SOLID LUBRICATION MECHANISMS IN LASER DEPOSITED NICKEL-TITANIUM-CARBON METAL MATRIX COMPOSITES

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A Ni/TiC/C metal matrix composite (MMC) has been processed using the laser engineered net shaping (LENS) process from commercially available powders with a Ni-3Ti-20C (atomic %) composition. This processing route produces the in-situ formation of homogeneously distributed eutectic and primary titanium carbide and graphite precipitates throughout the Ni matrix. The composite exhibits promising tribological properties when tested in dry sliding conditions with a low steady state coefficient of friction (CoF) of ~0.1 and lower wear rates in comparison to LENS deposited pure Ni. The as deposited and tribologically worn composite has been characterized using Auger electron spectroscopy, scanning electron microscopy (SEM), X-ray diffraction, high resolution transmission electron microscopy (HRTEM) with energy dispersive spectroscopy (EDS), dual beam focused ion beam SEM (FIB/SEM) serial sectioning and Vickers micro-hardness testing. The evolution of subsurface stress states and precipitate motion during repeated sliding contact has been investigated using finite element analysis (FEA). The results of FIB/SEM serial sectioning, HRTEM, and Auger electron spectroscopy in conjunction with FEA simulations reveal that the improved tribological behavior is due to the in-situ formation of a low interfacial shear strength amorphous carbon tribofilm that is extruded to the surface via refined Ni grain boundaries.
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CHAPTER 1
INTRODUCTION AND LITERATURE REVIEW

Metal matrix composites (MMCs) are a combination of a metallic matrix, usually a refractory metal, and a reinforcing secondary phase that is typically a ceramic [1]. This combination of material classes leads to the tailoring of specific material properties that are dependent on volume fraction, size, shape and distribution of the reinforcing phase, interfacial strength, and the material properties of the constituents [1-5]. As a result of optimization of these parameters, MMCs can exhibit an improvement of specific stiffness, high temperature creep resistance, thermal stability, Young’s modulus, coefficient of thermal expansion, compression and tensile strength over the individual constituents that they are comprised [6-8]. MMCs can be classified as either continuously or discontinuously reinforced where the previous contains directionally oriented fibers or filaments and the later contains distributed particulates. Continuously reinforced MMCs have a high degree of anisotropy with respect to mechanical properties and are more expensive to fabricate in comparison to discontinuously reinforced MMCs [7,8]. The focus of this work remains on discontinuously reinforced MMCs.

Processing of discontinuously reinforced MMCs can be categorized as either ex-situ or in-situ. In processing of ex-situ MMCs, the reinforcing phase is processed independently and prior to the fabrication of the composite, while in in-situ MMCs, the reinforcing phase is created by chemical reactions during processing. Ex-situ processed MMCs often result in an undesirable microstructure with unequal distribution of reinforcing particle spacing and size, poor wettability between the reinforcement and the matrix due to surface contamination and interfacial reactions between the reinforcement and the matrix [9,10]. Thus in-situ processed MMCs offer improvements in control over the resultant microstructure and mechanical properties. In-situ
processing routes of MMCs have been categorized by Tjong et al. [10] according to the temperature of the metal and the reactants as solid-liquid reactions, vapor-liquid reactions, solid-solid reactions and liquid-liquid reactions. The most common of these reaction processes used to process MMCs is the solid-liquid reaction process whereby the reinforcing particles are formed in-situ by diffusion of reactants in the liquid metal solvent. The processing techniques that use this reaction process are self-propagating high temperature synthesis [11,12], exothermic dispersion [13,14], reactive hot pressing [15,16], combustion assisted cast [17], direct reaction synthesis [18,19], flux assisted synthesis [20], reactive spontaneous infiltration [21,22], direct melt metal oxidation [23], reactive squeeze casting [24] and rapid solidification process [25-29]. The process used for deposition of this study is a rapid solidification process by laser engineered net shaping (LENS).

