INVESTIGATION OF MECHANICAL PROPERTIES OF COPPER AND ALUMINUM CUVERTICS USING NANOINDENTATION

BY

SAKSHI BRAROO

THESIS

Submitted in partial fulfillment of the requirements for the degree of Master of Science in Civil Engineering in the Graduate College of the University of Illinois at Urbana-Champaign, 2013

Urbana, Illinois

Advisers:

Professor Iwona M. Jasiuk
Assistant Professor Paramita Mondal
Covetics are novel metal-carbon materials invented by Third Millennium Metals, LLC (TMM). Covetics involve copper, aluminum, tin, zinc, silver, gold and other metals or their alloys which are infused with a high weight percent of carbon powder (up to 10%). The amount of carbon in covetics far exceeds the solubility limits of these metals and carbon. The covetics are made using a proprietary method of carbon catalyzation which uses molten metal or metal alloys as an ionizing medium.

In this thesis we study local mechanical properties of copper and aluminum alloy based covetics using the nanoindentation technique. Covetic copper 10200 and aluminum 6061 alloy samples along with standard, commercially available copper 10200, obtained from TMM, were tested. All the samples were as-cast and not heat treated. The copper covetic samples had carbon contents of 0, 3, 5 and 9 weight percent whereas the aluminum covetic samples had carbon contents of 0 and 2.3 weight percent as reported by TMM. Elastic modulus, hardness and friction coefficients were measured. In addition, viscoelastic properties such as storage and complex moduli were assessed for all the covetic samples and standard sample. The obtained values were compared with each other and with those available in literature.

The value of elastic modulus for standard copper 10200 was found to be lower by 7% from the literature reported value. The copper covetic samples studied here were found to have lower elastic modulus and hardness values by 13.5% - 16.8% and 4.8% - 10.8%, respectively when compared to those measured for a standard copper 10200 sample. The results did not show a clear trend with an increase in carbon content. The aluminum covetic samples also exhibited lower elastic modulus than the modulus of aluminum 6061 reported in literature. However, the aluminum covetic samples exhibited a clear increase in modulus and hardness with an increase in carbon content.

In addition, 200 nm thick thin-film samples made of pure copper and
copper covetic (carbon content 5 wt.%) were procured from University of Maryland. Several nanoindentation tests were performed at multiple times on these samples to measure their elastic modulus and hardness. Different mean hardness and elastic modulus values were obtained at different times possibly due to spatial heterogeneity in material properties and possible changes in the thin-films over time. The elastic modulus and hardness values measured in this study for covetic thin film were, in general, lower than those for the pure copper thin film of the same thickness.

All results reported in this study are based on results obtained from one sample of each material type and testing only few locations on each sample. More comprehensive analysis should be done in the future.
To my parents, for their love and support.
I would like to sincerely thank my adviser, Dr. Iwona Jasiuk, for her support and excellent guidance while working on this thesis. I would also like to express my heartiest gratitude to my co-advisor, Dr. Paramita Mondal, for her advice and support.

I thank Jason Shugart, Lou Luedtke and Harry Couch from Third Millennium Metals, LLC, for helpful discussions and for supplying covetic materials for this study. I also thank Prof. Lourdes Salamanca-Riba for supplying thin-films and for discussions. Special thanks to Dr. Francis Ted Limpoco, Dr. Timothy Spila and the staff at the Frederick Seitz Material Research Laboratory for their training and valuable assistance with the nanoindentation equipment.

Finishing this thesis would have been impossible without my family’s love and unwavering belief in me. I am blessed to have their support and I am indebted to them forever. Lastly but not the least, I would like to convey my deepest thankfulness to Suvrat Bhargava for his constant support, patience and invaluable advice while completing this thesis.

This material is based upon work supported by the National Science Foundation under Grant Numbers NSF MRI-0923428 and NSF CMMI-1234130. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.
# TABLE OF CONTENTS

CHAPTER 1  INTRODUCTION ........................................ 1  
1.1 Covetics .................................................... 1  
1.2 Nanoindentation .............................................. 2  
1.3 Motivation ................................................... 2  

CHAPTER 2  BACKGROUND AND LITERATURE REVIEW ............. 3  
2.1 Metal-Nanocarbon Composites .................................. 3  
2.2 Covetics ..................................................... 6  
2.3 Nanoindentation Technique - The Oliver-Pharr Method ...... 12  

CHAPTER 3  EXPERIMENTS AND METHODS .......................... 17  
3.1 Sample Information ............................................ 17  
3.2 Sample Preparation ............................................ 18  
3.3 Surface Roughness Measurement ................................ 19  
3.4 Measurements of Mechanical Properties ..................... 19  
3.5 Instrument Calibration ......................................... 23  

CHAPTER 4  RESULTS AND DISCUSSION ............................. 26  
4.1 Copper and Aluminum Bulk Samples ............................ 26  
4.2 Pure Copper and Copper Covetic Thin-Films ................... 51  

CHAPTER 5  CONCLUSIONS ........................................ 63  

CHAPTER 6  LIMITATIONS AND FUTURE WORK .................... 65  

CHAPTER 7  REFERENCES .......................................... 66
1.1 Covetics

The interest of the scientific community in creating novel materials is now long standing and has proved to be highly fruitful. Man-made materials have mostly taken the form of composites where two or more naturally occurring materials are combined by a variety of techniques to create a new material with properties better than those of the constituents alone. Concrete, polymer matrix reinforced with nanoparticles or Chobham Armor are some of the examples of composite materials developed by scientists. Composite science and technology has developed and diversified to a great extent; there are now several classes of composites, one of which is metal-matrix composites with nano-carbon. Though these metal-carbon composites have demonstrated improved properties, there are several challenges in their processing which include an inhomogeneous distribution of carbon reinforcement and inadequate bonding between the carbon and metal.

Covetics have been reported to be a new type of metal-carbon materials in which a metal and carbon form a strong bond [1]. Covetics were invented by Jason Shugart and Roger Scherer, Ph.D. of Third Millennium Metals, LLC (TMM) [2]. Covetics are produced by reacting carbon with metal at high temperatures in an ionizing environment and it is believed that under these conditions, carbon nanostructures form in-situ and bond with the metal [2]. Reports state that these carbon-metal bonds are stable and the carbon and metal do not separate after remelting and re-solidification [1].

Currently, covetics have been created by combining carbon with 15 different metals and alloys. TMM owns the intellectual property for the metal-carbon composition and the invention of silver covetic [2].
1.2 Nanoindentation

The experimental technique of nanoindentation consists of driving a probe of a particular shape and type into the material which needs to be tested. The motion of the probe can either be load- or displacement-controlled and the load exerted on the material/probe and the penetration of the probe into the material are continuously monitored. A load-displacement plot is generated and the area of indentation impression on the tested material is determined using known geometry of the probe. Principles of contact mechanics are used to derive the hardness and modulus values of the material that was indented.

