td>
<td></td>
<td>M. Gomez et al. [66], J. Romero et al. [67]</td>
</tr>
<tr>
<td>SiC/Al</td>
<td>Carbide</td>
<td>N. Chawla et al. [68], S. Lotfian et al. [16, 69], C. Mayer et al. [70], D. Singh et al. [71–73], G. Tang et al. [74], X. Deng et al. [75]</td>
</tr>
<tr>
<td>TiC/Fe</td>
<td></td>
<td>C. Liu et al. [76], J. He et al. [77]</td>
</tr>
<tr>
<td>TiC/Cu</td>
<td></td>
<td>J. He et al. [77]</td>
</tr>
<tr>
<td>TiC/Al</td>
<td></td>
<td>J. He et al. [77]</td>
</tr>
<tr>
<td>TiC/Mo</td>
<td></td>
<td>J. Wang et al. [78]</td>
</tr>
<tr>
<td>TiC/W</td>
<td></td>
<td>J. He et al. [77]</td>
</tr>
<tr>
<td>WC/Ni</td>
<td></td>
<td>T. Moustakas et al. [79]</td>
</tr>
<tr>
<td>WC/Co</td>
<td></td>
<td>T. Moustakas et al. [79]</td>
</tr>
<tr>
<td>Al2O3/Al</td>
<td>Oxide</td>
<td>R. Springer et al. [80], Y. Ding et al. [81], Z. Farhat [45]</td>
</tr>
</tbody>
</table>
Initial research that was performed in literature showed similar trends for both metallic/ceramic nanolaminates (≤ 100 nm layers) and multilayers (> 100 nm layers) for different material systems. Using an Al/SiC nanolaminate system, it was shown that by performing adhesion testing, that there is a higher critical load in the nanolaminate coatings than in monolithic coatings [82]. Adhesion testing is similar to a scratch test where the load is slowly increased during a linear scratch. During the scratch, the load at which cracking and delamination are recorded to determine when failure occurs. The researchers found that the metallic/ceramic nanolaminate showed a higher critical load because the composite coating provides a compromise of metallic and ceramic properties by having a good interface and providing both increased toughness and strength [82]. M. Gomez et al. research on Cr/CrC displayed similar results to the Al/SiC work previously described [66].

For Ti/TiN, which is the material system used in this research, it was displayed that as the layer thickness is decreased or the interfacial density is increased, the hardness, resistance to friction, and resistance to wear increases [8, 9, 11, 33, 34, 39, 81, 83]. It was also shown that increasing the ceramic-to-metallic ratio of layer volume increases the hardness and resistance to wear further [34]. Another study found that decreasing the ceramic-to-metallic ratio of layer volume displayed that the erosion rate of the coating decreases, while the abrasion wear rate increases [83]. These conflicting results heightens the need to fully understand what controls or influences the wear mechanisms and wear rates of metallic/ceramic nanolaminates.
3.2. Experimental Methods

3.2.1. Fabrication of Metallic/Ceramic Nanolaminates

Ti/TiN nanolaminates were deposited at Clemson University. Coatings of $\approx 1 \mu$m total thickness were deposited using the Edwards ESM 100 Deposition system. These coatings were deposited with 20 nm or 100 nm alternating layers with Ti on the base in contact with the native SiO$_2$ layer on the Si substrate and TiN exposed to the environment. These coatings were deposited at a base pressure of $< 5.0 \times 10^{-6}$ torr, a working pressure $\approx 5.0 \pm 0.2 \times 10^{-3}$ torr, 0.4 kW DC, and at room temperature (RT). For the 20 nm and 100 nm layered nanolaminates, TiN was deposited using a gas ratio of 1:1.5 and 1:1 of nitrogen to argon (N$_2$:Ar) during TiN deposition (Table 3.2). The gas flow rates of the argon were always at 6.0 sccm for both the Ti and TiN layers. For the two different ratio TiN layers, either a nitrogen flow rate of 4 sccm or 6 sccm was used during deposition.

**Table 3.2-** Deposition parameters of the Ti/TiN nanolaminates. The estimated residual stress was calculated using Stoney’s equation [84]. All samples were deposited using a 4” diameter Ti target and working distance $\approx 1”$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Deposition Power (W)</th>
<th>N$_2$:Ar Flow Ratio</th>
<th>Ar + N$_2$ Working Pressure (10$^{-3}$ torr)</th>
<th>Residual Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti/TiN 100 nm</td>
<td>400</td>
<td>1:1.5</td>
<td>$4.8 \pm 0.3$</td>
<td>89</td>
</tr>
<tr>
<td>Ti/TiN 20 nm</td>
<td>400</td>
<td>1:1.5</td>
<td>$5.0 \pm 0.1$</td>
<td>49</td>
</tr>
<tr>
<td>Ti/TiN 100 nm</td>
<td>400</td>
<td>1:1</td>
<td>$5.1 \pm 0.1$</td>
<td>239</td>
</tr>
<tr>
<td>Ti/TiN 20 nm</td>
<td>400</td>
<td>1:1</td>
<td>$5.1 \pm 0.1$</td>
<td>28</td>
</tr>
</tbody>
</table>

3.2.2. Pre-and Post-Wear Characterization

Sample characterization was performed at Clemson University and the Center for Nanophase Materials Sciences (CNMS) at Oak Ridge National Laboratory (ORNL) (ShaRE Facility User Grant: 2013-Kennedy_269). To determine the crystal orientation of the nanolaminates, out-of-plane x-ray diffraction (XRD) was performed at ORNL using
the PANalytical X’Pert PRO 2-circle XRD and at Clemson University using the Rigaku Ultima IV powder diffractometer. Additional in-plane XRD was performed at ORNL using a Rigaku SmartLab four-circle diffractometer. To measure the radius of curvature, a Veeco Dektak³ contact profilometer was used pre- and post-deposition in order to calculate the residual stress of the nanolaminate using Stoney’s equation. The Olympus OLS4000 Laser Scanning Microscope (LSM) was used to determine volume lost during wear.

To prepare transmission electron microscopy (TEM) cross sections, a focused ion beam (FIB) (Hitachi NB5000 nanoDUE’T FIB-SEM) was used to obtain samples inside and outside the worn region (wear scar). Bright field (BF) and high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) images of the specimens were acquired using a Hitachi HF3300 STEM that was operated at 300kV. A Gatan Quantum ER detector was used to perform in situ electron energy loss spectroscopy (EELS) to determine the chemical composition of each layer of the nanolaminate systems. TEM was performed at ORNL (ShaRE Facility User Grant: 2013-Kennedy_269). Electron microscopy was performed at Clemson University using the Hitachi S-4800 Field Emission Scanning Electron Microscope (FE-SEM).

Hardness and elastic modulus of the nanolaminates were calculated from load-displacement measurements using a Hysitron Triboscope nanoindentation system with a three-sided diamond Berkovich nanoindentation probe. Fifteen displacement controlled indents were taken at least 10 μm apart to reduce the influence of deformation zones from other indents and had a depth \( \leq 100 \text{ nm} \) to lessen the effect of the substrate on the results.
3.2.3. Macrowear Testing

Once the nanolaminates had initial characterization performed, they were worn using a CETR UMT-2 to perform linear reciprocating wear tests with a 9.5 mm diameter 440C stainless steel hemispherical pin counterface. All wear tests were performed with a load of 0.5 N (max Hertzian contact stress of $\approx 222$ MPa), a velocity of 0.5 mm/s, a scratch length of 2 cm, and 20 reciprocating scratch passes. The load cell has a sensitivity of 1 mN.

3.3. Results and Discussions

3.3.1. Initial Characterization of Nanolaminates

BF and HAADF STEM micrographs of the 100 nm 1:1.5 N$_2$:Ar Ti/TiN nanolaminates are shown in Figure 3.3. The image displays the nanolaminate architecture, as well as the microstructure of the coating. In the as-deposited films, the TiN layers displayed columnar grains, while the Ti layers exhibited more crystalline grains. The grain size of the Ti was similar or larger than the thickness of the individual layer thickness, which results in the layer thickness influencing the strengthening mechanisms more than the grain size [30]. Additionally, there were columnar grains that run throughout the entire nanolaminate.
Figure 3.3- BF and HAADF-STEM images of the 1:1.5 Ti/TiN nanolaminates with 100 nm individual layer thickness.  a) The BF-STEM image shows the grain structure and texturing in the Ti and TiN, as well as a significant amount of diffraction contrast consistent with stress/strain within the layers. b) HAADF-STEM micrograph displays a change in chemical composition in the Ti/TiN nanolaminate by a change in image contrast.

To determine the composition and orientation relationship of the nanolaminate systems, out-of-plane XRD was used. In-plane XRD was used to look at the Ti/TiN nanolaminates in the parallel direction, compared to the perpendicular diffraction that is used in out-of-plane XRD. Figure 3.4 displays out-of-plane XRD of the monolithic and nanolaminate coatings that were used in this experiment. For the monolithic TiN, there is a change in dominant orientation by altering the amount of nitrogen during deposition. For the 1:1.5 N$_2$:Ar TiN, there is a domination orientation of (111), while the 1:1 N$_2$:Ar TiN has a dominant orientation of (200). This change cannot be seen in the nanolaminates (Figure 3.4b). For all four nanolaminate system, the (111) is the most dominant TiN orientation.
In Figure 3.5b, there is up to a ≈ 0.5° shift to the right in the peaks for Ti and TiN in the 20 nm and 100 nm nanolaminates, compared to the monolithic coating. Similarly to the change in dominant orientation in the TiN, the shifting of peaks is due to the residual stress that is built up during deposition of the nanolaminate systems. The 100 nm nanolaminates have a higher determined residual stress, which correlates to a larger shift to the right from the as-deposited Ti and TiN peaks. In addition to the residual stress, there is a peak broadening in the observed peaks found in nanolaminates. In-plane XRD was also implemented on the nanolaminate systems to evaluate the texturing. Figure 3.5a displays a comparison of the in- and out-of-plane XRD of the 100 nm 1:1.5 nanolaminate. The results show different dominant orientations for the Ti/TiN system, which is representative of a highly textured coating.
**Figure 3.5-** a) XRD spectra of the out-of-plane vs. in-plane diffraction of the 100 nm 1:1.5 nanolaminate. The change in dominant peaks displays that the coating is highly crystalline. b) XRD spectra of 1:1.5 Ti/TiN 20 and 100 nm layer nanolaminates compared with monolithic Ti and TiN. The nanolaminates exhibited a peak shift to higher 2θ (indicating residual stresses), as well as a peak broadening, compared to the monolithic films.

The hardness of the nanolaminates for both gas ratios, shown in Table 3.2, indicates that by decreasing the individual layer thickness from 100 nm to 20 nm, the hardness increases, which is a similar trend that has been observed with other nanolaminate studies [85, 86]. Similarly, the elastic modulus of the nanolaminate increases with decreasing layer thickness. The hardness values that were determined for the 100 and 20 nm layered nanolaminates (Table 3.2) are lower than values found in literature. Literature shows that the hardness for 100 nm layered Ti/TiN nanolaminates should be 16.9 GPa and 11.4-17.8 GPa for 20 nm layered nanolaminates [43, 44]. This reduced hardness could be possibly caused by a poor columnar structure that is seen in the deposited nanolaminates or the increasing interfacial roughness.
3.3.2. Macrowear Testing

Once the wear testing was completed, the wear scar was examined to identify the dominant wear mechanisms that occurred. All of the nanolaminates had some degree of micro-cutting taking place during wear, which is evident by smooth lines that are parallel to the deep wear track. The dominant wear mechanism that was observed for the four nanolaminate coatings varied based on interfacial density. The 20 nm layered coatings displayed a dominant wear mechanism of wedging, while the 100 nm layered coatings exhibited many asperities relating to third-body abrasion (Figure 3.6).

The factor that gas ratios played for the wear mechanisms was the 1:1 gas ratio nanolaminates displayed more asperities in the 100 nm layered coating and less wedging in the 20 nm layered coating. This can potentially be attributed to the higher hardness and more brittle TiN in the nanolaminate. The layer thickness and the interfacial strength have been proposed as exerting the greatest influence on the mechanical properties of nanolaminates [16]. In the metal, the layer thickness controls the flow stress; in the ceramic, the layer thickness controls the failure strength [16].
Figure 3.6- Micrographs of the most deformed region of the wear scar for the a) 100 nm 1:1.5 N₂:Ar, b) 20 nm 1:1.5 N₂:Ar, c) 100 nm 1:1 N₂:Ar, and d) 20 nm 1:1 N₂:Ar. Both samples showed similar wear mechanisms characterized by micro-cutting and plowing, but had different dominant wear mechanisms. The 20 nm layered nanolaminates (b & d) were dominated by wedging, while the 100 nm layered nanolaminates (a & c) were dominated by third body abrasive wear. The 1:1 N₂:Ar (c & d) had less plastic deformation and most asperities due to an increase in the brittle ceramic from a higher nitrogen content.

The COF was determined by taking the ratio of the normal force to the frictional force during wear testing. For COF, the 1:1.5 100 nm layer nanolaminate had a decrease in friction after the initial run-in (Figure 3.7), which led to a steady-state COF of 0.25 ± 0.01. The 1:1 100 nm layer nanolaminate had a similar trend with a steady-state COF of 0.27 ± 0.02, except the run-in resulting in a COF of 0.80, instead of the COF of 0.45 in the 1:1.5 nanolaminate. This is thought to be a result of the increased brittle TiN in the 1:1 nanolaminate, resulting in a higher friction while the ceramic layers are being abraded.
during sliding wear and resulting in the formation of more asperities. Both thicker layered nanolaminates had a lower COF than the 20 nm layered nanolaminate (Figure 3.7), which were 0.56 ± 0.06 and 0.48 ± 0.06 for the 1:1.5 and 1:1 gas ratio nanolaminates, respectively.

**Figure 3.7** - COF vs. scratch passes for 20 nm and 100 nm layered Ti/TiN nanolaminates with a) 1:1.5 and b) 1:1 N₂:Ar ratio. The COF for the 20 nm layered coatings had similar friction trends where the COF slowly increased with each pass. For the 100 nm layered coatings, there was a run-in, followed by a decrease in friction to obtain a lower steady-state COF for the 100 nm than the 20 nm.

In contrast, previous studies have shown that nanolaminates with smaller individual layer thickness tend to have a lower COF when compared to films with larger layer thicknesses [9, 45, 81]. This may be a result of increased fracture toughness in the thinner layered nanolaminate. It has been shown that decreasing the layer thickness, increases the hardness and fracture toughness [27]. If this is the case, the COF results would be accurate due to the higher fracture toughness trying to inhibit the fracture of the TiN layers and resulting in a higher COF. The wear system properties, as well as the as-deposited mechanical properties of the Ti/TiN nanolaminates are displayed in Table 3.3.
**Table 3.3** - The wear and mechanical properties of the nanolaminates are shown. The wear rate showed in inverse relationship with the hardness and COF for the 1:1.5 N₂:Ar nanolaminates, but not with the 1:1 gas ratio films. This can be attributed to the higher hardness and lower ductility in the 1:1 N₂:Ar nanolaminates.