MMCs used in tribological applications can include particles that are harder than the matrix, softer than the matrix or both. Commonly used hard particles include Al$_2$O$_3$, SiC, WC, TiN and TiC and commonly used soft particles include MoS$_2$ and graphitic C. Wear rates in aluminum metal matrix composites have been shown to decrease with increasing volume fraction of either soft or hard particles [2]. This reduction in wear is contributed to two factors; one due to reduced adhesive wear via the reduction of real area contact between the composite and counterface with increasing hardness of the matrix; and two the reduction of interfacial shear strength and adhesion via the formation of tribofilms containing the softer phase [2,30]. Jinfeng et al. [31] and Riahi et al. [32] have reported wear results that follow the same trend in Al/SiC/graphite composites and suggest that the load bearing capacity of the hard reinforcing SiC particles in conjunction with a lubricating graphitic tribofilm are the main contributors to this observation.
Sliding friction values in lab atmosphere conditions are also shown to decrease with increasing volume fraction of graphite within the composite up to a value of approximately 20% where the friction coefficient reaches a steady value of approximately 0.2 [2,30]. This reduction of sliding friction is suggested by the authors to be due to saturation and complete coverage of the worn area by graphite that is “squeezed” out of the subsurface of the composite and smeared about the surface of the contact area. The addition of graphite to the surface is suggested to reduce interfacial shear strength due to the lamellar structure of graphite. This lamellar structure which contains much stronger bonds within the (0002) basal plane versus between basal planes is contributed with the reduced interfacial shear strength by slip between them. It has been well documented in [2] that this reduction in friction for graphitic materials is only observed in environments that contain water vapor.

Subsurface deformation and formed tribo-layers have been analyzed for Al/SiC/Graphite composites by Riahi et al. [32]. The surface film consisted of fractured SiC and NiAl$_3$ intermetallic particles intermixed with iron oxides that were likely introduced during testing from the steel counterface. They also observed subsurface formation of lamellar graphite films within the tribo-layers on the order of 1-5 µm thick that are suggested to form at high subsurface shear stress regions. These lamellar graphite tribo-layers were observed to be at the boundary between the heavily deformed surface region and the relatively undeformed bulk of the composite. This high shear accommodation of subsurface regions with strain reported to be on the order of 2-10 suggest that subsurface graphite also plays a role in the mitigation of subsurface deformation and subsequent wear.

The present investigation attempts to provide the following insights into solid lubrication mechanisms of MMCs:
1. Determine the structure and composition of the interfacial tribofilms that develop after sliding wear. For example, it is commonly thought that graphite tribofilms present on the sliding surfaces mitigate friction and wear. Is this carbon allotrope phase correct? Does it intermix with the metal matrix or particle reinforcements?

2. Resolve the pathway for carbon to provide solid/self-lubrication. Does it involve subsurface to surface plastic shear? What are the roles of the metal matrix grains and reinforcing particles during sliding?

3. Couple contact mechanics continuum modeling to experimentally observed phenomena. Does the finite element modeling agree with experiments? Are there new computational insights into sliding deformation modes?
CHAPTER 2
MATERIALS AND EXPERIMENTAL PROCEDURES

2.1 Materials and Preparation

The materials used to fabricate the Ni-TiC-C MMC were near spherical gas atomized powders of pure Ni, pure Ti and Ni coated graphite purchased from Crucible Research™. All powders were sieved through -100/+325 mesh which results in a particle distribution with nominal diameter between 44-149 µm. The Ni coated graphite powder is comprised of 25% Ni and 75% C by weight. Ni coated graphite powders were chosen over pure graphite particles to reduce flow constriction in the LENS powder delivery system to provide more precise mass flow during deposition. Two samples were prepared for analysis, one of pure Ni and one of 3% Ti, 20%C balance Ni (Ni-3Ti-20C) in atomic percent. Both compositions were premixed by ball milling with tungsten carbide spheres using a twin roller mixer for 6 hours at 300 rotations per minute to ensure a near homogeneous mixture of the unlike powders and equal preparation processes.