Nanoindentation allows for localized property measurement and this has resulted in the widespread use of this technique in characterizing all kinds of materials such as metals, ceramics, polymers, composites as well as biological materials, over the past couple of decades. This technique will be discussed in more detail in Chapter 2.

1.3 Motivation

The covetics are new materials with limited published data about them. Research is needed to understand the chemical nature and microstructural organization of these materials as well as to test its mechanical, thermal, and electrical responses.

This dissertation explores the mechanical properties of covetics made from copper and aluminum alloys and compares them with those of standard, commercially available alloys which haven’t gone through the covetic process. The technique of nanoindentation has been employed as it allows for localized property measurement and makes the relationship between microstructural properties and bulk mechanical properties easier to establish. The results of this study complement other microstructural tests and mechanical, electrical and thermal property measurements performed in our group.
CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

This chapter discusses covetics and metal-nanocarbon composites of aluminum and copper, in general. A brief overview of the nanoindentation technique and its history is also presented.

2.1 Metal-Nanocarbon Composites

Metals have now been used for thousands of years to meet mankind’s ever-increasing needs. The main attribute that makes metals so versatile is their combination of high ductility and strength. Over the past decades, as advances in aviation and automobile industry have made leaps forward, traditional metals and metal alloys have been found to be lacking and the need to produce reinforced metal composites was felt.

Carbon nano-particles in the form of carbon nanotubes have been shown to have extraordinary mechanical characteristics such as a modulus up to 1000 GPa and tensile strength greater than 100 GPa [3–7]. Their light-weight combined with their high strength makes them ideal reinforcing media for metals. Metal and carbon-nanotubes have been successfully combined to form what are commonly called carbon nanotube reinforced metal matrix composites (CNT reinforced MMCs). Figure 2.1 and 2.2 are SEM images of Cu- and Al-CNT composites showing the distribution of CNTs in the metal matrix.
Many researchers have shown that CNT reinforced metal composites possess improved mechanical properties when compared with pure metals and
metal alloys from which the composites were made. Tensile tests done by Kuzumaki et al. [10] on CNT reinforced aluminum demonstrated an improvement in tensile strength over pure aluminum as can be seen in Figure 2.3. Similarly, nanoindentation tests done on CNT-reinforced copper by Kim et al. [8] revealed an increase in hardness with increasing carbon content with values of 0.57 GPa, 1.11 GPa and 1.75 GPa for pure copper, Cu-CNT 5 vol.% and Cu-CNT 10 vol.%, respectively. Tensile test results reported in the same study (Figure 2.4) show an improvement in strength over pure copper with increase in carbon content of the composite [8].

![Figure 2.3: Tensile strength vs. annealing time for CNT reinforced aluminum composites [10].](image)

These composites have been produced by a variety of methods, all of which involve mixing or combining ex-situ produced carbon-nanotubes or fibers with the metal. The success of these composites depends highly upon homogeneous distribution of nanotubes throughout the metal and also, on the nature and the strength of the bonds between the CNTs and the metal matrix [9]. Introducing carbon particles into the metal matrix as a reinforcing media does improve the material properties when high homogeneity and good interfacial bonding is achieved. Research done by Noguchi et al. to develop aluminum composites with uniformly dispersed CNTs and testing them has shown a clear improvement in the moduli as interpreted from stress-strain curves obtained from testing [11]. However, Salas et al. reported a reduc-
tion in hardness values which was attributed to heterogeneity produced by agglomeration of CNTs in the matrix [12].

![Graph showing strength and elastic modulus as functions of volume fraction of the carbon-nanotubes in CNT-reinforced copper.](image)

Figure 2.4: Strength and elastic modulus as functions of volume fraction of the carbon-nanotubes in CNT-reinforced copper. [8].

The problem of inhomogeneous distribution of CNTs in the production of these composites has been attributed to entangling of the carbon nanotubes due to their slender nature [11] and the agglomeration of CNTs because of their large surface area which induces large van der Waals forces of attraction. The poor wetting affinity shown by carbon for aluminum [11] and copper [13] contributes to weakening of the interfacial bonding between carbon and the metal [9]. Several techniques [14–16] have been proposed to facilitate uniform distribution of CNTs in the metal, but many of them have associated disadvantages [9].

2.2 Covetics

Though metal-nanocarbon composites have shown improved mechanical performance, their large scale production with uniform distribution of nanocarbon particles and good interfacial bonding remains a problem. In contrast to the method of mixing separately produced CNTs with the metal, covet-
ics are produced by a novel technique that leads to the formation of carbon nanostructures in-situ [2]. This can be hypothesized to have alleviated the problem of poor wetting between carbon and metal that gets enhanced when carbon-nanotubes are introduced into the metal.

Some of the earlier studies such as LECO Combustion Analysis and Glow Discharge Mass Spectrometry done on covetics to study their carbon content failed to identify majority of carbon, indicating that it is very well bonded and dispersed in the metal medium [17]. Use of techniques such as Transmission Electron Microscopy (TEM), X-ray Spectroscopy, Raman Spectroscopy and Electron Energy Loss Spectroscopy (EELS) by Salamanca-Riba et al. [1] have revealed that carbon is incorporated in two different levels in the metals. They reported that some carbon was in the form of particulate nano-carbon of particle size 50-200 nm. Figure 2.5 is the He-ion fractured image of as-extruded aluminum 6061 covetic 3% carbon showing that these carbon particles are uniformly distributed in the metal. They reported the other form of carbon as 5-100 nm regions in which the carbon particles are connected in a network. Testing done on copper and aluminum-covetics by the same group also revealed that lattice-incorporated carbon takes up different forms in different metals. In aluminum, lattice-carbon was shown to form strips oriented mostly along the preferred crystallographic directions (Figure 2.6), whereas in copper, carbon forms modulation along various crystallographic directions (Figure 2.7). Electron Energy Loss Spectroscopy and Raman Spectroscopy were also performed in that study on Al- and Cu-covetics to understand in what form carbon is present inside the metal lattice, which suggested graphite like sheets and $sp^2$ bonding indicative of CNTs [1].

Mechanical testing done by Forrest et al. [17] confirmed improvement in yield strength and tensile strength with increasing carbon content as shown in Figure 2.8 in aluminum-7075 covetics. As-extruded aluminium 6061 covetic sample (3 wt.% carbon) tensile tested along with non-covetic sample revealed a 30 % higher yield strength (Figure 2.9). Similar testing on centrifugally cast covetic and non-covetic copper revealed a much higher value of yield strength of the covetic sample. However, the covetic sample failed sooner which has been suggested to be caused by porosity (Figure 2.11). Nanoindentation tests results reported in the study by Jasiuk et al. [18] show an increase in hardness as carbon content increases for Al 7075 covetics of 0, 3 and 5 wt.% carbon.
Figure 2.5: He-ion fractured image of as-extruded aluminum 6061 covetic containing 3 wt.% carbon [1].
Figure 2.6: SEM image of as-extruded Al 6061 3 wt.% carbon covetic sample showing carbon network [1].