<table>
<thead>
<tr>
<th>Sample</th>
<th>N₂:Ar Flow Ratio</th>
<th>Wear Rate (mm³/Nm)</th>
<th>Coefficient of Friction</th>
<th>Hardness (GPa)</th>
<th>Elastic Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti/TiN 100 nm</td>
<td>1:1.5</td>
<td>2.83 x 10⁻⁷</td>
<td>0.25 ± 0.01</td>
<td>7.6 ± 0.6</td>
<td>171.5 ± 6.7</td>
</tr>
<tr>
<td>Ti/TiN 20 nm</td>
<td>1:1.5</td>
<td>1.75 x 10⁻⁷</td>
<td>0.56 ± 0.06</td>
<td>9.3 ± 0.8</td>
<td>180.6 ± 7.6</td>
</tr>
<tr>
<td>Ti/TiN 100 nm</td>
<td>1:1</td>
<td>1.97 x 10⁻⁸</td>
<td>0.27 ± 0.02</td>
<td>8.2 ± 0.7</td>
<td>174.2 ± 7.8</td>
</tr>
<tr>
<td>Ti/TiN 20 nm</td>
<td>1:1</td>
<td>2.02 x 10⁻⁷</td>
<td>0.48 ± 0.06</td>
<td>10.2 ± 0.6</td>
<td>185.6 ± 5.5</td>
</tr>
</tbody>
</table>

The specific wear rate was calculated by determining the volume lost with non-contact profilometry. The wear rate of the four nanolaminates calculated are shown in Table 3.3. The measured wear rate is an averaged wear rate for the entire length of the test. For this experiment, one volume loss measurement was performed at the end of the entire test. In reality, the wear rate is going to change during the evolution of the wear test until a steady-state wear rate is measured (associated with a steady-state COF). This evolution of the wear rate is not expressed in the results. The trend in wear rate is inverse for the two gas ratio nanolaminates. This may be a result of an increased fracture toughness and hardness in the 1:1 gas ratio nanolaminates. In summary, the COF and wear data indicates that the potential increased fracture toughness of the thinner layered nanolaminate resulted in a higher resistance to wear.
3.3.3. Formation of an Amorphous Metallic Layer

The 1:1.5 N$_2$:Ar Ti/TiN nanolaminates had their structure and chemical composition further characterized by cross-sectional TEM and EELS. The 20 nm and 100 nm nanolaminates had specimens prepared by FIB and characterized using the Hitachi HF-3300 STEM. BF and HAADF STEM images of the 100 nm Ti/TiN can be observed in Figure 3.3. The morphology of the nanolaminate surface varied with the nanolaminate layer thickness. As the amount of layers increased, the roughness of the increased, as well as the amount of observable voids.

Chemical composition of each layer of the 100 nm layered nanolaminate was determined using EELS. The 20 nm layered nanolaminate was too thin for chemical analysis using EELS. For the 100 nm layered coating, it was determined that the titanium layers were pure titanium and the titanium nitride layers had an average of TiN$_{0.7}$ ratio, which falls into the compositionally stable region of TiN [87]. Although EELS was not performed on the 1:1 gas ratio Ti/TiN nanolaminates, it is proposed that the ‘x’ in TiN$_x$ would be larger than 0.7, due to the increased amount of nitrogen in the deposition chamber, as well as the increased hardness. The color of the top TiN layer was still gold, which leads us to believe that ‘x’ is below 1.2, allowing the TiN to still be compositionally stable.

As-deposited and worn Ti/TiN nanolaminates were evaluated to determine the effect of sliding wear on the overall structure, particularly the amount of interfacial density. Representative BF and HAADF STEM images of the post-worn 100 nm layered nanolaminates can be observed in Figure 3.8. In the circled region, the titanium layer is
deformed to fill in the unoccupied regions of the TiN layers. Although this region is between two TiN that have been deformed on the edge of the wear scar, this observation has been seen on a smaller scale when the metallic layer fills in micro-fractures of the ceramic layers [68]. This worn sample indicates that the wear scar has removed material into the seventh layer (Ti) of the nanolaminate. Even with the deformation in the worn region, there was no chemical mixing between the Ti and TiN.

![Figure 3.8- BF and HAADF STEM micrographs of the edge of the wear track in the 100 nm layered Ti/TiN nanolaminate. The wear track has worn to the seventh layer (Ti) from the substrate. The micrographs display that the more ductile metallic layer (Ti) fills in the voids in the brittle ceramic layer (TiN).](image)

Above the sixth layer (‘D’ - TiN) in the 100 nm layered nanolaminate, there was two small layers (‘B’ - Ti and ‘C’ – amorphous Ti) separating the TiN from the environment (‘A’ – carbon layer). These layers in the wear zone are labeled ‘A’ through ‘D’ in Figure 3.9a. The material composition of the layers was determined using EELS, which the results of which are shown in Figure 3.9. Based on the energy loss plot, the presence or absence
of C, Ti, and N can be determined by a peak on the corresponding line for each labeled layer. Layer ‘A’ was 100 at% carbon, which corresponds to the protective ion beam deposited carbon that was deposited on the surface of the nanolaminate prior to FIB milling. Layers ‘B’ and ‘C’ were found to be all titanium and ‘D’ had both titanium and nitrogen. Layer ‘B’ is the remaining material from the worn seventh layer of the 100 nm layered nanolaminate. The ‘C’ layer was unlike the nanocrystalline titanium layer immediately above as there were no ordered structures observed.

![Image](image_url)

**Figure 3.9**  a) BF-STEM cross-sectional image of the worn region in the 100 nm layer Ti/TiN nanolaminate. (b) The labels in (a) correlate to the acquired EEL spectra from each layer, which show that ‘A’ is the carbon layer deposited for FIB preparation, ‘B’ is the remainder of the Ti layer that was worn off, ‘C’ is an amorphous Ti layer, and ‘D’ is a TiN layer. (c) A high-resolution TEM image shows a magnification of the amorphous Ti layer.

A Fourier transform diffraction pattern program was used to analyze the layers and no diffraction pattern was observed in the non-structured titanium layer. A TEM
micrograph showing the structure above and below the amorphous region, as well of lack of structure in the amorphous, is shown in Figure 3.10. The results show that the layer ‘C’ is an amorphous titanium layer that was formed during the wear process, and is only observed in the worn region. Once outside of the pile-up region on the outside of the wear scar, the amorphous layer is not observed (Figure 3.11a). The amorphous layer can be better seen in comparison to the nanocrystalline titanium layer above and the columnar titanium nitride layer below in Figure 3.9c. The amorphous region was not found in the 20 nm layered nanolaminate (Figure 3.11b).

Figure 3.10- HRTEM micrograph showing the magnified region around the amorphous region (‘C’). The amorphous region would have observed lattice fringes if the atomic structure had order, compared to the Ti (‘B’) and TiN (‘D’) region where distinct ordering can be seen.
3.4.3. Amorphization of Bulk Materials

Literature shows there has been a vast amount research on understanding amorphous structures. Researchers have been focusing on how materials under pressure may undergo a crystalline to amorphous phase change for both electronic and mechanical properties to enhance microelectromechanical and nanoelectromechanical systems [88]. Most literature focuses on silicon [88], silicon carbide [89], and germanium [90], although some other materials have been found to have this transition of crystalline to amorphous material under pressure [91]. Past research on Si showed that amorphization takes place during indentation at slow loading-unloading rates and a minimum pressure of 24 GPa [88]. Researchers also observed nanoindentation induced amorphization in silicon carbide that is driven by a coalescence of dislocation loops and that there is a correlation between...
load-displacement response and ring distribution [89]. Molecular dynamic simulations looked at the effect of strain rate on f.c.c. metal alloys and found that at constant temperature, a perfect crystal can be transformed continuously to an amorphous metal by applying a large strain rate [91], which is opposite of what found with Si [88]. Most studies that found a transition from a crystalline metal to an amorphous structure involved the annealing of the material [92–94]. There has been no record of the amorphization of hexagonal closed packed (h.c.p.) materials, but Ti, which is typically has an h.c.p. structure, can transform into a f.c.c. structure at small length scales [95]. J. Chakraborty deposited Ti on Si and found an h.c.p. structure with films > 720 nm and an f.c.c. structure with films < 144 nm, where there was a meta-stable transition period between [95].

3.4. Conclusions

In this study, the wear of Ti/TiN nanolaminates was characterized. It was determined that the nanolaminates with thinner individual layers, or increased interfacial density, showed a higher hardness than the thicker individual layers, which is a similar trend with previous research. [86]. For coefficient of friction, the steady-state COF decreased as the layer thickness increased. The COF for the 100 nm layered nanolaminates were ≈ 0.25, while the COF for the 20 nm layered nanolaminates had a steady-state ≈ 0.50. The 100 nm nanolaminates displayed an initial run-in, while the 20 nm nanolaminates had a slowly increasing COF throughout the test. These results were contrary to previous results from similar nanolaminates, who showed that the thinner layered coatings had a
lower COF [9, 45, 81], but could agree with the idea that decreasing the layer thickness, increases the fracture toughness, resulting in a higher steady-state COF [27].

The dominant wear mechanism that was observed for the four nanolaminates varied based on interfacial density. The 20 nm layered coatings displayed a dominant wear mechanism of wedging, while the 100 nm layered coatings exhibited many asperities relating to third-body abrasion. The amount of nitrogen that was in the TiN\textsubscript{x} played more of a role in the brittleness of the nanolaminate coating. The 1:1 N\textsubscript{2}:Ar ratio coatings has more asperities in the 100 nm layered nanolaminate and less wedging in the 20 nm layered nanolaminate than the 1:1.5 N\textsubscript{2}:Ar.

EELS determined that the titanium layers showed no nitrogen within and the titanium nitride had a composition of TiN\textsubscript{0.7}. STEM showed the formation of an amorphous titanium layer between the TiN layer below and the remnants of a recrystallized nanocrystalline titanium layer above in the worn region of the 100 nm layered nanolaminate. EELS analysis and Fourier Transform software confirmed the layer as 100 at.% Ti and was amorphous by revealing no diffraction pattern in the amorphous region. This amorphous layer was neither observed in the thinner layered coating, nor has it been previously recorded in the literature. This compelling finding is expected to be useful in elucidating a novel phase change in certain layer thickness coatings that may be caused from the load under the contact area during wear. Research involving the 1:1.5 N\textsubscript{2}:Ar Ti/TiN nanolaminates can be seen in published work in Tribology Letters [54].

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CHAPTER FOUR
THE NANOWEAR OF METALLIC/CERAMIC NANOLAMINATES

4.1. Introduction to Layered Coatings

One recent advancement is the layering of synthetic protective coatings. The additional interlayer between the ceramic coating and the substrate can be used to inhibit pinholes from creating a pathway through the coating to the substrate and for increasing the adhesion between the substrate and coating [1]. Furthermore, researchers have deposited coatings with multiple alternating layers to increase the amount of interfacial density for additional protection. The amount of interfacial density began to be studied and coatings when sub-100 nm layers, known as nanolaminates, produced mechanical properties that deviated from the Hall-Petch relation. An extensive description of what nanolaminates are and their strengthening mechanisms can be found in Chapter 3.1.1. More research is needed to understand the tribological properties of metallic/ceramic nanolaminates. Part of this research will be comparing hardness-to-elastic modulus (H/E) ratios versus the wear rate of Ti/TiN coatings to determine if this mechanical property ratio has a major influence on the tribological properties of these nanolaminate coatings. Ti/TiN nanolaminates are the most studied system for metallic/ceramic nanolaminates due to the ability to deposit both layers from the same target (TiN reactive sputtered) [2–8].

J. Lackner and M. Kot did a series of technical papers on the mechanical and tribological properties of TiN and Ti/TiN nanolaminate systems [9–15]. One of the elements that their research stressed was how the mechanical properties affected the
tribological response. They claimed that the H/E ratio was the dominant factor influencing the wear rate of the tribosystem [11, 14], which had also been studied by A. Leyland [16].

4.1.1. Objective of Research

There are two main goals for this research project- 1) to compare this work to literature (J. Lackner and M. Kot) and 2) to determine how contact stress affects the strain and wear properties of metallic/ceramic nanolaminates. This work will use Ti/TiN to be able to compare nanolaminate systems from J. Lackner and M. Kot’s work to ours. J. Lackner and M. Kot claimed that the H/E ratio is the dominant factor in the wear rate of the material [11]. Normally when a series of layered systems are produced with a fixed total thickness, but altered amount of layers with equal thicknesses (i.e. 1 µm coating with fifty 20 nm layers or ten 100 nm layers), the elastic modulus is remains relatively constant for all the coatings. But J. Lackner and M. Kot altered the ceramic to metallic thickness ratio by have 2:1 and 4:1 [11]. Changing the ratio of material thickness altered the elastic modulus, which is why they believed that H/E played a larger role in wear, instead of the hardness independently. J. Lackner and M. Kot’s work displayed a trend in H/E versus wear rate, where it was shown that decreasing the H/E ratio, increased the wear rate ($R^2=0.76$) (Figure 4.1). The research in this project will produce four Ti/TiN nanolaminates with a lower H/E ratio than in J. Lackner and M. Kot’s work and determine if the trend in wear rate continues. Based on Figure 4.1, the H/E ratios for the nanolaminates would fall in the circled region if the wear rate trend applies to these systems.
Figure 4.1- The hardness/elastic modulus vs wear rate for work presented by J. Lackner and M. Kot [11]. The circled region is where the H/E ratios of the nanolaminates in this work would belong if the trend were to continue.

Although the tribosystems are not completely similar, this research will be comparing the works based off of contact pressure. J. Lackner and M. Kot used a 1 mm diameter Al₂O₃ bearing with a load of 1 N, while this work used a 10 µm cono-spherical diamond tip with a 100 µN load. Although these systems used different counterfaces and loads, the tests had similar contact stresses of ≈ 3 GPa, based on Hertzian contact stresses.