2.2 Laser Engineered Net Shaping (LENS)

The LENS process is a computer numerically controlled (CNC) deposition process similar to that of stereolithography. Figure 1 shows a schematic diagram of the LENS system. Deposition begins with a three dimensional computer aided design (CAD) solid model. This model is then converted into a standard tessellation (STL) file which converts the solid design into a three dimensional array of triangles that define the surface geometry of the solid. This array is then imported into a slice program that uses the boundaries and dimensions of the STL file to generate a stack of planar vector tool paths with user defined spacing’s between vectors and each stack called hatch width and layer spacing respectively. These tool paths are used for
motion control of the X-Y stage and Z axis which controls the laser focus point. Deposition is done by focusing the laser onto a substrate creating a molten pool while simultaneously feeding powder from the hopper with an inert Argon gas flow through a four nozzle assembly converging at the same point. This focal point is then scanned via relative motion along the planar vector tool paths by the X-Y stage generating deposition lines of controlled width and height. After a layer of deposition is completed the focal point and converging four nozzle assembly are moved a vertical distance equal to the layer spacing by the Z axis. This process is shown in Figure 2 and repeated until the solid object is completed.

Figure 1. Schematic diagram of LENS system.

The LENS system used for deposition is an Optomec, Inc. 750 equipped with a 500W Nd: YAG laser which emits radiation with a wavelength of 1.064 µm. Depositions were made with a laser power of 350 W in the geometry of a 10 mm diameter circle of 10 mm height on 0.5 inch stainless steel substrate. The hatch width was 0.018 inch with a layer spacing of 0.010 inch. Each layer of planar vector tool paths was comprised of one circumferential pass with linear vectors contained within this circumference. Each subsequent layer was scanned with a rotation of the linear vectors by 60° to reduce the chance of over deposition within one region. All depositions were made in an inert Argon atmosphere with a mean pressure of 6 bar while maintaining less than 10 parts per million of oxygen. The volumetric flow rate of the powder
carrying Argon was maintained at 3 liters/min. The completed cylindrical depositions were then removed through the ante chamber for sample preparation.

Figure 2. Schematic of LENS deposition process. (Image courtesy of Optomec Inc.)

### 2.3 Sample Preparation

The cylindrical deposits were first sectioned into smaller cylinders with a height of 3mm using a CNC wire electric discharge machine (EDM). EDM machines are commonly used to cut and machine extremely hard conductive materials that would be difficult to shape using conventional methods. A wire EDM works by passing a brass wire with variable high voltage through the sample while it is submerged in a dielectric fluid. As the local charge between the sample to be cut and the brass wire overcomes the strength of the dielectric fluid (in this case deionized water) a conduction pathway is generated and results in a plasma arc that removes small amounts of mass from both materials surfaces that is subsequently flushed from the cutting region with a dielectric jet [33]. As a result of the mass loss a continuous supply of new brass wire is fed into the system and a cut is generated in the sample with a precision of 0.001 inch.

The 3 mm height cylinders were then encased in a conductive polymer for ease of manual polishing and to ensure proper conduction for future imaging techniques. Each sample was polished using a progression of 400, 600, 800, 1200 grit silicon carbide paper in wet conditions.
Further polishing to a metallographic finish was conducted using suspended alumina powders in a progression of nominal size from 1 µm, 0.3 µm and 0.05 µm. The polished samples were then ultra sonicated in acetone and then methanol baths each for 20 minutes to remove remnants of alumina powders form the surface. After sonication the samples were placed on a hot plate at 150ºC for 10 minutes to evaporate any remaining solvents.

2.4 Characterization

2.4.1 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) is a method of determining crystal structure of materials through the reflections of the source radiation with crystallographic planes according to their planar spacing defined by the reciprocal lattice vector and Bragg’s law. The collected data for a bulk sample of randomly oriented grains is known as a powder diffraction file (PDF) which is a plot of reflected intensity versus twice the angle of incident irradiation. The experiments conducted here within were done using a Rigaku Ultima III diffractometer equipped with a Cu Kα X-ray source generated at 40 kV and 44 mA which has a 1.54 Å wavelength. The experimental parameters used were sample step size of 0.01º, scan speed 1º/min, start angle: 20º, stop angle 90º, attenuator: open and receiving slits: DS=3 mm, SS=1 mm, RS=1 mm. The data collected was then processed using Jade v7.0 software.