Figure 2.7: HRTEM image of a Cu 5 wt.% carbon covetic sample showing modulation [1].
Figure 2.8: Yield strength and tensile strength vs. weight % of carbon for Al-7075 covetics [17].

Figure 2.9: Stress vs. strain behavior comparison of covetic and non-covetic as-extruded Al-6061 [17].
2.2.1 A Note on Mixing of Carbon and Copper by Ball-Milling

Another technique that has been used to incorporate high amounts of carbon into metals is ball-milling or mechanical alloying. Based on the success of
this technique in creating supersaturated solutions of immiscible solids [19,20] researchers like Marques et al., Wang et al. and Liu et al. [21–23] used this method to infuse carbon into copper with considerable success. These studies report on the effect of carbon assimilation into the metal lattice structure either as solid solution of carbon and metal [23] or formation of small carbon clusters [21]. Inclusion of carbon has been attributed to cause an increase in lattice parameter and lattice strain. However, these studies do not report any results of mechanical testing on bulk form of these materials.

2.3 Nanoindentation Technique - The Oliver-Pharr Method

Nanoindentation is a technique in which a tip or a probe is driven into a material under a specific load as a function of time and then unloaded in a specified time while force and displacement are continuously monitored. This data generates load vs. displacement curve of the form shown in Figure 2.12. Important quantities are measured from this curve which include the maximum load, $P_{\text{max}}$, the maximum indentation depth achieved, $h_{\text{max}}$, the slope of the upper portion of the unloading curve or the contact stiffness, $S = \frac{dP}{dh}$, and the residual depth of penetration remaining on the material after the indenter has been removed after unloading, $h_f$. 

12
Oliver and Pharr [24] proposed a power law fitting to the unloading curve instead of a linear fit approximation proposed by Dorner and Nix [25]. The power law equation of the fitted unloading curve is [24]

\[ P = \alpha (h - h_f)^m \]  

(2.1)
Table 2.1: Power law parameters for different materials as determined by Oliver & Pharr [24].

<table>
<thead>
<tr>
<th>Material</th>
<th>$\alpha$</th>
<th>$m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>0.265</td>
<td>1.38</td>
</tr>
<tr>
<td>Soda-lime glass</td>
<td>0.0279</td>
<td>1.37</td>
</tr>
<tr>
<td>Sapphire</td>
<td>0.0435</td>
<td>1.47</td>
</tr>
<tr>
<td>Fused Silica</td>
<td>0.0500</td>
<td>1.25</td>
</tr>
<tr>
<td>Tungsten</td>
<td>0.141</td>
<td>1.51</td>
</tr>
<tr>
<td>Silica</td>
<td>0.0215</td>
<td>1.43</td>
</tr>
</tbody>
</table>

Another important parameter to be determined is the actual depth over which the indenter is in contact with the material. Figure 2.13 shows a schematic of the indentation process on the surface of the material. Note that in this figure the term indenter is refers to indenter tip or probe. The contact depth $h_c$ is actually different from the maximum penetration depth $h_{\text{max}}$ which also includes the sink-in of the surrounding area which is assumed to be an elastic half-space.

![Figure 2.13: Schematic of unloading part of the indentation process [26].](image)

The Berkovich indenter tip is modeled by a conical tip of half angle $\phi = 30^\circ$ which has the same depth-area relationship as the Berkovich tip to meet the basic assumption that the surrounding area near the indentation sinks in a manner predicted by models for indentation based on rigid indenter probes of simple geometry [27–31]. These models give the following relationship for the sink-in of the contact periphery, assuming there is no pile-up:
\[ h_s = \epsilon \frac{P_{\text{max}}}{S} \]  

(2.2)

where \( P_{\text{max}} \) is the maximum applied indenter load, \( S \) is the contact stiffness, and \( \epsilon \) is a constant that depends on the geometry of the indenter shape. For the conical indenter \( \epsilon = 0.72 \) [26].

From eq. (2.2) and Figure 2.13 an expression for the actual contact depth between the indenter and the material can be derived as:

\[ h_c = h_{\text{max}} - \epsilon \frac{P_{\text{max}}}{S} \]  

(2.3)

Before the elastic modulus and hardness values can be computed the projected area of the indenter at the contact depth has to be determined. This is achieved by using an experimentally generated indenter tip area function which is obtained by making multiple indents over a load range on a material of known elastic moduli and whose response to indentation is mostly plastic. The unloading curves of these various indents are then fitted to eq.(2.7) to compute the tip area as a function of depth, \( A = f(h_c) \). Details of this procedure have been reported by Oliver and Pharr [24]. For an ideal Berkovich indenter tip the area function is given by eq. (2.4).

\[ A(h_c) = 24.5h_c^2 \]  

(2.4)

Due to tip rounding that might occur because of grinding of the tip over many uses, the actual area function for the Berkovich tip can be of the following form:

\[ A(h_c) = 24.5h_c^2 + C_1h_c^{\frac{1}{3}} + C_2h_c^{\frac{1}{3}} + C_3h_c^{\frac{1}{3}} + ... + C_8h_c^{\frac{1}{128}} \]  

(2.5)

where \( C_1 \) to \( C_8 \) are constants that arise due to changes in the tip geometry.

The hardness of the material being tested is now given by

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

(2.6)

The reduced elastic modulus \( E_r \) of the combined indenter tip and specimen
system is related to contact stiffness, $S$ and contact area, $A$ by eq. (2.7),

$$E_r = \frac{S\sqrt{\pi}}{2\beta \sqrt{A}}$$

(2.7)

where $\beta$ is a factor that takes into account any deviations in the axial symmetry of the indenter tip. However, it has been found to have a value other than 1 (it would be unity for a perfectly axis-symmetric tip) even for axially symmetric tips and has thus, been included in the eq. 2.7 whereas, originally, it was assumed to be unity [24].