The second objective of this research will be to determine how contact stress affects the strain and wear properties of metallic/ceramic nanolaminates. In addition to the contact stress that will be used to compare the work of J. Lackner and M. Kot, five further contact stresses will be used to elucidate if varying the contact stress will alter the strain that is produced beneath the surface during the wear of these nanolaminate systems.
4.2. Experimental Methods

4.2.1. Fabrication of Metallic/Ceramic Nanolaminates

Ti/TiN nanolaminate systems were deposited at Clemson University and the Center of Integrated Technologies (CINT) and Los Alamos National Laboratory (LANL). For this experiment, four nanolaminate systems were deposited with various thicknesses and deposition parameters. At Clemson University, coatings with a total thickness of 1 µm were deposited with either 20 nm or 100 nm alternating Ti or TiN layers using an Edwards ESM 100 deposition system with a DC power supply. These coatings were deposited at a base pressure of < 5.0 x 10^{-6} torr, a working pressure ≈ 5.0 ± 0.2 x 10^{-3} torr, 0.4 kW DC, and at room temperature (RT). The Ti and TiN had an argon flow rate of 6 sccm and a flow rate of 4 sccm of nitrogen to reactive deposit the TiN. At CINT, coatings with a total thickness of 3 µm were deposited with 100 nm alternating Ti or TiN layers using a AJA International deposition system with a DC power supply. One of these coatings was deposited at room temperature and the other was deposited at 500 °C. These coatings were deposited at a base pressure of > 5.0 x 10^{-8} torr, a working pressure ≈ 3.0 x 10^{-3} torr, 0.3 kW DC, and a substrate bias of 20 W. The Ti and TiN had an argon flow rate of 30 sccm and a flow rate of 3 sccm of nitrogen to reactive deposit of the TiN. All four nanolaminate systems had a top layer of TiN and a base layer of Ti that was in contact with the native SiO₂ layer on the Si substrate.
4.2.2. Initial Characterization of Nanolaminates

Sample characterization was performed at Clemson University and the Center for Nanophase Materials Sciences (CNMS) at Oak Ridge National Laboratory (ORNL) (ShaRE Facility User Grant: 2013-Kennedy_269). To determine the crystal orientation of the nanolaminates, out-of-plane X-ray diffraction (XRD) was performed at ORNL using the PANalytical X’Pert PRO 2-circle XRD and at Clemson University using the Rigaku Ultima IV powder diffractometer.

Hardness and elastic modulus of the nanolaminates were calculated from load and displacement measurements using a Hysitron Triboscope nanoindentation system with a three-sided diamond Berkovich nanoindentation probe. Fifteen displacement controlled indents were taken at least 10 μm apart to reduce the influence of deformation zones from other indents and had a depth ≤ 100 nm to lessen the effect of the substrate on the results.

4.2.3. Nanowear Testing

Nanowear boxes were produced using the Hysitron TriboIndenter 900, using a 1 μm, 10 μm, and 100 μm diameter cono-spherical diamond tip at 40 μm/sec and 256 lines (512 due to trace and re-trace). The counterface was rastered across the film surface to replicate unlubricated sliding wear. Wear boxes with an edge length of 40 μm were produced with one or ten passes to determine how increased wear affects the wear rate. Normal loads of 100 μN and 1,000 μN were used to determine the effect of load on the wear boxes. With the two loads, three different tips, and two amounts of passes, there were twelve wear boxes produced on each sample. Between each of the wear boxes, the cono-
spherical tip was cleaned by performing three 10,000 µN indentations on single crystal aluminum to remove any potential material debris or build-up.

With the varied loads and tips, six different contact stresses were used for this experiment. The maximum contact stresses ranged from ≈ 0.6-30.0 GPa, where the same tip and load had a different maximum contact stress for each of the four samples due to material properties. The maximum contact stresses for all of the systems can be observed in Table 4.1. The contact stresses calculated are for an ideal material that is purely elastic using the Hertz equation. In the real experiment, these values would be expected to be lower due to the plastic deformation and true surface area interaction. Additionally, once the nanoindentation probe begins its lateral movement, there is more surface area in contact and more material will resist the movement of the tip, therefore reducing the contact stress further.

**Table 4.1**- The contact stresses of the six load and tip combinations for the four samples are listed below. The units of the contact stress are GPa.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tip 100 µm</th>
<th>Tip 100 µm</th>
<th>Tip 10 µm</th>
<th>Tip 10 µm</th>
<th>Tip 1 µm</th>
<th>Tip 1 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Load 100 µN</td>
<td>Load 1,000 µN</td>
<td>Load 100 µN</td>
<td>Load 1,000 µN</td>
<td>Load 100 µN</td>
<td>Load 1,000 µN</td>
</tr>
<tr>
<td>3 µm – 100 nm RT</td>
<td>0.6</td>
<td>1.3</td>
<td>2.8</td>
<td>6.0</td>
<td>12.9</td>
<td>27.8</td>
</tr>
<tr>
<td>3 µm – 100 nm 500 °C</td>
<td>0.6</td>
<td>1.4</td>
<td>3.0</td>
<td>6.4</td>
<td>13.8</td>
<td>29.7</td>
</tr>
<tr>
<td>1 µm – 100 nm RT</td>
<td>0.6</td>
<td>1.3</td>
<td>2.7</td>
<td>5.8</td>
<td>12.6</td>
<td>27.1</td>
</tr>
<tr>
<td>1 µm – 20 nm RT</td>
<td>0.6</td>
<td>1.3</td>
<td>2.8</td>
<td>6.0</td>
<td>13.0</td>
<td>27.9</td>
</tr>
</tbody>
</table>
4.2.4. Post-Wear Characterization

To determine if changing the load and dimensions of the wear box has an effect on the mechanical properties, a 3 by 3 nanoindentation grid with a Berkovich tip was performed inside the created wear boxes to determine the hardness and elastic modulus. All of the indents had a 10 µm spacing between each other to avoid any interaction between the adjacent deformation caused by the previous indent.

For the indents, there was a 5-step load controlled indent where the max loads for each step went from 1,000 to 5,000 µN with a 1,000 µN step increase and a 50% unload after each three second hold. The indents loaded and unloaded at a rate of 1,000 µN/sec. The use of the 5-step indent was to obtain multiple hardness values, from the measured load-displacement curves, as a function of depth. The indent depth did not exceed greater than 10% of the total film thickness due to a potential influence of the substrate on the mechanical properties of the film [17, 18].

Between each grid of indents, the Berkovich tip was cleaned by performing three 10,000 µN indentations in single crystal aluminum to remove any potential material debris or build-up. Indents that were observed to not be within the wear box region were removed from analysis.

The Olympus OLS4000 Laser Scanning Microscope (LSM) was used to image the wear boxes. A Veeco (Digital Instruments) Dimension 3100 atomic force microscope (AFM) was used to determine the surface and edge features of the wear boxes, as well as the volume lost to determine the wear rate.
4.3. Results and Discussions

4.3.1. Initial Characterization of Nanolaminate Coatings

Four Ti/TiN nanolaminate samples were brought to CINT to have various nanowear testing performed. Quasi-static indentation was performed on the coatings to determine the mechanical properties from the measured load-displacements curves (Table 4.2).

Table 4.2- Ti/TiN nanolaminate coating characteristics and mechanical properties. *produced at CINT; ^ produced at Clemson University

<table>
<thead>
<tr>
<th>Layer Thickness</th>
<th>Total Thickness</th>
<th>Deposition Temperature</th>
<th>Substrate</th>
<th>H (GPa)</th>
<th>E (GPa)</th>
<th>H/E</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 nm^</td>
<td>1 µm</td>
<td>RT</td>
<td>Si</td>
<td>9.3 ± 0.8</td>
<td>180.6 ± 7.6</td>
<td>0.051</td>
</tr>
<tr>
<td>100 nm^</td>
<td>1 µm</td>
<td>RT</td>
<td>Si</td>
<td>7.6 ± 0.6</td>
<td>171.5 ± 6.7</td>
<td>0.044</td>
</tr>
<tr>
<td>100 nm*</td>
<td>3 µm</td>
<td>RT</td>
<td>Si</td>
<td>7.9 ± 0.6</td>
<td>179.0 ± 6.2</td>
<td>0.044</td>
</tr>
<tr>
<td>100 nm*</td>
<td>3 µm</td>
<td>500 °C</td>
<td>Si</td>
<td>7.4 ± 0.6</td>
<td>201.0 ± 9.2</td>
<td>0.037</td>
</tr>
</tbody>
</table>

To determine the effects of mechanical properties and deposition parameters on the nanowear of the Ti/TiN nanolaminates, the four different coatings were selected to have comparable aspects, such as total film thickness, layer thickness, or deposition temperature. In order to determine if the mechanical properties of the coatings were different, statistical analysis was performed to conclude if there is a significant difference between the nanolaminates. Using the elastic modulus, hardness, and H/E values in Table 4.2, the values had an analysis of variance (ANOVA) test and a Least Significant Difference (LSD) [t-test] test run on them to determine if there is a statistical difference between the groups of values. The ANOVA tests showed at least one mean is different between the samples in the three groups. Further results from the LSD test are shown in Table 4.3. P-values > 0.05 (no marker) have equal variances assumed (no difference) and p-values less than or equal to 0.01 or 0.05 (* or **, respectively) have equal variances not assumed (difference).
From the table, it can be observed that the few differences are between CINT and CU samples, which is allowable due to the difference in total coating thickness (1 and 3 µm).

**Table 4.3**- Significance values for Fishers’ LSD tests. Values with p-value > 0.05 (no marker) have equal variances assumed (no difference) and p-values less than or equal to 0.01 or 0.05 (* or **, respectively) have equal variances not assumed (difference).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Comparison</th>
<th>Sig. E</th>
<th>Sig. H</th>
<th>Sig. H/E</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 µm – 100 nm</td>
<td>3 µm, 500 °C</td>
<td></td>
<td>**</td>
<td></td>
</tr>
<tr>
<td>RT</td>
<td>1 µm, 100 nm</td>
<td>**</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 µm, 20 nm</td>
<td>*</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>3 µm – 100 nm</td>
<td>3 µm, RT</td>
<td>*</td>
<td>**</td>
<td></td>
</tr>
<tr>
<td>500 °C</td>
<td>1 µm, 100 nm</td>
<td></td>
<td>*</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 µm, 20 nm</td>
<td>*</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>1 µm – 100 nm</td>
<td>3 µm, RT</td>
<td>**</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RT</td>
<td>3 µm, 500 °C</td>
<td></td>
<td>*</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 µm, 20 nm</td>
<td>*</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>1 µm – 20 nm</td>
<td>3 µm, RT</td>
<td></td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>RT</td>
<td>3 µm, 500 °C</td>
<td></td>
<td>*</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 µm, 100 nm</td>
<td>*</td>
<td>*</td>
<td></td>
</tr>
</tbody>
</table>

To obtain an understanding of the structure of the four nanolaminate systems, cross-sectional SEM was performed (Figure 4.2). Both coatings made at CINT were ≈ 3 µm, while the 20 nm layered 1 µm nanolaminate deposited at Clemson was ≈ 1 µm and the 100 nm layered coating was slightly larger than 1 µm. For an unknown reason, the micrographs display the layers in groups (Ti and TiN), where there are 5 and 15 layers instead of 10 and 30 individual layers. Due to the smooth surface roughness of the Si wafer (Ra < 5 nm), the interfaces of the room temperature nanolaminates are fairly parallel to the substrate-first Ti layer roughness. There is a slight increase in interface roughness with each increasing layer. The nanolaminate deposited at 500 °C (Figure 4.2d) has somewhat wavy interfaces, which has been seen in literature with other elevated temperature work [19].
**Figure 4.2**- Cross-sectional SEM of the four nanolaminate systems used in this experiment. a) has a total film thickness of 1 µm, a layered thickness of 100 nm, and was deposited at room temperature. b) has a total film thickness of 1 µm, a layered thickness of 20 nm, and was deposited at room temperature. c) has a total film thickness of 3 µm, a layered thickness of 100 nm, and was deposited at room temperature. d) has a total film thickness of 3 µm, a layered thickness of 100 nm, and was deposited at 500 °C. Figures ‘a’, ‘b’, and ‘c’ have similar structures due to the RT deposition temperature, while ‘d’ has more wavy-like interfaces due to the heated substrate.
XRD diffraction patterns confirmed that $\text{(111)}_{\text{TiN}}$ and $\text{(002)}_{\text{Ti}}$ were the dominant orientations within the nanolaminate (Figure 4.3), which are comparable to literature [20–22]. The one nanolaminate that was deposited at 500 °C had two unique features in the diffraction pattern compared to the three nanolaminates deposited at room temperature. The 500 °C coating was shifted approximately 0.7° to the left, which is potentially due to a change in residual stress in deposition or it could be a possible misalignment during XRD analysis.

![XRD diffraction pattern of the four Ti/TiN nanolaminates in this study. All of the samples have the same dominant Ti and TiN peak, but the sample deposited at 500 °C has additional peaks that are created due to the higher deposition temperature.](image)

**Figure 4.3-** XRD diffraction pattern of the four Ti/TiN nanolaminates in this study. All of the samples have the same dominant Ti and TiN peak, but the sample deposited at 500 °C has additional peaks that are created due to the higher deposition temperature.

### 4.3.2. Wear Characterization

The four Ti/TiN nanolaminate systems were worn using a maximum contact stress ranging from ≈ 600 MPa to ≈ 30 GPa (Table 4.1). Optical characterization was performed to visual inspect the deformation created by wear. All of the wear boxes produced with 1,000 µN are shown in Figure 4.4. The wear boxes produced in this study were different.
in shape from the wear boxes produced in Chapter 2. For this experiment, these wear boxes were produced with the Hysitron TriboIndenter (TI) 900 and not the TI 950 system. The wear box produced had a shape more similar to a parallelogram, instead of a square (Figure 4.5). The shape shift was consistent for all of the wear boxes produced in this study. Since all of the wear boxes produced displayed a parallelogram shape, the effect is either caused by a default system setting or a drift in the instrument during wear.

Figure 4.4- Optical micrographs of the wear boxes produced in the Ti/TiN nanolaminates with the various tip diameters and cycles. All of the wear boxes here were produced with 1,000 µN. The associated roughness measurements for the wear boxes are shown in Table 4.4. The wear boxes were worn in a parallelogram shape. Scale bar is 40 µm.
Figure 4.5- AFM images of the 1 µm/100 nm/RT Ti/TiN nanolaminate produced with the 1 µm diameter tip, 100 µN load, and 10 passes. a) is the height scan and b) is the phase image to better display the parallelogram shape of the wear box. The height scale is only for Figure a). The scan is 60 µm x 60 µm.