2.4.2 Scanning Electron Microscopy (SEM)

SEM is used here to image the microstructure of the material to determine phase structure and distribution. A FEI Nova NanoSEM 230 was used in back scattered electron mode to image with greater contrast between elemental atomic mass. The microscope was operated at 15 kV with a field emission current between 3-6 nA. Area fraction measurements were done using ImageJ software.
2.4.3 Vickers Micro-Hardness Testing

Vickers micro-hardness measurements were conducted on the pure Ni and Ni-3Ti-20C composite using a Shimadzu Vickers hardness tester. The tests were performed at room temperature with a normal load of 300 g and a hold time of 15 seconds. Test locations were taken at random from the metallographically polished surface and measured using a 40X magnification optical microscope and attached viewing scale. Hardness measurements were taken at 10 different locations with a spacing of at least 300 µm between each measurement. The Vickers hardness number (HV) is obtained by the following expression:

\[ HV = \frac{F}{A} \approx \frac{1.8544F}{d^2} \]

where \( F \) is the normal load in kgf, \( A \) is area in mm\(^2\) and \( d \) is the average length of the diagonal left by the indenter in millimeters. The corresponding units of HV are then kilograms-force per square millimeter (kgf/mm\(^2\)).

2.4.4 Tribology

Unidirectional sliding friction and wear testing is used to determine the coefficient of friction (CoF), defined as the ratio of tangential to normal force, in a specific environment as well as produce a wear track that can be measured to determine the wear rate. An Implant Sciences Falex ISC-200 pin-on-disc (POD) tribometer was used to collect the CoF data which is plotted versus distance traveled. Tests were performed with 1/8 inch diameter Si\(_3\)N\(_4\) ball with an applied normal load of 0.49 N and 2.45 N which corresponds to an initial max Hertzian point contact stress (\( P_{\text{max}} \)) of 1.11 GPa and 1.50 GPa respectively. Sliding speed during testing was maintained between 20-22 mm/sec out to 140 m total sliding distance. All tests were conducted at room temperature in lab air (~40% Relative Humidity).
Wear rates were analyzed using a scanning micro-profilometer. The micro tip of the profilometer was first scanned normal to the direction of sliding across the wear track with a minimum of 100 µm of unworn area scanned on each side of the wear track to normalize the depth versus scan distance plot. This procedure was repeated at eight separate locations on the wear track and the calculated cross-sectional area of wear averaged between these results. The averaged cross-sectional area is then multiplied by the circumference of the wear track to calculate volume of material removed. The wear rate of the material is then determined as the ratio of material volume removed to normal load times total sliding distance and is reported in the units of mm³/Nm.

2.4.5 Auger Electron Spectroscopy (AES)

AES is a chemical analysis tool that uses an electron gun to produce Auger escape electrons very near the surface from orbital shell transitions that have a unique energy. The energy of these Auger electrons collected by a spectrometer identifies the element probed by the gun. The current analysis used a PHI 670xi scanning Auger nanoprobe operating at 20kV and 10nA to map the elemental distribution of the as deposited sample and worn surfaces of the tribologically tested sample. Collected spectra were data shifted to C1s energy of 284.6eV for precise identification.

2.4.6 Dual Beam Focused Ion Beam SEM (FIB/SEM) Serial Sectioning

FIB/SEM serial sectioning is a method of imaging a materials microstructure in three dimensions through repeated ion milling of small sections and imaging of the newly generated surface. Conventional FIB/SEM serial sectioning is conducted by first milling trenches around the volume to be analyzed and then sectioning the exposed volume still attached to the bulk as shown in Figure 3.
Figure 3. Conventional FIB/SEM serial sectioning configuration. White lines signify milling patterns [36].

A more involved technique given by Schaffer and Wagner requires several more steps of preparation over conventional FIB/SEM serial sectioning which are shown in detail in Figure 4 [36]. Figure 4 (a) shows deposition of a protective Pt layer to mitigate effects of ion beam scatter milling areas of interest while milling the trench patterns shown in white rectangles. Figure 4 (b) and (c) show the undercut milling patterns and resultant block of material supported by two beams connected to the bulk. Figure 4 (d-f) shows the use of the Omniprobe needle to remove the volume of interest and mounting to a separate post through Pt deposition. This technique has several advantages over the conventional technique which are listed below.