The reduced modulus is related to the Young’s modulus $E$ and Poisson’s ratio $\nu$ of the material and the indenter tip by the relation:

$$\frac{1}{E_{reduced}} = \left(\frac{1-\nu^2}{E}\right)_{\text{indenter}} - \left(\frac{1-\nu^2}{E}\right)_{\text{sample}}$$

(2.8)

These values of experimentally obtained elastic modulus and hardness are not accurate in cases where pile-up of the material is observed and can deviate as much as by 60 % [32]. During the pile-up, the material undergoing indentation flows plastically and collects around the indent on the surface, thereby, increasing the actual contact area over and above the projected tip cross-sectional area. This phenomenon and a correction for it has been explained in more details in Chapter 3 - Experiments and Methods.
3.1 Sample Information

In this study, the following materials were tested:

1. Standard, commercially available copper 10200 alloy referred to as standard Cu-10200 hereon.

2. Copper 10200 covetic with 0 wt.% of carbon (material underwent covetic process but no carbon was added).

3. Copper 10200 covetic with 3 wt.% of carbon.

4. Copper 10200 covetic with 5 wt.% of carbon.

5. Copper 10200 covetic with 9 wt.% of carbon.

6. Aluminum 6061 T0 covetic with 0 wt.% of carbon (material underwent covetic process but no carbon was added).

7. Aluminum 6061 T0 covetic with 2.3 wt.% of carbon.

8. Pure copper thin-film, 200 nm thick.

9. Copper covetic thin-film with 5 wt.% of carbon, 200 nm thick.

All the copper covetic and aluminum covetic samples were received from TMM in the form of as-cast rods with no heat treatment and of dimensions 2 cm x 2 cm x 20 cm. The as-cast standard Cu-10200 material which was used by TMM to produce the copper covetics was also received in form of a thick plate (∼1 cm thick). The thin-film samples were received from Professor Lourdes Salamanca-Riba at University of Maryland.
3.2 Sample Preparation

Three millimeter thick samples were cut from the rods perpendicular to their lengths at two locations: near the edge and about 2.5 cm away from the edge. The machining work was performed in the machine shop of Mechanical Science and Engineering department at the University of Illinois at Urbana-Champaign. The surfaces for all bulk samples (i.e. all samples other than thin-film samples) were prepared by mechanical polishing followed by vibro-polishing. The complete polishing regime consisted of the following steps.

1. The samples were polished with Buehler silicon carbide polishing paper of the following grit measures in order P600, P800 and P1500, moving from the coarsest to the finest sized papers. These steps constituted coarse polishing.

2. Fine polishing was carried out with alumina powders of 1 μm and 0.3 μm diameter particle sizes used with 3 μm and 0.25 μm polishing cloths, respectively, and in that order.

3. The samples were then placed in the vibro-polisher for ~48 hours using 50-70 nm diameter alumina colloidal gel. Samples were mounted on aluminum stubs of ~2.5 cm diameter using superglue before being placed in the vibro-polisher.

Table 3.1: Grit size and particle size of polishing papers/cloths used in sample preparation.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Particle Size</th>
<th>Grit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coarse polishing</td>
<td>26 μm</td>
<td>P600</td>
</tr>
<tr>
<td>Coarse polishing</td>
<td>22 μm</td>
<td>P800</td>
</tr>
<tr>
<td>Coarse polishing</td>
<td>12.5 μm</td>
<td>P1500</td>
</tr>
<tr>
<td>Fine polishing</td>
<td>3 μm</td>
<td>-</td>
</tr>
<tr>
<td>Fine polishing</td>
<td>0.25 μm</td>
<td>-</td>
</tr>
<tr>
<td>Vibratory polishing</td>
<td>50-70 nm</td>
<td>-</td>
</tr>
</tbody>
</table>

For coarse and fine polishing the MetaServ® 250 polisher-grinder from Buehler was used and for vibro-polishing the Syntron vibro-polisher was used. Both the equipments are housed at the Fredrick Seitz Material Research Laboratory at the University of Illinois at Urbana-Champaign.
3.3 Surface Roughness Measurement

The surface roughness of polished samples was measured to verify their compliance with ASTM E2546-07 and ISO standards 14577 of metal specimen preparation for nanoindentation. The measurements were performed in the imaging mode of the Hysitron TriboIndenter TI 950 using a Berkovich tip. A setpoint force of 3.00 µN and a scan rate of about 1.00 Hz were used to scan and image over 10 µm x 10 µm squares. The average roughness $R_a$ and root mean square roughness $R_q$ values over 10 µm lateral length were calculated by the Triboview software using images saved during the scans. The scans were done on 5 different locations on each sample and over several profile lines on each scan. Figure 3.2 shows one such measurement.

ASTM E2546-07 recommends to maintain the profile surface roughness parameter $R_a < 10$ nm over a trace length of 10 µm in order to minimize the effect of surface condition on measured values. ISO 14577 recommends $R_a < h_{max}/20$ where $h_{max}$ is the maximum depth of the tip achieved while indentation. Roughness values measured by Hysitron TI-950 TriboIndenter were all found to have a roughness parameter $R_a < 10$ nm.

3.4 Measurements of Mechanical Properties

3.4.1 Indentation

Hysitron TriboIndenter TI 950 was used to perform the indentations on all samples. Number of indents (>150) were performed on each sample with load functions of varying loading-, hold- and unloading-times and peak loads. Specific load functions and peak load values are mentioned along with their results in the Chapter 4 - Results and Discussions chapter. The standard Berkovich diamond indenter tip was used to perform all the indents. The unloading segments of the resulting load-displacement curves were analysed by the TriboScan software as per the Oliver-Pharr method to give the reduced modulus and hardness values.
Figure 3.1: Surface scan, line-profile and roughness measurement over profile.

Pile-Up Correction

The scanning mode of the TriboIndenter was used to scan the indents to check for pile-up and create pile-up profiles. The semi-ellipse method developed by Kese et al. [33] was used to apply a pile-up correction. The pile-up occurs as a result of plastic flow of the material around the indenter tip which collects on the surface as the tip is being forced into the material. Kese et al. have defined the total indentation area $A$ to be made up of area determined by Oliver-Pharr method $A_{OP}$ and area contributed by pile-up $A_{PU}$. Pile up area $A_{PU}$ has been approximated by projecting a semi-ellipse of major axis $b$ and minor axis $a_i$ where $b$ is the side of the projected triangular cross section of the Berkovich indenter tip as shown in Figure 3.2. Kese et al. obtained $a_i$ from the cross-sectional image and profile of the indent using Atomic Force Microscopy (AFM). In this study, the same profile was generated by using the scanning mode of the Hysitron TriboIndenter.
Figure 3.2: Line diagram of an indent and its profile generated by a Berkovich indenter tip. Only one pile-up peak is shown on the right for clarity [33].

The area of an equilateral triangle of side \( b \) is given by eq. (3.1) and, if assuming a perfect Berkovich indenter tip, the projected contact area \( A_c \) at depth \( h_c \) is given eq. (3.2).

\[
A_{eq} = \frac{b^2}{4} \tan 60^\circ = 0.433b^2 \quad (3.1)
\]
\[
A_c = 24.56h_c^2 = 0.433b^2 \quad (3.2)
\]

From eq. (3.1) and (3.2)

\[
b = 7.531h_c \quad (3.3)
\]

The area of each semi-elliptical pile-up lobe/peak is computed by \( \frac{\pi b}{4}a_i \). Then, eq. (3.4) is used to compute the area of all the pile-up lobes as

\[
A_{PU} = \frac{\pi b}{4} \sum a_i \quad (3.4)
\]
The true contact area now becomes

\[ A_{PU} = A_{OP} + A_{PU} = A_{OP} + \frac{\pi b}{4} \sum a_i \]  

(3.5)

where \( A_{OP} \) is the area output by the indenter using the Oliver-Pharr method.