4.3.3. Wear Rate Comparison to Previous Studies

All of the wear boxes were scanned using the AFM to determine the volume loss for a wear rate (Table 4.4). The specific wear rate was found using Equation 1.7 with the measured volume losses from AFM. The wear boxes that could not have a determined volume loss due to the resolution of the AFM are not listed in Table 4.4.
Table 4.4- Comparison of the specific wear rates for the Ti/TiN wear boxes. The wear boxes not listed could not be determined to have volume lost. The bolded selections are the wear boxes created with similar contact stresses ($\approx 3.0$ GPa) to J. Lackner and M. Kot [11].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tip Diameter (µm)</th>
<th>Load (µN)</th>
<th>Cycle</th>
<th>Volume Lost (µm$^3$)</th>
<th>Specific Wear Rate (10$^{-4}$) (mm$^3$/Nm)</th>
<th>Wear Rate Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 µm 100 nm RT</td>
<td>1 1,000</td>
<td>1</td>
<td>95.1</td>
<td>46.4</td>
<td>0.037</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 1,000</td>
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<td>73.6</td>
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<td></td>
</tr>
<tr>
<td><strong>10 100</strong></td>
<td>1 100</td>
<td>1</td>
<td><strong>11.8</strong></td>
<td><strong>57.4</strong></td>
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<td></td>
<td>10 100</td>
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<td>28.8</td>
<td>1.4</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>100 1,000</td>
<td>10</td>
<td>5.1</td>
<td>0.3</td>
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<td></td>
</tr>
<tr>
<td>3 µm 100 nm 500 °C</td>
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<td>90.2</td>
<td>44.1</td>
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<td></td>
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<tr>
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<td>1 100</td>
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<tr>
<td>1 µm 100 nm RT</td>
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<td>1 100</td>
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<tr>
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<td>&lt; 0.001</td>
<td></td>
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</tbody>
</table>

The wear rates for the 1 and 10 cycle wear boxes did not have a significant difference, as a result, the single cycle wear box has a specific wear rate with an order of magnitude higher than the 10 cycle wear boxes. The 1 µm/20nm/RT Ti/TiN had the least wear of the other samples for two possible reasons: (1) this sample had the highest hardness, therefore resisted wear the most and (2) it was the last sample to be tested of the four, so the probes were worn down.
The samples were worn in the order of 3 µm/100 nm/RT, 3 µm/100 nm/500 °C, 1 µm/100 nm/RT, and finally 1 µm/20 nm/RT, which is how the samples are oriented from left to right in Figure 4.4. As the wear tests proceeded, the wear boxes became less visually pronounced, especially with the 1 µm diameter probe. The potential cause of this is the progressive wear the cono-spherical tips, which can be observed in Figure 4.6. Although the probe is made of diamond, it can still lose volume as it is worn against another hard ceramic, due to the system response to each other.

**Figure 4.6**- a) Micrograph of the 1 µm diameter cono-spherical probe used for the wear boxes produced with the highest maximum contact pressures. The tip is worn down, which could have affected the wear as the tests proceeded. b) Micrograph of the 10 µm diameter cono-spherical probe used for the wear boxes. This probe also had some wear damage, but not as much as the 1 µm diameter probe.
The deterioration of the counterface changes the contact mechanics during the testing. Depending on how the tips are worn, the maximum contact pressure can either increase (if worn to a point) or decrease (if worn into a flat geometry). This change in probe shape, as well as the potential increase in contact stress, could have an effect on the wear boxes surface roughness and depth. The surface roughness analysis of the wear boxes produced with a 1,000 µN load is shown in Table 4.5. To understand the structure changes in the surface would allow for the possibility of determining if the change in the counterface changes how the Ti/TiN surface is worn.
Table 4.5- Various roughness and surface feature measurements calculated by a laser profilometer. ‘$S_a$’ represents the arithmetic average roughness, ‘$S_q$’ represents the root mean squared roughness, ‘$S_p$’ represents the maximum peak height, and ‘$S_v$’ represents the maximum valley depth. The associated images for these wear boxes can be seen in Figure 4.4.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ideal Tip Diameter ($\mu$m)</th>
<th>Applied Load ($\mu$N)</th>
<th>Cycles</th>
<th>Maximum Contact Pressure</th>
<th>$S_a$ [nm]</th>
<th>$S_q$ [nm]</th>
<th>$S_p$ [nm]</th>
<th>$S_v$ [nm]</th>
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<td>1 µm 20 nm RT</td>
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The average surface roughness ($S_a$) and mean squared roughness ($S_q$) were relatively the same for the wear boxes to the as-deposited material, except in the 1 µm/100 nm/RT sample. The 1 µm, 100 nm nanolaminate had the highest as-deposited $S_a$ and $S_q$, so the already roughened surface could have influenced the wear to create an even rougher surface. The 1 µm, 100 nm nanolaminate also has the largest peaks ($S_p$) and lowest valleys ($S_v$), compared to the as-deposited material, furthering the belief that the initial surface roughness and features influenced the post-wear surface profiles and roughness.

In addition to the specific wear rate, the wear rate coefficient was calculated using Archard’s law, which incorporates hardness. As stated in Chapter 1.3.1., if the wear rate coefficient is $> 0.001$, it is deemed ‘severe wear’ [23]. Most of the wear boxes that were able to have their wear rates calculated had ‘severe wear’, except for the 1 µm/20/RT sample that had no wear boxes with a wear rate coefficient $> 0.001$.

These wear boxes were compared to work by J. Lackner and M. Kot [11]. Adding the wear rates determined in this experiment to J. Lackner and M. Kot’s work (Figure 4.1) is shown in Figure 4.7. Their work displayed a smaller range of wear rates ($2.1 \times 10^{-6} - 23 \times 10^{-6}$ mm$^3$/Nm) for a larger range of H/E ratios (0.660 – 0.103), while the wear rates determined from nanowear were higher and with a wider range ($0.1 \times 10^{-4} - 153.1 \times 10^{-4}$ mm$^3$/Nm) and a lower and smaller H/E ratio range (0.037-0.051). Additionally, the wear rates from the macro-linear reciprocating wear testing from Chapter 3 have been added to Figure 4.7. The wear rates ($2.0 \times 10^{-8} – 2.8 \times 10^{-7}$ mm$^3$/Nm) are lower than both the nanowear testing and J. Lackner and M. Kot’s work.
Figure 4.7- Comparison of the wear rate to the H/E ratio for the Ti/TiN wear boxes in this study compared to J. Lackner and M. Kot [11]. The dashed black line is the trend for J. Lackner and M. Kot. The dotted black line is the trend for this study.

The results display that the trend found by J. Lackner and M. Kot is not universal for all H/E ratios. While their results show a distinct linear relationship in the H/E ratio to the wear rate, this is not shown the same for either the macro or nanowear experiments on similar Ti/TiN nanolaminates.

Three reasons the relationships in H/E ratio and wear rate may have been different are: (a) their study involved pin-on-disk with 2,000 passes, while this study had at max 20 passes (10 cycles, trace and retrace), (2) the counterface and the load were three orders of magnitude larger than this study (1 mm diameter and 1 N load), creating a large difference in testing parameters, even though the contact stress was comparable, and (3) the structures and compositions of their films are different than the films in this study. The H/E ratio takes into account how the structure and composition changes the mechanical properties of
the films, but the composition and structure (columnar grains, smooth interfaces) can influence the wear differently.

4.3.4. The Effect of Wear on the Mechanical Properties

The worn samples had nine multi-step static indentations performed within the deformed region to calculate the hardness from the measured load-displacement curves. From section 4.3.3., it was determined that there was no significant difference in the wear volume for the 1 and 10 cycle wear boxes. Due to this outcome, the calculated hardness as a function of depth was compared for the 1 and 10 cycle wear boxes in the 3 µm/100 nm/RT sample (Figure 4.8).

![Figure 4.8](image)

**Figure 4.8** - The average hardness as a function of contact depth for the 1 and 10 cycles wear boxes created in the 3 µm/100 nm/RT Ti/TiN nanolaminate. ‘T’ represents tip diameter and ‘L’ represents the normal load during wear. Based off Hertz contact stress, all of the steps max contact depth are within the plastic zone created during wear.
There is no significant difference between the same contact stresses and steps for
the 1 (Figure 4.8a) and 10 (Figure 4.8b) cycles (i.e., no difference between step 3 in the T-
10, L-1,000 µN sample). Since there was no difference in wear volume for the two cycles,
it was expected that the hardness was going to be higher in the 10 cycle film due to a higher
amount of potential deformation in the sample. In order for there to be no wear addition
wear in the 10 cycle sample, the wear box has to strain harden at the first cycle and not
allow more wear (wear rates in Table 4.4). If this is the case, the additional wear should
potentially strain harden the deformed region more and increase the hardness, but this result
did not occur (Figure 4.8).

All four samples 10 cycle wear boxes were compared to determine if there were a
difference in trends in the hardness (Figure 4.9). Opposite to the copper and gold in
Chapter 2, these coatings displayed an increase in hardness as a function of contact depth.
Based on the tip function calibration, it was deemed that steps 1 and 2 are too shallow for
accurate analysis. These indents were removed for the analysis in Figure 4.10.
Figure 4.9 - The average hardness as a function of depth for all four Ti/TiN nanolaminates. The graphs only display the values for the wear boxes created with 10 cycles. All of the wear boxes increase hardness as a function of depth. ‘T’ represents tip diameter and ‘L’ represents load during wear. Based off Hertz contact stress, all of the steps max contact depth are within the plastic zone created during wear.
The overall average hardness for the wear boxes remained not significantly different to the as-deposited material for most of the deformed regions. Apart from all of wear boxes in the 1 µm/100 nm/RT and two wear boxes in the 3 µm/100 nm/500 °C and 1 µm/20 nm/RT samples, more of the wear boxes were not statistically different from the as-deposited material. Since the hardness does not often differ from the as-deposited material and the wear does not change from the 1 to the 10 cycle wear boxes, it is possible that the complex metallic/ceramic layered system is not being affected by the wear as much as a monolithic metallic film or a metallic/metallic nanolaminate. All the wear created during nanowear had a depth that was within the top hard ceramic layer (Table 4.4), and the plasticity of the metallic Ti may be allowing the layers to plastically deform with no significant change to the mechanical properties.
Figure 4.10 - After removal of indents influenced by the surface effects (steps 1 & 2), the average hardness of all of the indents are displayed. The solid black line is the average for the as-deposited Ti/TiN sample and the dashed line is one standard deviation. The black and grey stars represent a significant difference in hardness from the as-deposited sample for the 1 cycle and 10 cycle, respectively. Based off Hertz contact stress, all of the steps max contact depth are within the plastic zone created during wear.
4.3.5. Plastic Radial Strain of Ti/TiN

Using the calculated hardness, elastic modulus, and testing parameters, the flow stress and plastic radial strain were estimated for the indents into the deformed wear boxes using Equation 2.3, 2.4, and 2.5. The calculated values can be compared to estimate the power-law relationship that is needed to determine strain hardening exponent and strength coefficient from Hollomon’s relation, which are shown in Figure 4.11. The nanolaminate systems used a Poisson’s ratio of $\nu=0.29$. This was calculated using the rule of mixtures with the Poisson’s ratio of Ti ($\nu=0.34$ [24]) and TiN ($\nu=0.23$ [25]).
Figure 4.11- The mechanical response of the deformed Ti/TiN nanolaminate systems. To estimate the strain hardening relationship for these coatings, the Hollomon’s equation was used. These plots were formed from estimated flow stress (Tabor relationship) and plastic radial strain. The 1 µm nanolaminates showed more strain hardening than the 3 µm nanolaminates.
The strain hardening exponent \((n)\) that was estimated using Hollomon’s relation were 0.50-0.64. These values were larger than values found in literature for Ti and TiN thin films and bulk materials. Z. Shan et al. found that the \(n\) for a 1 \(\mu\)m CP-Ti thin film was 0.35, which was estimated from both experimental data (nanoindentation) and finite element simulation [26]. Next, J. Kim et al. investigated the strain hardening of Ti-6Al-4V bulk material with high velocity impact. They determined that the \(n\) changed from 0.09-0.18, based on different strain rate [27]. Finally, M. Qin et al. investigated the strain hardening exponent of 800 \(\mu\)m TiN thin film by tensile testing. They estimated that the \(n\) for the TiN thin film was 0.36 [28]. Based on the values found in literature, it would be expected that the strain hardening exponent would fall between the Ti and TiN.

Between the four Ti/TiN nanolaminates, there are a few factors that could influence the strain hardening. The potential influential parameters are layer thickness (interfacial density), total film thickness, deposition temperature, and ceramic composition. Layer thickness does not alter the strain hardening of the layered structures. The 1 \(\mu\)m/100 nm/RT (Figure 4.11c) and the 1 \(\mu\)m/20 nm/RT (Figure 4.11d) have all of the same deposition parameters, except for the layer thickness (interfacial density) and these two nanolaminates have identical estimated strain hardening exponents. This outcome is surprising since in metallic/metallic nanolaminate systems, it was determined that the layer thickness had the largest effect on the strain hardening exponent, which is due to the dislocation strengthening mechanisms [29]. The lack of effect of layer thickness on the Ti/TiN nanolaminates may be a result of the hard ceramic layer.
Deposition temperature has a similar result as the layer thickness. Both the 3 µm/100 nm/RT (Figure 4.11a) and the 3 µm/100 nm/500 °C (Figure 4.11b) Ti/TiN systems had similar strain hardening exponents (0.60 and 0.64, respectively). The only different parameters that could potentially be altering the $n$ values are the total film thickness and the composition of the TiN. The composition of the 1 µm films are TiN$_{0.7}$, while the composition for the 3 µm films are unknown. The 3 µm films appear to be more ‘silver-like’ in color, which could possibly mean a lower nitrogen value ($x < 0.7$), but this has not been confirmed. The 1 µm nanolaminates had a strain hardening exponent of 0.50, while the two 3 µm systems had a $n$ of 0.60 and 0.64. Since the two total thickness systems were deposited on different systems, there may be a different amount of residual stress that was deposited into the system, changing the nanolaminate response to the deformation. This increased strain hardening exponent in the 3 µm nanolaminates will result in the flow stress rising higher and faster than in the 1 µm nanolaminates when a strain is introduced into the system. All of the calculated power law relationships from Hollomon’s equation were replotted to investigate the overlap of the strain hardening exponent and strength coefficient of the four nanolaminate systems (Figure 4.12). The two 1 µm layered systems have an overlapping relationship, where the 3 µm nanolaminates have a slightly different slope.
Figure 4.12- Comparison of strain hardening relationships for the four Ti/TiN nanolaminate samples. Both 1 µm total thickness samples (dashed lines) are overlapped.

4.4. Conclusions

There were no significant changes in surface roughness from the as-deposited material to the worn regions, except in the 1 µm/100 nm/RT sample. This increase in roughness and maximum peaks and valleys may be a result of the already increased surface roughness influencing the post-wear surface roughness. Also, the wear boxes produced were in the shape of a parallelogram and not a square, which is a potential error in the drift of the system or a system programming error.