1. Improved image contrast by removing “shadows” created in the conventional method as a result of secondary electron trajectories from the bottom of the area of interest to the detector being blocked by the surrounding bulk. An example can be seen in Figure 4 (b).

2. Consistent phase contrast throughout the serial sectioning volume due to the removal of the “shadow” effect and reduction of secondary electron noise from the surrounding bulk.
3. Removal of surrounding re-deposition surfaces that can build up over time during sectioning of large volumes and completely block the area of interest from view of the detector.

![Figure 4. SEM images of block lift-out technique. (a-c) Milling patterns and resulting block. (d-f) Removal and mounting to post [36].](image)

The technique for serial sectioning employed for the current analysis includes one more preparation step between those shown in Figure 4 (d) and (e) where the Omniprobe with attached lift-out is rotated about its axis 180°. When the lift-out is attached to the post in this orientation it results in the area of interest being on the top surface of the volume so that sectioning can be done in a vertical manner as shown in Figure 5. This vertical orientation was chosen for two reasons.

1. The block lift-outs analyzed were larger in the dimension of sectioning than the allowable SEM beam deflection which would require stage movements during sectioning using the other methods and introduce drift.

2. The surface exposed to the incident FIB can be selected through stage rotation before sectioning to further mitigate beam scatter damage of sensitive tribo-layers.
Figure 5. Schematic of lift-out and area of interest relative to FIB and SEM beams in the vertical orientation.

The serial sectioning experiments here within were completed using a FEI Dual Beam FIB/FESEM Nova 200 with the SEM column operating at 5 kV and 3 nA and the FIB column operating at 30 kV and 0.3 nA.

2.4.7 High Resolution Transmission Electron Microscopy (HRTEM)

HRTEM is a method by which high energy electrons are used to image microstructures by tunneling of the electrons through the sample and is capable of resolving individual atomic planes. The method requires the sample to be electron transparent to the potential of the microscope gun and thus must be extremely thin. The sample preparation process was carried out using the aforementioned FIB/SEM by first removing a lift-out from a site specific location and subsequently mounting and polishing it to electron transparency using the FIB. A FEI Tecnai F20 field-emission gun (FEG) TEM operating at 200keV which produces electrons with a wavelength of approximately 0.025 Å was used for analysis. This equipment also has an energy dispersive spectroscopy (EDS) detector with the capability of generating line profiles of the spatial distribution of elements in the sample. EDS utilizes X-ray photon emission from electron transitions to lower energy orbitals after being excited by the incident high energy beam of the
FEG. These emitted X-rays are collected by a spectrometer and indexed according to their energy. This method was used in conjunction with HRTEM bright field micrographs to analyze the tribologically worn samples.

2.5 Finite Element Analysis (FEA)

FEA was conducted using ABAQUS Standard version 6.x to investigate the subsurface stress states and precipitate motion during repeated sliding contact in plane strain analysis. The material model was comprised of a rectangular half-space with a total depth 400 times and a width 1000 times that of the largest precipitate modeled to reduce errors from boundary conditions. Each side edge boundary condition allowed zero displacement in the X direction and the bottom edge boundary condition allowed zero displacement in the Y direction. Figure 6 shows the global coordinate axis with the mesh scheme of triangular elements. The mesh in Figure 6 was generated by first seeding the side edges with a linearly increasing spacing from the surface to a final equivalent spacing at the bottom and a spacing of the top surface that linearly increased from the center to the edges. This configuration was chosen to minimize the calculation time while maintaining a high density of elements near the precipitates and resulted in approximately 17,500 elements. Also shown in Figure 6 is the rigid indenter which was modeled using a 20° arc with a radius equivalent to the 1/8 inch Si₃N₄ ball used in the POD experiments. This rigid indenter was restricted by zero rotation about its center of mass.
Figure 6. Finite element mesh arrangement and rigid indenter.