The modified area is used in eq. (2.6) and eq. (2.7) to compute corrected reduced modulus and hardness.

### 3.4.2 Scratch Testing

Hysitron TriboIndenter TI 950 was used in nanoscratch mode to perform scratch tests on all samples. Several scratches (>45) were made on each sample with load functions shown in Figure 3.3. The standard Berkovich diamond indenter tip was used to make all the scratches. During the test, the indenter tip was driven into the sample with a pre-determined normal force as a function of time (see Figure 3.3) while it was moved to a fixed distance in the lateral direction for a specified time. The normal and the lateral forces measured continuously by the instrument were then used to calculate the coefficient of friction.

![Figure 3.3: Load and displacement functions used for scratch testing of all samples.](image)

### 3.4.3 Dynamic Mechanical Analysis

The NanoDMA III mode of the Hysitron TriboIndenter TI 950 was used to perform the dynamic indentations on all samples. Several indents (>40) were performed on each sample with load functions shown in Figure 3.4. The
standard Berkovich diamond indenter tip was used to perform all the indents. The NanoDMA mode allows for continuous stiffness measurements and in this technique the instrument applies a smaller sinusoidal load along with a higher static force to perform the indent. The storage, loss and complex moduli along with the phase shift between force and displacement signals are measured by the instrument.

![Figure 3.4: Load function used for NanoDMA testing of all samples.](image)

3.5 Instrument Calibration

Before testing a specimen (indentation, scratch testing or scanning) in the Hysitron TriboIndenter a number of calibration checks are performed to ensure maximum accuracy in the results generated and a safe operation of the equipment. These checks are:

1. Current system parameters are checked against those provided by the manufacturer to ensure a match.

2. The instrument consists of a stage on which the specimen is placed and an indenter which is driven into the specimen (see Figure 3.5). The Hysitron TriboIndenter has an additional optical microscope to facilitate the user-selection of indent locations on the sample. To ensure perfect coordination between optical view points and actual indent locations, a stage-optic calibration is performed where a specific pattern of indents is made on an opaque material, such as aluminum, that leaves a noticeable residual impression at a location chosen from the optical microscope. After making this pattern the indents are located
under the microscope and the instrument then calibrates the stage location accordingly.

3. The assembly into which the tip or probe is attached has many delicate springs and plates that control and precisely monitor tip’s location in the X-, Y- and Z-directions. This assembly needs to be calibrated so that precise displacement measurements can be made. This is achieved by performing an indent in the air and checking to see if the resulting noise and maximum displacement is within the limits set by the manufacturer.

4. The correct tip-area function is confirmed by indenting on a material such as quartz of known elastic modulus and hardness and checking to see if the instrument generates reasonably correct values of these quantities within acceptable error bounds.

5. Before performing an indent, a drift check is performed to capture the thermal drift rate of the tip and/or the specimen i.e., any displacement that might be due to thermal expansion/contraction and not due to actual indenter load. This displacement is then subtracted from the actual displacement of the indenter during the test.
Figure 3.5: A schematic of a nanoindenter.
CHAPTER 4

RESULTS AND DISCUSSION

This chapter discusses the results obtained by nanoindentation testing of a set of samples of copper 10200 and aluminum 6061 covetics as well as standard Cu 10200, provided to us by TMM. Elastic (Young’s) modulus, hardness and friction coefficients as well as viscoelastic properties of the samples are compared and plausible explanation for any trends observed has been presented. Results from testing of pure copper and copper covetic thin films have also been presented and discussed.

4.1 Copper and Aluminum Bulk Samples

4.1.1 Optical Images

Optical images were taken of the covetic samples using the Triboindenter optical microscope. The microstructures of covetics containing different amounts of carbon shown in Figures 4.1, 4.2, 4.3, 4.4, 4.5 and 4.6.
Figure 4.1: Cu 10200 with 0 wt.% carbon made using covetic process.

Figure 4.2: Cu 10200 covetic with 3 wt.% carbon.
Figure 4.3: Cu 10200 covetic with 5 wt.% carbon.

Figure 4.4: Cu 10200 covetic with 9 wt.% carbon.
4.1.2 Static Indentation

Indents (>150) were made on the copper- and aluminum-covetic and standard copper 10200 samples using 10s loading time, 10s hold time and 10s
unloading time, trapezoidal load function with peak load of 5000 \( \mu N \). Indentations were performed in a grid format (20 \( \mu N \) spacing between indents) at two different locations and the data was combined to calculate the mean elastic modulus and hardness. The mean of the modulus and hardness data was computed after removing outliers (values beyond \( \pm \) from mean). The modulus and hardness values were corrected for pile-up according to the semi-ellipse method suggested by Kese et al. [33]. Figures 4.7 and 4.8 show a comparison between mean Young’s modulus and hardness of the standard Cu-10200 and copper covetic samples of carbon percentages 0, 3, 5 and 9 percent. Figures 4.13 and 4.14 are mean modulus and hardness plots of Al-covetic 0 % and 2.3 % carbon contents. Young’s modulus and hardness values obtained from individual indents were sorted in the ascending order and plotted against the measurement indent number (stated as measurement number in plots) to check for any clumping of data that might indicate different phases/ grains in the microstructure seen in the optical images in the previous section of this chapter (See figures 4.9, 4.10, 4.11, 4.15 and 4.16).

![Figure 4.7: Young’s modulus (mean and standard deviation) of standard Cu 10200 and Cu-covetic samples.](image)
Figure 4.8: Hardness (mean and standard deviation) of standard Cu 10200 and Cu-covetic samples.

Figure 4.9: Young’s modulus measured in each indent (outliers removed).
The results show that the covetic samples received from TMM exhibited different mechanical properties. The modulus and hardness values of Cu-covetic samples tested were smaller than the corresponding values measured for standard Cu-10200 sample tested. The plots of the sorted data for both
copper and aluminum do not reveal any clumping. However, they do reveal
that the variation in the standard copper measurements is similar to that
seen in covetic samples tested in this study. One can conclude that the
variation seen in the measurements on covetic samples are not due to material
heterogeneity. Indeed, Energy Dispersive Spectroscopy (EDS) testing done
in our group on the covetic samples at different locations didn’t reveal any
spatial variation in carbon composition on the indentation surface of each
sample. The modulus values of Cu-covetic samples with all carbon contents
tested were very similar in magnitude to each other with no clear trend with
carbon content but the differences between them were statistically significant
except for modulus of the 0 and 5 % Cu-covetic samples and the hardness of
3 and 5 % Cu-covetic sample. The aluminum covetics samples did show an
improvement in properties with an increase in carbon content.