The wear of the nanolaminates in this study were compared to previous work performed by J. Lackner and M. Kot. Not all of the wear rates for this study could be determined due to resolution in the AFM scan. For the wear boxes that could be measured, it was found that there was not a difference in volume loss from the 1 to the 10 cycle, resulting in an order of magnitude higher wear rate for the 1 cycle wear boxes. Most of the wear boxes also had a wear rate coefficient $> 0.001$, which signifies severe wear.
While their results show a distinct linear relationship in the H/E ratio to the wear rate, this is not shown the same for either the macro or nanowear experiments on similar Ti/TiN nanolaminates. This may be a result of J. Lackner and M. Kot using a 1 mm counterface, 1 N load, and 2,000 passes on a pin-on-disk tribometer, while this study had 20 passes with a counterface diameter and normal load three orders of magnitude lower. Additionally, the structures and compositions of their films are different than the films in this study. The H/E ratio takes into account how the structure and composition changes the mechanical properties of the films, but the composition and structure (columnar grains, smooth interfaces) can influence the wear differently.

For the mechanical properties of the deformed regions, the hardness was found to increase as a function of contact depth. There was also no significant difference between the steps in the 1 cycle wear box to the 10 cycle wear box at the same contact stress. In addition, most of the calculated hardness values were similar in the deformed regions to that of the as-deposited material, except for in the 1 µm/100 nm/RT sample. The flow stress and plastic radial strain were estimated using calculated mechanical properties. From Hollomon’s relation, it was found that the strain hardening exponent was most influenced by the total thickness than any other parameter. The $n$ for the 1 µm coatings was 0.50 and the $n$ for the 3 µm coatings was 0.60 (RT) and 0.64 (500 °C). This signifies that the flow stress will increase higher and faster when more strain is applied to the 3 µm nanolaminates.

4.5. Reference Cited in Chapter Four

1. Massiani, Y., Medjahed, A., Crousier, J., Gravier, P., Rebatel, I.: Corrosion of


5.1. Summary of Research Results

This work focused on electronic devices and specifically looked at how the metallic films within these devices responded to external mechanical loading. For this work, the effect of wear overlap and contact pressure was studied to quantify the strain hardening exponent in metallic f.c.c. films with and without passivation layers. Additionally, the wear of metallic/ceramic nanolaminates was investigated to quantify the impact of ceramic interlayers within f.c.c. metallic layers on the strain hardening relationship and the evolved structure during nano-sliding wear in metallic/ceramic nanolaminates. The outcomes of this dissertation yielded both interesting results and additional research questions. The following sections highlight some of the key research findings and also potential areas that should be investigated.

5.1.1. Tribological Performance of Monolithic Face Centered Cubic Thin Films - (Chapter Two)

The mechanical properties of the as-deposited and worn f.c.c. films were calculated from nanoindentation load-displacement curves. As the contact pressure during sliding contact increased, the hardness of the film was shown to significantly increase. This change in hardness resulted from the increased dislocation density from the sliding contact. All of the average hardness values were significantly different from the as-deposited material except when a potential maximum sliding contact pressure of 10.4 GPa (400 µN)
was applied. In addition, increasing the overlap between the plastic zones around the parallel passes also resulted in a measurable increase in film hardness. These studies also allowed us to calculate the strain hardening of the Cu films. Using only worn samples with the homogenous deformation along the surface (closely spaced passes), we calculated the strain hardening exponent to be 0.11 for the Cu films.

To compare the response of the f.c.c films with passivation layers (Cu) to those without passivation, we also repeated a similar set of experiments on Au thin films. The relationship of film hardness to the applied contact pressure during sliding contact and increased wear track overlap was unclear and there was no statistical trend. However, these studies did allow to better understand the morphological changes of the Au surface during sliding contact. The greater the contact pressure, the more evident it was that stick-slip occurred since the film surface evolved a wavy-like structure similar to prior work [1, 2].

5.1.2. Identifying the Wear Mechanisms and the Formation of an Amorphous Metallic Layer During the Sliding Wear of Metallic/Ceramic Nanolaminates - (Chapter Three)

Using a series of metallic/ceramic nanolamine systems, we studied both the mechanical and tribological performance as a function of architecture changes. We initially showed that thinner individual layers, or increased interfacial density, had a relatively higher hardness than thicker individual layers. Then, we characterized the films using macrowear systems and our results showed that the steady-state COF decreased as the layer thickness increased. The COF for the 100 nm layered nanolaminates were approximately 0.25, while the COF for the 20 nm layered nanolaminates had a steady-state
around approximately 0.50. The 100 nm nanolaminates displayed an initial run-in, while the 20 nm nanolaminates had a slowly increasing COF throughout the test. These results were contrary to previous results which showed that the thinner layered coatings had a lower COF [3–5]. However, our work did align with a publication that showed that the decreasing the layer thickness within a nanolaminate could increase the fracture toughness and result in a higher steady-state COF [6].

EELS results helped us to determine that the titanium layers within the metallic/ceramic nanolaminates had no significant nitrogen and that the ceramic layers were TiN$_{0.7}$ for the 1:1.5 N$_2$:Ar films. In addition, STEM characterization revealed the formation of an amorphous titanium layer in the worn region of the 100 nm layered nanolaminate. This layer was below a recrystallized nanocrystalline titanium layer. This amorphous layer was neither observed in the thinner layered coating, nor has it been previously recorded in the literature.

5.1.3. The Nanowear of Metallic/Ceramic Nanolaminates - (Chapter Four)

In addition to macrowear, we also studied the deformation and properties of metallic/ceramic nanolaminates under nanowear conditions. The results in our study were then compared to previous work performed by J. Lackner and M. Kot [7]. While their results show a distinct linear relationship in the H/E ratio to the wear rate, this is not shown for either our macro or nanowear experiments on similar Ti/TiN nanolaminates. This difference in results may be due to either the test set up or the film systems being studied. The J. Lackner and M. Kot study employed a 1 mm counterface, 1 N load, and 2,000 passes.
on a pin-on-disk tribometer, while this study had 20 passes with a counterface diameter and normal load three orders of magnitude lower (1-100 μm diameter and 100-1000 μN).

For the mechanical properties of the deformed regions, the hardness was found to increase as a function of contact depth. There was also no significant difference between the steps in the 1 cycle wear box to the 10 cycle wear box at the same contact stress. In addition, most of the calculated hardness values in the deformed regions were similar to the as-deposited material, except for in the 1 μm/100 nm/RT sample. The flow stress and plastic radial strain were estimated using calculated mechanical properties. From the Hollomon’s relation, it was found that the strain hardening exponent was most effected by the total thickness than any other parameter. The $n$ for the 1 μm coatings was 0.50 and the $n$ for the 3 μm coatings was 0.60 (RT) and 0.64 (500 °C). This signifies that the flow stress will increase higher and faster when more strain is applied to the 3 μm nanolaminates.

5.2. Future Work - Effect of Extreme Environments on Wear and Corrosion

Metals can be exposed to high temperature [8], aqueous environments [8, 9], irradiation [10, 11], in addition to the mechanical loading discussed within this dissertation. Therefore, future studies of nanolaminates should be expanded to better understand how these materials respond to these conditions and the options for optimizing their structure and subsequent performance. The following sections will review work performed to understand both irradiation and corrosion as primary environments and highlight new search avenues to understand these mechanisms.
5.3. The Irradiation of Metallic Structures

[Section formed using proposals submitted by M. Kennedy]

Radiation of metallic structures has been shown to impact structure and subsequent component lifetimes. In reactors (structures where materials are subjected to controlled nuclear reaction with release of energy [12]), medical devices (x-ray, CT [13]), or deep space [14], the interaction between energetic particles and the metallic structure can result in atomic displacement damage, such as clusters of implanted ions, dislocation loops, vacancies, or interstitials [10, 15, 16]. This irradiation damage can cause phase transformations, crystallization of amorphous layers, amorphization, interdiffusion, or intermixing [17–21]. The resulting damage is influenced by the size and energy of the impacting particle, including neutrons, electrons, and light or heavy ions. For both bulk and thin film Cu, the dominate defect type that is produced by radiation are stacking fault tetrahedra (SFT). These are normally observed with an additional lower number density of partially dissociated Frank loops (also known as overlapping, truncated stacking fault tetrahedra) [22].

When materials are exposed to the interior of nuclear reactors, the effects of radiation can damage the material [23–25]. One way the exposure can damage the structural materials of a reactor is the bombardment of helium (He) ions [23–25]. In bulk material, imbedded He ions will imbed themselves into the material and coalesce into the He bubbles at the grain boundaries [23] or inside the grains [25]. These bubbles can increase the stress required for yield, which leads to hardening [25], reduced fracture toughness [26], and embrittlement [27]. When these reactors are run at high temperatures,
the growth and interaction of the helium bubbles can change the microstructure, leading to blistering and volumetric swelling [25]. Radiation of metallic structures has been shown to impact structure and subsequent component lifetimes, as well as the service life of the reactor.

For future work, I propose that Cu thin films be exposed to high energy He\(^+\). These high energy ions can sometimes result in the formation of He\(^+\) clusters and bubbles to form due to the low solid solubility of the He. The effects of He\(^+\) bubbles on the mechanical properties of metals are caused by two primary hardening mechanisms- the cascade-induced source hardening model and the dispersed barrier hardening model [16]. Source hardening is the result of dislocation interactions on a glide plane, while dispersed barrier hardening is when created defects block the dislocation motion. The issue with this model is that it does not describe the dose dependence of hardening and is incapable of describing the post-yield drop in strength [16]. The dispersed barrier hardening model is applied to correlate changes in yield strength to the irradiation induced defect density of metals [16]. An example of dispersed barrier hardening is the interaction between irradiated induced He\(^+\) bubbles acting as Orowan barriers. These produced bubbles and clusters can cause changes in the mechanical properties by increasing a metal’s yield strength, increasing its hardness, and decreasing its ductility due to the ability to block the dislocation movement. Since He\(^+\) bubbles coalesce into voids, increasing the amount of interfacial density can improve the performance of a materials resistance to radiation damage. The interfaces that are found in nanolaminate coatings act as He\(^+\) sinks and suppress or distribute the bubble nucleation [10, 15]. Metallic nanolaminates are a radiation-resistant coating design that
have been starting to gain interest for this application. By decreasing the layer thickness of the nanolaminates, there is an increase in interfacial density for a system that is already high [28], which also leads to a relatively high hardness, while retaining a ductility similar to the bulk, non-treated metals used in this study (Cu/Nb) [29].

The goal of this research experiment is to improve the current understanding of He\(^+\) bubble formation within f.c.c./b.c.c. nanolaminates that have been strengthened with increased strain. Based on preliminary studies from our group and in literature, it is hypothesized that the size of He\(^+\) bubbles under wear tracks caused by sliding wear is related to the strain hardening prior to implantation due to the increased amount of dislocations and potential nucleation sites.

5.3.1. The Irradiation of Metallic/Metallic Nanolaminate Systems for Damage Resistance

Structures that are layered with coherent interfaces have identical crystal structures with a minimal mismatch in the lattice spacing, which provides the minimum amount of strain necessary for a continuous crystalline plane across the interface. When the lattice mismatch becomes too large or there are two different crystal structures, the interfaces are then considered incoherent and the slip systems are discontinuous across the interface. The most common incoherent interface system that has been studies, especially for irradiation work, is Cu/Nb [30–35]. Many studies have also been conducted for purposes of determining the radiation tolerance of nanolaminate structures, as shown in Table 5.1.
Table 5.1: Irradiation data of various nanolaminates used in a range of systems

<table>
<thead>
<tr>
<th>NMM Used in Irradiation Studies</th>
<th>Interface</th>
<th>Irradiation Type</th>
<th>Nominal Individual Layer Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/Nb [15, 17, 36]</td>
<td>f.c.c./b.c.c.</td>
<td>He⁺</td>
<td>2.5-100 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>He⁺</td>
<td>50 nm</td>
</tr>
<tr>
<td>Cu/V [37, 38]</td>
<td>f.c.c./b.c.c.</td>
<td>He⁺</td>
<td>1-200 nm</td>
</tr>
<tr>
<td>Al/Nb [10]</td>
<td>f.c.c./b.c.c.</td>
<td>He⁺</td>
<td>1-200 nm</td>
</tr>
<tr>
<td>Au/Fe [39]</td>
<td>f.c.c./b.c.c.</td>
<td>Ar⁺</td>
<td>0.3-1.2 nm</td>
</tr>
<tr>
<td>Cu/Mo [40]</td>
<td>f.c.c./b.c.c.</td>
<td>Xe⁺</td>
<td>2.5 nm</td>
</tr>
<tr>
<td>Cu/W [41]</td>
<td>f.c.c./b.c.c.</td>
<td>He⁺, Kr⁺</td>
<td>7.5 nm</td>
</tr>
<tr>
<td>Ni/W [42]</td>
<td>f.c.c./b.c.c.</td>
<td>Au⁹⁺</td>
<td>25 Å</td>
</tr>
<tr>
<td>Al/Ti [43]</td>
<td>f.c.c./h.c.p.</td>
<td>Ar⁺</td>
<td>25 nm</td>
</tr>
<tr>
<td>Cu/Cu-Zr [44]</td>
<td>f.c.c./Amorphous</td>
<td>He⁺</td>
<td>2.5-150 nm</td>
</tr>
<tr>
<td>Fe/W [45]</td>
<td>b.c.c./b.c.c.</td>
<td>He⁺</td>
<td>1-200 nm</td>
</tr>
<tr>
<td>Ta/Ti [18]</td>
<td>b.c.c./h.c.p.</td>
<td>Ar⁺</td>
<td>17 nm Ta; 23 nm Ti</td>
</tr>
</tbody>
</table>

Initial studies on the irradiation of nanolaminates have shown that the damage is a function of layer thickness, the susceptibility of the layers to intermixing due to irradiation, and the shear strength of the layers [17]. By decreasing the spacing between the layers, the formation of He⁺ bubbles will be suppressed when the irradiated samples are annealed, which was shown using 1 nm and 50 nm layered Cu/Nb nanolaminates [15]. In addition to the suppression of large defect nucleation, the change between as-deposited and irradiated mechanical properties is a function of layer thickness [10, 45]. One study showed that the largest changes in hardness between the as-deposited and irradiated nanolaminates occurred when the individual layer thickness is above ≈ 5 nm, where the hardness decreases below this layer thickness. They displayed that the irradiated nanolaminate hardness was representative of [45]:

\[ H = H_0 + kd^{-\frac{1}{2}} \] (5.1)
where $H$ is the hardness of the nanolaminate, $H_o$ is coating hardness at infinitely large layers, $d$ is the layer thickness, and $k$ is a constant. One additional feature that was discovered was during the irradiation of 1 nm layered Fe/W nanolaminates, the defined interface was no longer visible due to intermixing of the layers [45].

Understanding how defects created by irradiation are altering the mechanical response of nanolaminate systems, molecular dynamic and finite element models have been developed for obstacles in the lattice and structure. The models suggest that the strengthening cannot be due to the weak obstacles alone, such as the Friedel-Kropa-Hirsh. Alternately, the defects, such as He$^+$ bubbles, should be considered when using the dispersed barrier-hardening model that was developed by A. Seeger [46], which displays a more acceptable model for He$^+$ strengthening. The estimated change in stress can be expressed as [10]:

$$\Delta\sigma = M\alpha\mu b\frac{1}{l} = M\alpha\mu b\sqrt{N/d}$$

(5.2)

where $\Delta\sigma$ is the change in stress, $N$ is the average loop density, $d$ is the loop diameter, $M$ is the Taylor Factor (3.06 for f.c.c. and b.c.c. metals), $\alpha$ is the barrier strength, $\mu$ is the shear modulus, $b$ is the burgers vector, and $l$ is the average spacing between obstacles. The typical value for $\alpha$ is 0.45 [47], but can be broken down further for dislocation loops ($\approx$ 0.3), SFT ($\approx$ 0.2), and voids ($\approx$ 1.0) [16, 48, 49]. The issue with this model is that it cannot be used to measure the barrier strength on interfaces, so it is invalid for nanolaminate systems.
5.3.2. Aim 1: Quantifying the Effects of Plastic Deformation on the Formation of Irradiation-Induced Defects

Research published by this group have recently displayed the extent of strain hardening that occurs during plastic deformation in Cu/Nb NMMs. The results showed that the strain hardening is dependent on the individual layer thickness. The implication of this conclusion is that the strain hardening exponent, which has served as an indirect measure of dislocation interaction with smaller strain hardening exponents, suggests that dislocations act more in isolation that previously determined. Literature provides a study that showed that Cu/Nb nanolaminates (30 nm layers) had a strain hardening exponent that was an order of magnitude lower than bulk values of Cu and Nb [50]. Their group determined that the strain hardening exponent for the Cu/Nb NMM system was 0.029, while bulk copper has an exponent of \( n \approx 0.35 \) [50] and niobium has an exponent of \( n \approx 0.2-0.25 \) [51]. The bulk strain hardening exponents fall in the range that is most common for bulk metals (\( n \approx 0.2-0.4 \) [52]). The nanolaminates in this study were deposited using magnetron sputtering, except in order to produce the various amount of strains, the coatings were rolled. The post-rolled nanolaminates were then indented to have the hardness measured [50]. The low strain hardening exponent measured can be compared to tensile fracture strains in several studies of Cu/Nb. Specifically, the predictions of the onset of necking (\( \varepsilon = n \)) was used to confirm the strain-hardening exponents of the nanolaminates [35, 53].

Additional work performed by this group include investigating the influence of the nanolaminate architecture on the strain hardening of f.c.c./b.c.c. NMM systems [54]. To determine the effect of lateral deformation (i.e. wear) on the strain hardening of Cu/Nb
systems, nanoindentation was performed inside nanowear boxes and as-deposited regions to obtain the mechanical properties to calculate the strain hardening.

Three layer thicknesses (2 nm, 20 nm, and 100 nm) and two total film thicknesses (1 µm and 10 µm) were deposited to examined the architecture and substrate influence on the strain hardening of the NMM system during deformation. There was a significant increase in hardness that was observed in the deformed regions compared to the as-deposited region. The hardness of the deformed region also increased as the load during wear was increased. After determining the flow stress and the plastic radial strain based of measured mechanical properties and material property constants, the strain hardening exponent was estimated. The strain hardening exponent for the thinner layer nanolaminates (2 nm and 20 nm, \( n \approx 0.018 \) and \( n \approx 0.022 \), respectively) were found to be less than the 100 nm layered nanolaminate (\( n \approx 0.041 \)), where total film thickness did not play a major role.

Based on the results surrounding the strain hardening exponents of the NMM systems, it can be suggested that the single dislocation based deformation mechanisms detected for the thinner layered nanolaminate limit the extent of strain hardening in the system. Consequently, due to the conclusions that have been determined in work performed by this group [54], both the architecture strengthening and strain hardening must be taken into account if the performance during sliding wear for the various layer thickness nanolaminate systems can be accurately predicted.

Literature has shown have strain hardening has affected materials that are irradiated. A. Takamura et al. presented that f.c.c. metals that have impurities, and/or cold worked or have had other plastic deformation, will have increased damage within the
structure when irradiated with electrons, neutrons, or deuterons [55]. In another study [56], Al and Cu samples were both cold worked and annealed and then exposed to a neutron flux of $5.5 \times 10^8$ n/cm$^2$·s. The damage that was produced in each sample was measured by comparing the electric resistance before and after the irradiation. The study showed that there was an increase in the damage for the cold worked Cu and Al (10% and 32%, respectively) than in the annealed samples. The results suggest that the dislocation density within the nanolaminate system should be taken into account and analyzed, in addition to understanding how the interfaces influences the formation of He$^+$ bubble nucleation and growth.

To be able to understand how various amounts of plastic deformation influences the formation of He$^+$ bubbles within a Cu/Nb nanolaminate system, a base of four samples structures will be analyzed: (1) an as-deposited nanolaminate, (2) an as-deposited nanolaminate after exposure to He$^+$ irradiation, (3) a worn nanolaminate, and (4) a worn nanolaminate after exposure to He$^+$ irradiation. For samples (3) and (4), there will be worn samples at both 100 µN and 1,000 µN to determine how the effect of deformation influences the formation of He$^+$ bubbles. Due to the magnitude of damage that is present below the wear track and the concentration of He ions varies from the surface of the sample towards the bulk region below the deformed region, the measurements of the strain and simulations of the expected He$^+$ concentration gradient must be performed, based on the ion fluency.

It is expected that the sliding contact should increase the number of dislocations due to the increased plastic deformation in the as-deposited Cu/Nb nanolaminates. Due to
the increased number of dislocations, the potential sites for nucleating and formation of He\(^+\) bubbles will also increase. It is theorized that the He\(^+\) bubbles that are created directly under the worn region will have a smaller dimension or completely suppressed at the same depths as in the as-deposited material. It is also anticipated that there will be a relationship between the dimensions of the He\(^+\) bubbles under the worn region and the strain hardening prior to implantation.

5.3.2.1. Experimental Methods for Aim 1

From each of the three alternative layered Cu/Nb nanolaminates (2, 20, and 100 nm layers), there will be four specimens that will be characterized and compared: (1) an as-deposited nanolaminate, (2) an as-deposited nanolaminate after exposure to He\(^+\) irradiation, (3) a worn nanolaminate, and (4) a worn nanolaminate after exposure to He\(^+\) irradiation. Once the nanolaminates have been deposited, wear boxes will be created using a nanoindentation system \([1, 54, 57–62]\), similarly to the wear boxes that were produced in Chapter 2 and 4. A 1 \(\mu\)m diameter diamond cono-spherical indentation probe will be rastered across the surface with a known applied load to produce the various nano-worn boxes for this experiment. The wear boxes will be 80 \(\mu\)m by 80 \(\mu\)m to have a larger test region than is what normally produced in other nanowear work \(\leq 40 \mu\)m by 40 \(\mu\)m \([54, 60–63]\)

Irradiation of the nanolaminate systems will also be performed at CINT with the assistance of Dr. Y. Wang. Irradiation damage is normally described as displacements per atoms (dpa) \([38]\). For irradiation, testing parameters of work previously performed at
CINT [44, 64] will be performed with the guidance of the Stopping and Range of Ions in Matter (SRIM) software [65]. This software uses a Monte Carlo Simulation to predict the He⁺ depth concentration profile of irradiated samples (Figure 5.1). The SRIM software assumes a homogeneous system, where the influence of interfaces is not considered. This research will use the depth profiles calculated from this software to identify the depth at which the anticipated maximum He⁺ concentration will occur and determine if that is the most prevalent location of He⁺ bubbles. The irradiation parameters that will be used for this experiment for He⁺ implantation are a base pressure of 1 x 10⁻⁴ Pa, an ion energy of 40 keV, and an ion flux on the order of 10⁻⁴ dpa*s⁻¹ at a constant beam current of 2.5 µA [44, 64]. This work will also investigate how the implantation temperature affects the hardening from irradiation. Based off literature, the largest increases in hardening are expected to occur when the metal is irradiated at a temperature between 0.3-0.4 the melting temperature (T_m) [38].
Figure 5.1- SRIM simulations of He⁺ irradiation into monolithic gold. The results show that as the ion energy increases, the max concentration shifts deeper from the surface, but the ion concentration is more distributed.
5.4. Introduction to the Corrosion of Protective Coatings

[This work was supported through funding by the South Carolina Space Grant Consortium.]

The corrosion of Ti/TiN was initially a portion of the intended research for this dissertation, but the tribology aspect of the project took more time than anticipated.

To enhance the corrosion resistance of metallic components, hard ceramic coatings have been traditionally deposited, such as titanium nitride (TiN) [66], titanium aluminum nitride (TiAlN) [67], silicon carbide (SiC) [68]. However, these coatings have low toughness, which can result in cracking and delamination. The increased potential to fracture or delaminate can advance the rate of corrosion. In addition, failure can also be caused by self-catalytic localized corrosion due to defects in the coating allowing the substrate to be exposed to the environment (pinholes [69]). The need to create protective coatings for corrosion resistance has a high importance to society due to corrosion having direct effects resulting in injury, contaminates to the environment, and financial costs [direct and indirect costs estimated ≈ $276 billion/year (3% of U.S. Gross Domestic Product)] [70].

Corrosion is the undesirable deterioration of a metal or alloy, where there is an electrochemical response involving electron transfer [9]. Thin film corrosion testing is used to determine the nobility and longevity of the system. The most common test method used is potentiodynamic polarization tests or cyclic polarization [71–75]. A polarization test is performed with a potentiostat, which is a three electrode apparatus where voltage is passed between the working electrode (sample) and the reference electrode and current is passed between the working electrode and the counter electrode (Figure 5.2) [9]. The test
analyzes the combination of a minimum of two half-cell reactions, where there is at least one anodic reaction (oxidation) and one cathodic reaction (reduction) [9]. From the intersection of these two reactions, a critical corrosion current density ($i_{\text{corr}}$) can be extrapolated, which determines if a system is more corrosive than another (Figure 5.3) [9, 76]. Another method that is often used for coatings is electrochemical impedance spectroscopy (EIS). This form of testing looks at applying alternating current (AC) potential to an electrochemical cell and measuring the current throughout the cell [9]. EIS will be used to determine the properties of characteristic films formed at the contact zone, which is performed before and after the wear test [77]. For EIS, the data is displayed in a Bode or Nyquist plot to determine the polarization resistance ($R_p$ or $R_{\text{ct}}$) and the solution resistance ($R_s$ or $R_\Omega$) [9]. These two variables can be used to determine the $i_{\text{corr}}$ and of the corrosion rate of the material based off variances in Faraday’s Law [9].
Figure 5.2- Schematic of a three cell polarization cell. AUX is the counter electrode, WE is the working electrode, and REF is the reference electrode. Taken without permission from [9].

Figure 5.3- Potentiodynamic polarization test results of Ti/TiN nanolaminates of different period sizes. Taken without permission from [78].
5.4.1. Aim 1: The Effect of Bilayer Thickness and Chemical Composition on The Corrosion of Metallic/Ceramic Nanolaminates

Understanding how to increase the resistance to corrosion has been an important topic of research for some time. One of the most popular methods to improve corrosion resistance that has been employed is using a protective coating. When hard ceramic coatings are used, there can be microstructural defects. Hard ceramic coatings often have cracks or pinholes in the films, resulting in potential film failure [69, 79, 80]. There are also large internal stresses that are created when deposited, so coatings, like TiN, can only be $\approx 6-7 \, \mu m$ thick before there is a high possibility of delamination due to a low adhesion with the substrate [79].

To improve the properties, capabilities, and longevity of the hard ceramic coatings, researchers have worked on altering the chemistry of the ceramic coating [81], altered the processing parameters [82–87], or adding a metallic interlayer between the ceramic coating and the substrate [80, 88]. The addition of a metallic interlayer can increase the adhesion energy between the film and substrate, allowing for a thicker film, decrease the pinhole density and inhibit pinhole paths from the surface to the substrate, therefore increasing corrosion resistance [80, 89]. Studies have shown that a titanium layer between TiN and a substrate decreases the critical corrosion current density [80, 89].

The idea of adding a single interlayer to increase the corrosion resistance has been advanced by multiplying the amount of layers to create multilayers (layers $> 100 \, \text{nm}$) and nanolaminates (layers $< 100 \, \text{nm}$). From previous literature, both multilayer and nanolaminates had similar results. Metallic/ceramic (Ti/TiN) [73, 78, 90, 91] and ceramic/ceramic (TiN/NbN) [92] multilayers or nanolaminates displayed better corrosion
resistance than the bare substrate. For both multilayers and nanolaminates, the results were inconclusive in the correlation between amount of layers and corrosion resistance. For Ti/TiN layered films, one researcher found that adding more bilayers decreased the amount of corrosion [73], while another found that by adding more layers, the amount of corrosion increased [72, 78]. Regardless, the corrosion resistance decreased compared to a monolithic layer [72, 78]. Although there are conflicting results, all systems showed an $i_{corr}$ value lower than the substrate.

5.4.1.1 Experimental Methods for Aim 1

For this experiment, understanding how the different layered thicknesses and chemical composition of the TiN layer effect the corrosion will be investigated. Four Ti/TiN nanolaminate systems, similarly to the coatings deposited in Chapter 3, will be deposited, as well as monolithic Ti and TiN films of equal total thickness. The coatings that will be deposited are shown in Table 5.2.

**Table 5.2** - The architectures and gas flow ratios of the four nanolaminates and three monolithic coatings for this experiment.