An interesting observation was made when sorted Young’s modulus data
of copper covetics and standard Cu-10200 with outliers were plotted against
the measurement number. Several outlier values were found to lie within 20-
25 GPa in the case of covetic samples but not for standard Cu-10200 (Figure
4.10). The indents corresponding to these outlier data points were found
to leave no residual impression. No relationship was found between these
indent locations and any specific phase/ grain type seen under the optical
microscope. The average hardness values corresponding to these outliers in
modulus measurements were slightly higher than the mean hardneses of
covetic samples as shown in figure 4.10. To better understand these outlier
points, load-displacement curves corresponding to these points were plotted
along with typical load-displacement curves for that sample. However, the
load-displacement curves of the outlier points did not differ from typical
load-displacement curves for other indent points on the sample. One such
comparison for copper covetic 5 wt. % carbon is shown in Figure 4.12. We
have no explanation for this behavior.
The modulus of standard Cu-10200 with value 107.3 ± 3.3 GPa measured by nanoindentation is lower but still comparable to the value of 115 GPa (ASM handbook) of Cu-10200 found in literature (values of 120 to 180 GPa obtained using nanoindentation technique for pure copper have been reported [34]). The hardness values measured by nanoindentation reported in literature for pure copper vary from 1.25 to 1.5 GPa [35, 36] which is slightly lower than 1.67 ± 0.07 GPa obtained for standard Cu-10200 in this study. ASM Handbook reports a smaller Rockwell hardness of pure copper as compared to that of Cu10200 and that trend might be reflecting in the nanoindentation results of this study when compared with literature values. The values measured in this study for copper-covetics are lower than those measured by Hysitron for cold-rolled Cu-Ni-C covetics [37].

Thus, we find that the elastic modulus and hardness of copper covetic samples tested in this study were lower than reported in literature for standard Cu-10200. Research done by Salamanca-Riba et al. [1] has revealed the presence of $sp^2$ bonding in covetic samples which can indicate combining or clustering of carbon atoms. Similar conclusions were drawn by Marques et al. [21] who showed that carbon clusters are more common in a carbon-metal composite that a solid solution of carbon and metal and that this cluster-
ing can cause an increase in the lattice parameter and lattice strain. If we assume that similar phenomena are occurring inside the covetics, one can then hypothesize that the assumed carbon clustering inside copper covetics is weakening the mechanical response by spreading of the crystal lattice. Although one can argue that particle reinforcements can have the effect of impeding dislocation motion inside the metal, leading to a stiffer response, the spreading of the lattice parameter and increasing of lattice strain [23] is a competing mechanism that can plausibly offset the dislocation impedance if a critical lattice parameter increase is reached. Note that the Cu-covetic sample with 0% carbon content has a similar response although no carbon is said to be present. More microstructural investigations are needed to understand the changes that the covetic process itself and not just inclusion of carbon might be inducing in the material. The fact that the properties of copper covetics sample of all carbon percentages tested in this study showed a more or less uniform response can indicate that the processing might be the game-changing factor rather than the carbon inclusion in case of copper covetics.

Figure 4.13: Young’s modulus (mean and standard deviation) of Al-Covetic 0% and 2.3% carbon content.
Figure 4.14: Hardness (mean and standard deviation) of Al-Covetic 0% and 2.3% carbon content.

Figure 4.15: Young’s modulus measured in each indent of Al-Covetic 0% and 2.3% carbon content (outliers removed).
Both aluminum covetic samples of 0 wt.% and 2.3 wt. % carbon content tested in this study were found to have lesser values of modulus (52.7 ± 7.21 and 67.3 ± 13.54 GPa) than those reported in literature for Al 6061-T0 which is about 69 GPa (ASM Handbook) although the Al-C 2.3 wt% modulus was much closer to this value. In the case of aluminum covetics, a clear improvement in properties is seen with increase in carbon content in contrast to the flat trend of copper covetics. Since the lattice parameter in pure aluminum is greater than the lattice parameter in copper, it can be hypothesized that the possible clustering of carbon atoms that could be causing lattice spreading in copper covetic may not be causing a significant increase in lattice parameter and strain in aluminum covetic. Perhaps, the carbon clusters, if present, are indeed impeding dislocation movement and causing the stiffer response in the 2.3% aluminum sample tested.

The experimental results shown above pertain to tests done on a sample taken 2.5 cm away from the edge of the as-cast rods supplied by TMM. Similar experiments were also performed on a sample taken from ends of the rods. Figures 4.17, 4.18, 4.19 and 4.20 compare the hardness and modulus values of the edge and the inner samples for copper and aluminum covetics. It is clearly seen that the end samples show poorer and unusually low
values in some cases. For example moduli of Cu covetic 9 wt.% carbon and hardness values for Cu covetic 5 wt.% carbon show a large variation. It can be hypothesized that such performance can be due to high heterogeneity of material and/or porosity at the edge of the rods (possibly caused due to non-uniformity in the rate of cooling process along the length of rods). Keeping this in mind, no further testing was performed on the edge samples and the results so forth will only pertain to the tests done on inner samples.

Figure 4.17: Young’s modulus comparison between end samples and inner samples of standard Cu-10200 and copper covetic.
Figure 4.18: Hardness comparison between end samples and inner samples of standard Cu-10200 and copper covetic.

Figure 4.19: Young’s modulus comparison of end and inner samples of aluminum covetic.
4.1.3 Pile-Up Correction

This section compares the elastic modulus and hardness values before and after applying pile-up corrections. Pile-up was observed in all samples. The area of contact in case of pile-up is higher than the actual projected area of the indenter tip at the depth of the indentation. Values of modulus and hardness for such a material are therefore overestimated. Once the correct area is determined it can then be used to recalculate the modulus and hardness values. The corrected modulus and hardness values in this case were similar to the values output by the instrument (details of the correction applied can be found in the Chapter 3 - Experiments and Methods). Figures 4.21, 4.22, 4.23 and 4.24 compare the corrected and uncorrected values of modulus and hardness.

Figure 4.20: Hardness comparison of end and inner samples of aluminum covetic.
Figure 4.21: Young’s modulus of standard Cu-10200 and copper covetic before and after pile-up correction.

Figure 4.22: Hardness of standard Cu-10200 and copper covetic before and after pile-up correction.
Figure 4.23: Young’s modulus of aluminum covetics before and after pile-up correction.

Figure 4.24: Hardness of aluminum covetics before and after pile-up correction.
4.1.4 Dynamic Indentation

Dynamic mechanical analysis was performed on the copper- and aluminum-covetic samples using a constant strain rate load function with peak load of 5000 $\mu N$ along with a superimposed sinusoidal load function to perform the indents. The load and displacement signals measured by the instrument were used to output storage, loss and complex moduli. The following plots in figures 4.25, 4.26, 4.27 and 4.28 were obtained by averaging the storage and complex moduli measured by the instrument over each indent.

Figure 4.25: Average moduli vs. indent depth curve of Cu 10200 0 wt.% carbon.
Figure 4.26: Average moduli vs. indent depth curve of Cu 10200 3 wt.% carbon.