<table>
<thead>
<tr>
<th>Material</th>
<th>Layer Thickness</th>
<th>Total Thickness</th>
<th>Substrate Material</th>
<th>N₂:Ar Flow Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti/TiN</td>
<td>100 nm</td>
<td>1 µm</td>
<td>Si</td>
<td>1:1.5</td>
</tr>
<tr>
<td>Ti/TiN</td>
<td>20 nm</td>
<td>1 µm</td>
<td>Si</td>
<td>1:1.5</td>
</tr>
<tr>
<td>Ti/TiN</td>
<td>100 nm</td>
<td>1 µm</td>
<td>Si</td>
<td>1:1</td>
</tr>
<tr>
<td>Ti/TiN</td>
<td>20 nm</td>
<td>1 µm</td>
<td>Si</td>
<td>1:1</td>
</tr>
<tr>
<td>TiN</td>
<td>-</td>
<td>1 µm</td>
<td>Si</td>
<td>1:1.5</td>
</tr>
<tr>
<td>TiN</td>
<td>-</td>
<td>1 µm</td>
<td>Si</td>
<td>1:1</td>
</tr>
<tr>
<td>Ti</td>
<td>-</td>
<td>1 µm</td>
<td>Si</td>
<td>-</td>
</tr>
</tbody>
</table>

The seven samples will be testing with a three-electrode potentiostat (Gamry Instruments, ParaCell electrochemical cell kit) in a solution of 5 wt.% sodium chloride.
(NaCl) and distilled water. The main corrosion testing that will be performed are cyclic polarization and electrochemical impedance spectroscopy (EIS). The results of these tests will be analyzed to determine how the individual layer thickness and the ceramic composition affects the corrosion rate. The monolithic coatings will be used as a comparison to the nanolaminate coatings.

Previous literature has suggested that increasing the Ti layer thickness will decrease the corrosion rate [78, 93]. Decreasing the amount of bilayers results in the current density increasing, which represents more corrosion occurring in the system [78, 93]. It is anticipated that increasing the bilayer thickness from 20 nm to 100 nm will increase the corrosion rates. The reason increased corrosion is anticipated with the thicker layers is due to the decreased amount of interfaces interfering with the defects that are often associated with TiN (pinholes, cracks). The potential opportunity of increased localized corrosion in the thicker TiN layers will result in more damage to the system and a higher critical current density than in the 20 nm layered systems.

Initial studies performed at Clemson University have shown that as you increase from a monolithic coating to a nanolaminate, the $i_{corr}$ decreases, which signifies a decrease in corrosion. Additionally, as the amount of interfacial density is increased, the $i_{corr}$ is further decreased (Figure 5.4). This finding, using cyclic polarization was further confirmed using EIS (Figure 5.5). The increasing hemisphere from the monolithic TiN to the 20 nm layered nanolaminate indicates a higher resistance to corrosion. The double hemispheres, shown in Figure 5.5b, indicate that the coating and the substrate are both being corroded, where the smaller hemisphere on the left is for the Si substrate.
Figure 5.4- Cyclic polarization measurements recorded from a thin film cell potentiostat. As the amount of interfacial density is increased, the resistance to corrosion increases.

Figure 5.5- Electrochemical impedance spectroscopy measurements recorded from a thin film cell potentiostat. As the amount of interfacial density is increased, the resistance to corrosion increases.

5.4.2. Aim 2: Investigation of the Corrosion Properties of a Metal/Ceramic Interface at the Nanoscale

Understanding how corrosion effects materials at the nanoscale has been a growing interest in the scientific world. Researchers have been developing in situ transmission electron microscopy (TEM) sample holders with electrochemical cells [94, 95]. R. Unocic et al., with the help of Protochips Inc., have developed an in situ electrochemical-
scanning/transmission electron microscopy (ec-S/TEM), which is a technique that utilized microfluidic electrochemical cells to characterize corrosion with microscopy, diffraction, or spectroscopy [95]. The system uses glassy carbon and platinum microband electrodes in a three-electrode cell arrangement with an underlying chip that is connected to a potentiostat on the outside of the TEM. An illustration of the system is shown in Figure 5.6.

![Figure 5.6](image)

**Figure 5.6-** Illustration of the Poseidon 500 ec-S/TEM system. The schematic displays the assembly of the silicon microchip devices within the tip of the TEM holder. Taken without permission from [95].

The importance of *in situ* work involving an electrochemical cell in a TEM allows one to understand the reaction process at the nanoscale. While testing a thin film, the results are a response to how the entire film corrodes on the given substrate. Being able to determine how an electrochemical response will react over a single interface will give great insight to how each layer will further influence the corrosion of the entire nanolaminate. If the amount of corrosion of a single interface is determined, a model can be created to
determine the optimal amount of layers to prevent corrosion, while still allowing for the designers to create a coating with the intended mechanical properties for an application.

For this experiment a single bilayer of titanium nitride on titanium will be deposited and have multiple samples prepared using a FIB. The cross-sections will have the ec-S/TEM electrodes placed over the interface of the metallic/ceramic interface and will be tested in various pH-level aqueous solutions to understand the electrochemical response across the interface.

5.4.2.1 Experimental Methods for Aim 2

For this experiment a Ti/TiN coating will be deposited on a silicon wafer. Each layer of the coating will be $\approx 1 \, \mu m$, resulting in a coating of $\approx 2 \, \mu m$ total thickness. These coatings will be deposited with Ti on the base in contact with the native SiO$_2$ layer on the Si substrate and TiN exposed to the environment. The deposition parameters can be found in Chapter 3.2.1. The TiN will be using a gas ratio of 1:1.5 and 1:1 of nitrogen-to-argon during TiN deposition. The different gas ratios will allow for two different ceramic compositions in the layered coatings. These two coatings will allow researchers to investigate the effect of composition on the corrosion of the individual interfaces.

Each of the two layered films will have three cross-sectional specimens prepared using a focused ion beam (FIB) (Hitachi NB5000 nanoDUE’T FIB-SEM) at the Center for Nanophase Materials Sciences (CNMS) at Oak Ridge National Laboratory. The thin cross-sectional specimens will be prepared to be introduced into the Poseidon 500 ec-S/TEM holder. Bright field (BF) and high angle annular dark field (HAADF) scanning
transmission electron microscopy (STEM) images of the specimens will be acquired \textit{in situ} using a Hitachi HF3300 STEM that was operated at 300kV. A Gatan Quantum ER detector will be used to perform \textit{in situ} electron energy loss spectroscopy (EELS) to determine the chemical composition of each layer of the nanolaminate systems.

5.4.3. Technical Summary

These two future projects will help further elucidate nanolaminate systems in extreme environments, specifically the wear of irradiated metallic/metallic systems and the corrosion of metallic/ceramic systems. The irradiation of metallic/metallic nanolaminates will further and combine initial wear studies performed at Clemson University [54] and irradiation studies at CINT [25, 36]. Additionally, the corrosion of metallic/ceramic nanolaminates has been briefly studied in literature, but conflicting results of various groups makes it difficult to fully understand how increasing the interfacial density of the films effects the corrosion. Furthermore, understanding the corrosion at the atomic scale across a metallic/ceramic interface will allow for the better understanding of how a single interface will influence a whole system once multiple interfaces are incorporated. These studies will further the base understanding of the nanolaminate systems.

5.5. Reference Cited in Chapter Five


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89. Massiani, Y., Medjahed, A., Crousier, J., Gravier, P., Rebatel, I.: Corrosion of


APPENDIX A

USER INSTRUCTIONS FOR EDWARDS ESM100 DEPOSITION SYSTEM

A.1. Components of The Edwards ESM100 Deposition System

In order to deposit the metallic/ceramic nanolaminates studied in Chapter 3 and 4, a system capable of high deposition rates, but with the capabilities of producing fine interfaces is needed. This system can be used to deposit metallic and ceramic monolithic thin films, reactive sputter films, or deposited layered films in a timely fashion, which is imperative due to the lack of automation. These instructions are crucial for users to repetitively create films with consistent properties and help with debugging any issues.

This unit has two positions within the platen to hold 3-4” wafers. The system has an Advanced Energy MDX-10K DC magnetron and a Plasma Products, Inc. RF sputtering power supply. The RF is not currently functioning due to lack of grounding of the deposition system. The vacuum system is comprised of two pumps, a mechanical roughing pump for high pressure pumping and a diffusion pump for low pressure pumping to obtain high vacuum. There are three pressure gauges on the system: two Pirani gauges and one Penning Gauge. In order to control the gas flow of the argon or nitrogen (or other gas if substituted), the system has a MKS 247c 4-channel readout and MKS 250 controller. To prevent gases and hot oil from leaving the diffusion pump and entering the chamber, a Polycold trap was inserted between the diffusion pump and chamber.
A.2. Layout of Sputtering System

Figure A.1 - Layout of Edwards ESM100 deposition system external.

Figure A.2 - Layout of the Edwards ESM 100 system internal.
A.3. Sputtering Procedure

A.3.1. Start-up

1. Turn on both chillers (Equilibrium temperature 15 °C).

2. Turn on main circuit breaker switch at wall.

3. Turn on MKS 247c 4-channel readout and the MKS 250 controller to warm up mass flow controllers (MFCs). These devices control the gas flow into the chamber during deposition. MFC # 1 is for argon and MFC # 2 is for nitrogen.

4. Turn on rotary pump (red switch).

5. Turn on gauge # 2 and wait for rotary pump to be below a pressure of 3x10^{-2} torr.

   a. Note pressure gauge positions:

      i. Pirani gauge (1) in vacuum chamber (high pressure)

      ii. Pirani gauge (2) at intake to rotary pump

      iii. Penning gauge (3) in vacuum chamber (low pressure)

      iv. H/L- Gauge 1 or 3 vacuum chamber, depending on the pressure

6. Turn valve to roughing position [arrow pointing right (turn base of handle to left)].

7. Turn to gauge # 1 and pump below 5x10^{-2} torr.

8. Open valve to backing position [arrow pointing left (turn base of handle to right)].

   a. Turn back to gauge # 2

   b. Handle should pop out ~ ½ inch

   c. In order to go back to roughing position, must push handle back in to turn

9. Once below 5x10^{-2} torr, turn on Polycold unit and the diffusion pump (yellow switch).
10. Wait 45 minutes for diffusion pump to heat up.
   
a. Keep in backing mode

11. To open high vacuum valve, slowly open the valve [move arrow from left to right pointing up (moving handle end from right to left)] while keeping an eye on the pressure gauge # 2. When the high vacuum valve opens, the pressure on gauge # 2 will rise. Keep the pressure on gauge # 2 less than 1x10^{-2} torr. Continue to slowly open the valve until fully open (if not opening, refer to section A.4.).

12. To load sample, turn handle to backing position, press air admittance (white switch).
   
a. Turn gauge to gauge # 1
b. Wait for chamber to equilibrate (wait for loud noise to stop)
c. Wiggle handle on top of chamber to loosen seal
d. Open chamber hatch and turn off air admittance
e. Insert samples and/or replace targets. Try to keep chamber open < 10 minutes
f. Repeat steps 4-8

g. Repeat step 11 to open high vacuum valve, turn to gauge # 3

13. Wait until the pressure in the vacuum chamber is 5x10^{-6} torr or below.

14. The system is now ready for deposition.

A.3.2. DC Magnetron Sputtering

1. Make sure pressure is below 5x10^{-6} torr on gauge # 3.

2. Open the argon valve and nitrogen valve at the tank.

3. Turn the key switch to the power supply to program the deposition run.
4. Press “off” to turn off the flashing light and allow for programming.

5. Set DC power to the desired operating power.
   a. Push “set point” and then hold down “level” button
   b. Move knob to desired power level/current/voltage and release “level”

6. Set desired sputtering time.
   a. Hold “ramp” and tap “set point”
   b. Turn knob to desired time amount, “-- --” for unlimited time

7. Set ramp up time.
   a. 1.50 minutes or more for first layer to clean target
   b. 0.25 minutes for each layer after if making nanolaminate

8. Once desired parameters are reached, switch system’s pressure gauge to gauge #1.

9. Turn on MFC #1 for argon. The gas flow and pressure will fluctuate wildly for a few minutes until flow stabilizes.

10. When MFC #1 becomes stable, adjust the chamber pressure to ~ 5x10⁻³ torr by partially closing the high vacuum valve.

11. Once at desired pressure, hit the run button to rotate sample stage.

12. Press “on” on the DC power supply. The power will gradually ramp up to the set max power determined during programming.

13. When the power set point is reached, the power supply will “ding”. Immediately open the shutter.

14. At the end of the set time, the power will turn off and extinguish the plasma. If running on unlimited deposition time, close shutter and hit “off” button to extinguish plasma.

15. Close the shutter immediately to prevent leftover plasma from falling onto the target.
16. Press the “off” button on the DC power supply.

17. Turn off the MFC # 1 on MKS 247c 4-channel readout.

18. Turn the key to off on the power supply.

19. Open the high vacuum valve.

20. If sample stage is rotating, stop it.

21. Turn off the gas on the tanks.

22. Close the high vacuum valve and put into backing mode.

23. Push the air admittance button (white switch).

24. Wait for chamber to equilibrate (wait for loud noise to stop).

25. Wiggle handle on top of chamber to loosen seal.

26. Open chamber hatch and turn off air admittance.

27. Remove sample and/or insert new samples and/or replace targets. Try to keep chamber open < 10 minutes.

28. Close chamber and turn valve to roughing to pump below $5 \times 10^{-2}$ torr.

29. Turn valve to backing position again.

30. To open high vacuum valve, slowly open the valve [move arrow from left to right pointing up (moving handle end from right to left)] while keeping an eye on the pressure gauge # 2. When the high vacuum valve opens, the pressure on gauge # 2 will rise. Keep the pressure on gauge # 2 less than $1 \times 10^{-2}$ torr. Continue to slowly open the valve until fully open (if not opening, refer to section A.4.).

31. Wait for chamber pressure on gauge # 3 to drop below $5 \times 10^{-6}$ torr if sputter again. If not, allow for $5 \times 10^{-5}$ torr to shut down the system.

A.3.3. RF Sputtering (not in service, must ground system)

1. Make sure source selector switch on controller is set to position # 2.
2. Open argon valve on the tank.

3. Set pressure gauge to gauge # 1.

4. Turn on MFC # 1 for argon. The gas flow and pressure will fluctuate wildly for a few minutes until flow stabilizes to set point gas flow rate.

5. Turn on RF-10 power supply.

6. Set RF Max Power to desired maximum operation power.

7. Turn on RF turning circuits.

8. Set RF tuning to “auto”.

9. On RF power supply, turn power control knob to zero watts.

10. When MFC # 1 is stable, adjust chamber pressure to 1.5-2.0x10^{-2} torr (measured on gauge # 1) by partly closing the high vacuum valve.

11. Turn on the RF power (red button, “RF ON”).

12. Turn up the RF power control knob, until plasma ignites (~ 7-10 watts).

13. Reduce pressure chamber to 1.5-2.0x10^{-3} torr (urgent!).

14. Increase RF power stepwise, as appropriate for target, until max power is reached.

15. For deposition, select sample position or turn on (run button) to rotate sample stage.

   a. If “1” is lit, sample “3” is in the RF position.

16. With plasma stable and at desired power, open shutter for desired time.

17. After closing shutter, you may repeat “Loop: Deposition” to sputter onto another sample.

18. Decrease RF power stepwise, as appropriate for target, to zero watts.

19. Turn off RF power.
20. Turn off MFC # 1 on the MKS 247c 4-channel readout.

21. Open high vacuum valve.

22. If finished with sputtering, turn off RF power supply and RF turning circuits.

23. Close argon valve on tank.

24. To remove sample, close the high vacuum valve and put into backing mode.

25. Push the air admittance button (white switch).

26. Wait for chamber to equilibrate (wait for loud noise to stop).

27. Wiggle handle on top of chamber to loosen seal.

28. Open chamber hatch and turn off air admittance.

29. Remove sample and/or insert new samples and/or replace targets. Try to keep chamber open < 10 minutes.

30. Close chamber and turn valve to roughing to pump below 5x10^{-2} torr.

31. Turn valve to backing position again.

32. To open high vacuum valve, slowly open the valve [move arrow from left to right pointing up (moving handle end from right to left)] while keeping an eye on the pressure gauge # 2. When the high vacuum valve opens, the pressure on gauge # 2 will rise. Keep the pressure on gauge # 2 less than 1x10^{-2} torr. Continue to slowly open the valve until fully open (if not opening, refer to section A.4.).

33. Wait for chamber pressure on gauge # 3 to drop below 5x10^{-6} torr if sputter again. If not, allow for 5x10^{-5} torr to shut down system.

A.3.4. Shutdown Procedure

1. Turn off the MKS 247c 4-channel readout and MKS 250 controller.

2. Make sure argon and nitrogen tanks are closed.

3. Pump vacuum to at least below 5x10^{-5} torr.
4. Close the high vacuum valve and leave in backing position.

5. Turn off diffusion pump (red button) and Polycold system.

6. Let the diffusion pump cool and the Polycold warm for 30-60 minutes to allow Polycold to release gases it has condensed.

7. Close the vacuum valve.

8. Turn off the rotary pump (yellow button).

9. Turn off water chillers.

10. Turn off main breaker switch on the wall.

A.4. Troubleshooting

There are a few potential issues that may prevent the process of deposition. There are a few safety features that are built into the deposition system to allow one to turn on the power supply to the DC magnetron system. First are the safety switches. There are three safety switches distributed around the deposition system. There is a safety switch attached to the valve to open the high vacuum valve (Figure A.3), as well as a safety switch that is attached to the door to the chamber (Figure A.4).
Figure A.3- Safety switch for the high vacuum valve. The button has been circled

Figure A.4- Safety switch for the deposition chamber door.

These safety switches can become stuck or loose. If an error message pops up on the DC power supply, one may have to remove the safety switch and either loosen the screws or add graphite lubricant to allow for movement in the switches. This will allow for deposition. There is a third switch that is located in the rear of the power supplies. There is a light switch that has replaced the switch for the water flow. Because this light switch bypasses the safety switch of the water, the water must be monitored to make sure there is continued water flow. If the flow has stopped, the water lines need to be cleaned out.
The major troubleshooting that may take place is when the high vacuum door does not open. If not operated for an extended period of time, the O-ring that is positioned to create a vacuum between the chamber and diffusion pump may become stuck and the door will not open. If this occurs:

1. Press air admittance to bring the chamber to atmosphere.

2. Turn off power to the roughing pump and diffusion power and power down the entire system. (Make sure the diffusion pump is at room temperature!)

3. One of the pipes between the roughing pump and the diffusion pump has to become detached to allow for equilibrium between diffusion pump and chamber (Figure A.5).

![Figure A.5](image)

**Figure A.5**- Photo of the pipe that must be removed in order to allow for equilibrium pressure between the diffusion pump and the chamber.

4. Once pressure is equal between the diffusion pump and the chamber, open the high vacuum valve to be all the way open.

5. While wearing gloves, reach hand in the chamber and under the safety plate to wiggle the diffusion pump door open.
6. Once open, place a very small amount of diffusion oil and carefully rub the O-ring with the oil to lubricate.

7. Close high vacuum valve and test to determine if it re-opens.

8. Re-attach pipe to diffusion pump.

9. Turn on power to deposition system and start section A.3.1. to turn on deposition system.

10. Determine if high vacuum door can open; if not, repeat the process.
    
    a. System may take longer to pump down due to opening the entire system to atmosphere.
APPENDIX B

USER INSTRUCTIONS FOR NANOINDENTATION AND NANOWEAR BOXES USING A HYSITRON TRIBOINDENTER 950

B.1. Introduction to the Hysitron TriboIndenter 950

The Hysitron TriboIndenter 950 is the newest of the nanoindenter series that is produced by Hysitron, Inc. (Figure B.1). This instrument played a large role in the research that was performed in Chapter 2. The research was performed on the TriboIndenter 950 at the Center of Integrated Nanotechnologies at Los Alamos National Laboratory because it is unlike any equipment located at Clemson University. The TI 950 can create wear boxes and locational indents with precision and accuracy that is unique in the tribological world. The methodology of the 950 is listed below so the work performed in this dissertation can be repeated, as well as save time for future researchers who will be performing nanowear experiments. Complete instructions can be found in Hysitron TriboIndenter 950 User Manual [1].
Depending on the instruments that are installed, the system has the capabilities of performing nanoindentation (both static and dynamic indentation at room and high temperature), atomic force microscopy/scanning probe microscopy (AFM/SPM), scratch testing, and nanowear tests (Figure B.2). The transducer specifications for the load is a resolution of < 1.0 nN and the noise floor of < 30 nN, while the displacement has a resolution of < 0.02 nm and the noise floor of < 0.2 nm. Unlike the TriboIndenter 900 and other older Hysitron nanoindenter models, the 950 incorporates the performech™ advanced control module, which improves the precision of the feedback-controlled nanomechanical testing and increased noise-floor performance [2].

Figure B.1- The Hysitron TriboIndenter 950 system. Taken without permission from [2]
Figure B.2- Photograph of the testing set-up. The high load and low load cell can be replaced with a high temperature cell or an AFM. Taken without permission from [2]

B.2. System Set-up and Calibrations

B.2.1. System Start-up

1. Turn on computer attached to the nanoindenter before turning on system.

2. Turn on both power boxes located in the lower cabinet of the instrument.

3. Initiate the software by selecting the Triboscan software. Select ‘Analysis Only’ if no testing is needed, otherwise, allow time for loading.

4. Select the devices present on the mounts (i.e. low load head, high load head, optical camera).

5. Click ‘OK’ to agree that the system has been setup for quasistatic analysis.

6. Let the software initiate the hardware connection and home the three axes.

B.2.2. Sample Preparation

1. Use superglue to attach sample to an AFM puck. Make sure the AFM puck is concave down to prevent any potential rocking of the sample during testing.
2. Open the front door of the system and place the sample on one of the magnets in the sample stage. This will further prevent movement of the sample.

3. Make sure the taller samples are stationed on the right so the tip does not hit a sample. This is due to the low load transducer and tip being lower than the optical camera.

**B.2.3. Establishing Safety Zones**

1. Turn on the microscope light located next to the nanoindenter computer.

2. Create a new workspace above the ‘Sample Navigation’ tab in the upper left corner. (An older personal workspace can be used if needed, but make sure the sample safety zones are re-established)

3. In the lower left of the ‘Sample Navigation’ tab, in the ‘Sample Boundaries’ region locating in Figure B.3, there will be only the listing ‘Stage’. The ‘Stage’ is a pre-programmed zone which cannot be removed. The geometry of the stage appears in the lower left hand corner with multiple indicators for navigation references: a pink diamond for the optical microscope location and a green diamond for the indenter tip location.
Figure B.3- Screenshot of Triboscan software. The image displays the home screen showing the camera video, the stage controls, and the sample boundaries. Taken without Permission from [1].

4. Select the ‘New Sample’ tab to create and name each of the samples that have been placed to the sample stage. Make sure that the aluminum and fused quartz calibration samples are added in addition to the testing samples.

5. Check both the ‘X-Y Safety DISABLED’ and the ‘Z Safety DISABLED’ buttons located in the ‘Stage Controls’ region in Figure B.3. Note: This is the only time these safeties should be disengaged.

6. Left-click and hold down anywhere in the blue X-Y crosshairs box in the ‘Stage Controls’ section. The further the crosshair is selected from the center, the faster the stage will move.

7. Once the optical camera is above the sample, use the ±Z bar in the ‘Stage Controls’ section to lower the camera to come into focus. Similarly, to the X-Y crosshairs, the further the ±Z bar is clicked from the center line, the faster the stage will move.

8. Navigate the optical camera around the sample and locate a corner or an edge of a sample. Once at a selected position, click the ‘Pos. Add’ button to add a safety zone. Continue until an outline of the sample is complete.

9. Once a sample is completed, repeat the process for all samples and a map of the stage can be observed on the ‘Stage Controls’ or ‘Sample Boundaries’ sections.
10. Uncheck the ‘X-Y Safety DISABLED’ and the ‘Z Safety DISABLED’ buttons so they are no longer red.

**B.2.4. Create an H-Pattern**

1. Position of the optical camera over the aluminum standard.

2. Perform an air indent.
   
   2.1. Go to the Calibration/System Calibration tab
   
   2.2. Under the Transducer Calibrations/Indentation Axis, click the ‘Calibrate’ button.
   
   2.3. Change the load to 1200 µN.
   
   2.4. Click the ‘Cal Air Indent’ button.
   
   2.5. The calibration is performed.
   
   2.6. When prompted, if the data is acceptable, click save.

3. After the air indent is performed, go to the Calibration/Stage Calibration Tab and select ‘Tip to Optic Calibration.’

4. Select ‘New H Pattern.’

5. A dialogue box will direct the user to locate a region where the H-Pattern will be performed. Make sure the optical zoom is set to 1X.

6. The desired load that should be selected for the H-Pattern is 8,000 µN.

7. Hit ‘OK.’

8. Once instructed to, lower the tip to be located approximately 1 mm from the sample. Use the ±Z button in the software to lower the tip. Make sure the actual instrument is being watched to prevent any potential damage or crashing of the tip into the sample/stage.

9. Click ‘OK’ once the desired distance from the sample. The H-Pattern will be automated.
10. Once completed, locate the H-Pattern (black triangles in Figure B.4).

![Figure B.4](image)

**Figure B.4** - The black triangles represent the H-Pattern performed for calibration. The grey triangle represents the indent that is performed once calibration is completed to indicate that this H-Pattern has been used so further testing will not be confused with this H-Pattern.

11. Center the cross-hair over the center of the center indent and click ‘OK.’

12. Once this is completed, perform an additional indent above or below the center indent so future users will know this is a previous calibration (Grey indent in Figure B.4).

13. Once the H-Pattern is complete, perform a ‘Quick Approach’ on the additional samples. Move the microscope over a sample and put the sample into focus. Click the ‘Quick Approach’ and wait for the automated process to complete.

**B.3. Indentation and Nanowear**

**B.3.1. Static Indentation**

1. Whether performing calibration indents for a tip function or a series of indents for testing, the set-up is the same.

2. First, go to the ‘Load Function’ Tab and create the indent test desired (i.e., load, hold, unload or multiple steps). Save the test set-up.

3. After test has been created, go to the ‘Automation’ tab. At this tab, a program can be created to indent a series of indents of the same or varying test procedures.

4. Move to a desired, clean, flat location on the sample that is intended to be indented.
5. Select ‘New Method’, name the method, and select the directory for the files to be saved.

6. Select the ‘Pattern’ tab located to the right of the ‘New Method’ button.

7. Create a new pattern based on the amount of indents desired for the test. Name the pattern. A grid of indents can be selected, the spacing between the indents, and where the indents will start. For example, if 50 indents are desired, a 5x10 or 10x5 grid can be created with 10 µm spacing and the first indent will be in the lower left.

8. Go back to the ‘Setup’ tab where the Method was created and select the desired pattern in the ‘Use Pattern’ box. A lay-out of the pattern will appear in the white box next to it.

9. Go to the ‘Position’ tab and select a new position and name the position. This step is needed to be done for every single method. Make sure the optical camera is moved to a new location before naming new locations.

10. On the ‘Setup’ tab, select the desired position in the position space.

11. Finally, click the ‘Load Function’ button and select the load function that was created before the program was started to be created. On this pop-up, you will also select what max load that will be used and also if there will be a change throughout the test, i.e. will the max load remain the same for all the indents or will the load, for example, increase from 50 µN to 2500 µN, by 50 µN, for the 50 indents in the grid.

12. If two or more methods are going to be run in consecutive order, at the end of the first method, select the name of the second method on the ‘Setup’ tab that states ‘When Method is Complete.’ Repeat for the series of methods that are intended to be run.

13. Once complete, click ‘Start Method’

B.3.2. Nanowear Testing

1. For the wear testing, the test is set-up similarly to that of an automated test for indentation.

2. First, go to the ‘Load Function’ tab and then click on the ‘Scanning Wear’ sub-tab. This will allow the user to make a wear load function similarly to a load
function for a static indent. Select load, amount of lines (select ‘256 lines, 1 Step’ for a full scan), the scan speed, and amount of passes.

3. After test has been created, go to the ‘Automation’ tab. At this tab, a program can be created to perform a series of indents of the same or varying test procedures.

4. Move to a desired, clean, flat location on the sample that is intended to be indented.

5. Select ‘New Method’, name the method, and select the directory for the files to be saved.

6. For ‘Method Type’, change to wear test.

7. Select the ‘Pattern’ tab located to the right of the ‘New Method’ button.

8. Create a new pattern based on the amount of wear boxes desired for the test. Name the pattern. A grid of wear boxes can be selected, the spacing between the wear boxes, and where the wear boxes will start. Note: it is best to next make an automated grid, but make the grid manually with one wear box at a time. This will allow the used to clean the tip between wear boxes with indents into the Al standard.

9. Go back to the ‘Setup’ tab where the method was created and select the desired pattern in the ‘Use Pattern’ box. A lay-out of the pattern will appear in the white box next to it.

10. Go to the ‘Position’ tab and select a new position and name the position. This step is needed to be done for every single method. Make sure the optical camera is moved to a new location before naming new locations.

11. On the ‘Setup’ tab, select the desired position in the position space.

12. Go to the ‘Wear Test’ sub-tab and open the load function for the wear test that was created. Enter in the load and amount of passes. This sub-tab dictates the actual test’s load and amount of passes, while the load function determines the amount of lines and speed.

13. Finally, click the ‘Load Function’ button and make sure the load function is the same that was entered in the ‘Wear Test’ sub-tab.

14. If two or more methods are going to be run in consecutive order, at the end of the first method, select the name of the second method on the ‘Setup’ tab that states ‘When Method is Complete.’ Repeat for the series of methods that are
intended to be run. Note: as recommended in step 8, it is better to have a new method for each wear box, allowing for three cleaning indents into the Al standard between wear tests.

15. Once complete, click ‘Start Method’

B.4. References Cited in Appendix B