Figure 4.27: Average moduli vs. indent depth curve of Cu 10200 5 wt.% carbon.
Figure 4.28: Average moduli vs. indent depth curve of Cu 10200 9 wt.% carbon.

Figure 4.29: Average moduli vs. indent depth curve of Al 6061 0% carbon content.
Figure 4.30: Average moduli vs. indent depth curve of Al 6061 2.3% carbon content.

As can be seen from the copper covetic plots above, very little, if any, difference is seen between the storage and complex moduli as the plots for complex and storage moduli are overlapping. This indicates that negligible viscoelastic behavior is exhibited by copper covetic samples tested in this study at room temperatures. Viscoelasticity is commonly observed in polymers and most metals including copper have not been shown to be viscoelastic at ambient temperatures and moderate loading [38]. Experiments, especially at higher temperatures, might be needed to understand the viscoelastic nature of those samples.

On the other hand, aluminum covetic samples show a viscoelastic response with loss moduli values of around 15 GPa. Loss modulus for pure aluminum has been reported to be only about 1 GPa. This indicates the the inclusion of carbon into aluminum has induced a polymer-like behavior.

4.1.5 Indentation Size Effect

Many researchers have observed and studied the indentation size effect (ISE), which is the increase in measured mechanical properties, especially hardness, as the depth of indentation decreases [39–41]. Several reasons have been
stated to explain this effect [42], including: presence of thin oxide film on the surface of specimen, residual stress and strain hardening due to surface preparation methods, area function calibration over higher load range only and pile-up. Particular care was taken in this study to correct for or avoid all of these factors. The oxide films that exist on copper and aluminum samples are of the order of 50-100 nm [43] and 5 nm [44], respectively, which are smaller when compared to the magnitude of indent depth for the smallest size indent made on the bulk samples in this study (≈ 250 nm). Mechanical polishing and grinding can induce residual stresses in the upper layer of the specimen. However, this layer can be completely removed or made negligible by vibro-polishing for long durations or by electro-polishing [45]. In this study, vibro-polishing for 24 to 48 hours was performed on all the samples to attain not just a smooth finish but to remove the residual stress layer created by grinding and polishing. The Berkovich indenter tip area function was calibrated for load and range of 100 \( \mu N \) to 8000 \( \mu N \) to ensure any effect of tip rounding is removed. Pile up correction performed at 5000 \( \mu N \) load didn’t reveal any significant corrections in modulus and hardness values.

Indentation size effect was studied by performing 25 indents on the copper covetic and base samples using different peak loads varying from 2000 \( \mu N \) to 7000\( \mu N \). Despite taking measures to curb ISE, all samples exhibited some degree of indentation size effect (Figures 4.31, 4.32, 4.33 and 4.34). A lesser degree of indentation size effect on hardness measurements is seen in covetic samples compared to standard Cu-10200 sample.
Figure 4.31: Young’s modulus variation with indent depth of standard Cu-10200 and copper covetic samples.

Figure 4.32: Hardness variation with indent depth of standard Cu-10200 and copper covetic samples.
Figure 4.33: Young’s modulus variation with indent depth of aluminum covetic samples.

Figure 4.34: Hardness variation with indent depth of aluminum covetic samples.
4.1.6 Friction Coefficients

Friction coefficients were measured by testing the copper and aluminum covetic and standard Cu-10200 in the scratch mode of the TriboIndenter where the indenter tip is made to scratch the surface at a constant normal load. While performing the scratch test the instrument measures the lateral resistance load and calculates the coefficient of kinetic friction. The coefficient of friction shows an increase with increasing carbon content. However, the values of several of the samples were not found to be statistically different due to large standard deviation in the mean. The mean friction coefficient of 0 % copper-covetic sample was not found to be statistically different from the mean friction coefficient of any other copper covetic sample. Also, the mean coefficients for the pairs Cu-covetic 3 % and Cu-covetic 9 % as well as Cu-covetic 5 % and Cu-covetic 9 % were not found to be different. No statistical difference was found between the mean coefficients of 0 wt.% and 2.3 wt.% carbon Al-covetic samples as well.

Figure 4.35: Friction coefficients of standard copper and Cu-covetic samples.
4.2 Pure Copper and Copper Covetic Thin-Films

4.2.1 Experimental details

Indentation tests to measure modulus and hardness of pure copper and copper covetic thin films were done at multiple locations and different testing dates. The table below summarizes the dates and the parameters of the different tests performed. Group 1 tests are the first experiments done on each film, Group 2 tests are the second experiments done on the films and so on. It should be noted that the pure copper film was produced in August 2013 and the covetic thin-film was produced in February 2013.
Figure 4.37: List of experiments done on thin-films and their details.

<table>
<thead>
<tr>
<th>S. No</th>
<th>Test Group</th>
<th>Test Date</th>
<th>Sample</th>
<th>Peak Load</th>
<th>Load Function</th>
<th>Number of Indents</th>
<th>Performed By</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Group 1</td>
<td>3/9/13</td>
<td>Cu-C 5%</td>
<td>200</td>
<td>10s-10s-10s</td>
<td>8 x 8</td>
<td>Alexander Setters</td>
</tr>
<tr>
<td>2</td>
<td>Group 1</td>
<td>9/13/13</td>
<td>Cu</td>
<td>200</td>
<td>10s-10s-10s</td>
<td>10 x 10</td>
<td>Sakshi Braroo</td>
</tr>
<tr>
<td>3</td>
<td>Group 2</td>
<td>9/11/13</td>
<td>Cu-C 5%</td>
<td>200</td>
<td>10s-10s-10s</td>
<td>10 x 10</td>
<td>Sakshi Braroo</td>
</tr>
<tr>
<td>4</td>
<td>Group 2</td>
<td>11/9/13</td>
<td>Cu</td>
<td>200</td>
<td>10s-10s-10s</td>
<td>10 x 10</td>
<td>Sakshi Braroo</td>
</tr>
<tr>
<td>5</td>
<td>Group 3</td>
<td>11/26/13</td>
<td>Cu-C 5%</td>
<td>200</td>
<td>10s-10s-10s</td>
<td>10 x 10</td>
<td>Sakshi Braroo</td>
</tr>
<tr>
<td>6</td>
<td>Group 3</td>
<td>11/26/13</td>
<td>Cu</td>
<td>200</td>
<td>10s-10s-10s</td>
<td>10 x 10</td>
<td>Sakshi Braroo</td>
</tr>
<tr>
<td>7</td>
<td>Group 4</td>
<td>11/25/13</td>
<td>Cu-C 5%</td>
<td>100</td>
<td>10s-10s-10s</td>
<td>10 x 10</td>
<td>Sakshi Braroo</td>
</tr>
<tr>
<td>8</td>
<td>Group 4</td>
<td>11/25/13</td>
<td>Cu</td>
<td>100</td>
<td>10s-10s-10s</td>
<td>10 x 10</td>
<td>Sakshi Braroo</td>
</tr>
</tbody>
</table>

Figure 4.38: Young’s modulus (mean and standard deviation) of pure copper and copper covetic films from different groups (see Figure 4.37) with outliers removed.
Figure 4.39: Hardness (mean and standard deviation) of pure copper and copper covetic films from different groups (outliers removed).

Figure 4.40: Young’s modulus (mean and standard deviation) modulus of thin-films measured from different groups (including outliers).
Figure 4.41: Hardness (mean and standard deviation) of thin-films measured from different groups (including outliers).

Figure 4.42: Young’s modulus (mean and standard deviation) comparison of pure Cu and Cu covetic thin-films obtained from tests done at the same time (outliers removed).
Figure 4.43: Hardness (mean and standard deviation) comparison of pure Cu and Cu covetic thin-films obtained from tests done at the same time (outliers removed).

Figure 4.44: Young’s modulus (mean and standard deviation) modulus comparison of pure Cu and Cu covetic thin-films obtained from tests done at the same time (including outliers).
Figure 4.45: Hardness (mean and standard deviation) comparison of pure Cu and Cu covetic thin-films obtained from tests done at the same time (including outliers).

Figure 4.46: Young’s modulus (mean and standard deviation) comparison of pure Cu and Cu covetic thin-films obtained from 100µN peak load tests (outliers removed).
Figure 4.47: Hardness (mean and standard deviation) comparison of pure Cu and Cu covetic thin-films obtained from 100µN peak load tests (outliers removed).

Figure 4.48: Young’s modulus (mean and standard deviation) comparison of pure Cu and Cu covetic thin-films obtained from 100µN peak load tests (including outliers).
Figure 4.49: Hardness (mean and standard deviation) comparison of pure Cu and Cu covetic thin-films obtained from 100µN peak load tests (including outliers).

Figure 4.50: Young’s modulus (mean and standard deviation) comparison of pure Cu and Cu covetic thin-films obtained from 100µN and 200µN peak load tests done at the same time (outliers removed).
Figure 4.51: Hardness (mean and standard deviation) comparison of pure Cu and Cu covetic thin-films obtained from 100μN and 200μN peak load tests done at the same time (outliers removed).

Figure 4.52: Young’s modulus (mean and standard deviation) comparison of pure Cu and Cu covetic thin-films obtained from 100μN and 200μN peak load tests done at the same time (including outliers).
Figure 4.53: Hardness (mean and standard deviation) comparison of pure Cu and Cu covetic thin-films obtained from 100µN and 200µN peak load tests done at the same time (including outliers).

Figure 4.54: Young’s modulus measurements comparison of pure Cu thin-film obtained from all indents for all test groups.
Figure 4.55: Young’s modulus measurements comparison of Cu covetic thin-film obtained from all indents for all test groups.

Figure 4.56: Hardness measurements comparison of pure Cu thin film obtained from all indents for all test groups.
Depth of indentation for 200 $\mu N$ and 100 $\mu N$ load test were around 15% and 10% of film thickness. For soft films like that of copper, indent depth of 15% of film thickness should produce results free from substrate effect [46].

Young’s modulus and hardness values were found to vary in each set of experiments with 200 $\mu N$ peak load, likely due to heterogeneity of samples. Also, since some of the tests were done after several months from procuring the film, changes in film chemistry could also have introduced variability in the results although no monotonic decrease in film properties is seen with time as might have been expected. The mean modulus of Cu and Cu-C films measured during 100 $\mu N$ peak load tests were not found to be statistically different although all the measurements done with 200 $\mu N$ peak load were statistically different even with large observed standard deviation. The 100 $\mu N$ tests had maximum indent depth of about 20nm and might have been inaccurate due to being so close to the instrument’s precision.

In general, the copper covetic film that was tested using 200 $\mu N$ was found to have lower modulus than the pure copper thin-film, possibly due to the same mechanism as hypothesized for bulk samples.
CHAPTER 5

CONCLUSIONS

The following points summarize the results and conclusions drawn from the data obtained from various tests that were performed on the standard Cu 10200, Cu 10200 covetics, Al 6061 covetics and pure copper and copper covetic thin-films samples that were tested:

1. Copper-covetic samples tested were found to have lower Young’s modulus and hardness when compared with literature values of these mechanical properties for standard Cu 10200 as well as those obtained by testing of the standard sample. For copper covetics, no trend in these properties was seen with an increase in carbon content. Aluminum covetics tested in this study also exhibited lower mechanical properties when compared to Al 6061 properties found in literature. However, Al-covetics did show a monotonic increase in properties with increase in carbon content.

2. Viscoelasticity was not observed in bulk copper covetic samples tested at room temperatures which is the behavior expected of standard copper. Aluminum covetic samples on the other hand did show viscoelasticity greater than reported for aluminum in literature, indicating that the inclusion of carbon has the effect of imparting polymer-like characteristics to aluminum.

3. Friction coefficients measured for these samples showed a monotonic increase with carbon content although a large scatter was observed in the data possibly because of low peak load function used in testing. However, the differences in the friction coefficient values for different carbon contents were not statistically significant.

4. Indentation size effect was observed in all the samples although careful steps had been taken to avoid it.
5. Covetic thin-film tested in this study was found to have lower modulus and hardness values than pure copper film tested. But due to large variation in results from different tests and a possible change that might have occurred in the thin-films over time, nothing conclusive can be said about the performance of the films.

6. In general, it can be concluded that adding carbon produces different results in different metals. More research needs to be done to understand the exact nature of interaction of carbon with metals in covetics and the resulting mechanical properties.
The aim of this study was to measure the local properties of copper and aluminum covetics and compare them with those of standard copper and aluminum alloys. The following points summarize the limitations of this study and make several suggestions for future work that will provide a better understanding of results obtained in this study, in particular, and of covetics in general.

1. Results reported in this study for bulk samples pertain to covetics produced from as-cast and non-heat treated aluminum 6061 and copper 10200 alloys only. Other post processing methods could produce other results.

2. The carbon contents reported in this study for all the covetic samples are those stated by TMM. These numbers reflect the amount of carbon that was used at the start of the covetic process. No conclusive data on carbon content was obtained due to challenges involved in those measurements.

3. The two copper thin-films tested and compared in this study were not produced at the same time (they were made six months apart) which made it difficult to draw clear conclusions from the results observed.

4. Nanoindentation is a very localized technique and in this study, all indents were done in a grid format on small regions of size 200 $\mu$m by 200 $\mu$m. More tests at different locations should be done to more accurately capture the properties of these samples.

These results are limited only to nanoindentation data. A more comprehensive characterization of the structure, composition and mechanical properties should be done to understand covetics and interpret these results. Such study is in progress and will be reported elsewhere.
REFERENCES