Tribological stresses were modeled by applying a normal load at the center of the rigid indenter of 98.9 mN/unit length which results in an equivalent initial Hertzian max line contact stress of 1.50 GPa for the POD test conducted with a 2.45 N load. The CoF between the rigid indenter and the surface of the rectangular half space was kept at 0.1 while sliding in the positive X direction. To return the indenter to the initial position after a frictional sliding contact the normal load applied to the rigid indenter was reduced to 0.05 N to avoid plastic deformation and the CoF taken to be zero.

Material behavior was modeled as isotropic perfectly elastic and perfectly plastic with elastic modulus, Poisson’s ratio and yield stress values for each material summarized in Table 1.

<table>
<thead>
<tr>
<th>Material</th>
<th>Elastic Modulus (GPa)</th>
<th>Poisson’s Ratio</th>
<th>Yield Stress (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix</td>
<td>200</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Graphite</td>
<td>15</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>TiC</td>
<td>450</td>
<td>0.3</td>
<td>2.5</td>
</tr>
</tbody>
</table>
A total of five different precipitate configurations were analyzed and their initial shapes are shown in Figure 7. Figure 7 shows graphite precipitates in green and TiC in red with (a) being only graphite, (b) only TiC, (c) graphite on the leading edge of TiC, (d) graphite above TiC and (e) graphite on the trailing edge of TiC with respect to indenter motion during frictional contact.

Figure 7. (a-e) Initial precipitate orientation in FEA models. Green is graphite, red is TiC.
CHAPTER 3

RESULTS AND DISCUSSIONS

3.1 X-Ray Diffraction (XRD)

Figure 8 shows the XRD scan of the as deposited Ni-3Ti-20C composite. The primary peaks observed are indexed according to crystallographic plane and show the existence of hexagonal graphitic C with a (0002) basal plane reflection as well as face centered cubic (FCC) Ni and FCC TiC which exhibits a NaCl rocksalt type structure. This indexing was consistent with PDF files 03-065-2865 for FCC Ni, 03-065-8805 for FCC TiC and 03-065-6212 for graphite. The relatively low intensity of FCC TiC reflections in Figure 8 with respect to FCC Ni indicates that there is a lower percent volume fraction of TiC which is to be expected due to only 3 atomic% of Ti used during deposition. The observed reflection of the FCC TiC phase also shows that it was formed by an in-situ reaction during LENS deposition due to the initial powder form of these elements being comprised of pure Ti and Ni coated graphite.
3.2 Scanning Electron Microscopy (SEM)

The as deposited microstructure of the Ni-3Ti-20C composite is shown as backscattered SEM images in Figure 9. Figure 9 (a) shows the homogenous distribution of the included particles throughout the Ni matrix and (b) highlights the primary and eutectic morphologies of both Graphite and TiC that follow from the solidification reaction of liquid Ni (Ti,C) → liquid Ni + TiC + C → eutectic (Ni + TiC + C). Although a reliable ternary diagram of the Ni-Ti-C system from liquidus to room temperature is not available the larger precipitates of TiC and C are referred to as primaries. The primary TiC forms a cuboidal structure in the liquid due to its rocksalt FCC structure while the more acicular TiC is eutectic precipitate formation which is in agreement with the TiC-Ni phase diagram given by Liu et. al [34]. The primary C forms predominantly spherical structure which is likely due to a combination of surface energy reduction and hydrostatic pressure imposed by the liquid Ni. This formation of primary and eutectic C precipitates is in agreement with the Ni-C phase diagram given by Lee [35].
Figure 9. Backscatter SEM images of Ni-3Ti-20C composite. (a) Low magnification. (b) Higher magnification.

Figure 10 (a) shows the area fraction of both the primary C and eutectic TiC and (c) shows just the selected primary C precipitates from the SEM image in (b). Table 2 summarizes the area fractions and average area in square microns. Average area values are obtained in ImageJ by first converting the SEM scale bar to a pixel equivalent whereby the enclosed features can be measured by square pixels then recalculated as square microns.

Figure 10. Area fraction measurement profiles and SEM image of Ni-3Ti-20C. (a) Area fraction of all precipitates. (b) Backscatter SEM image. (c) Area fraction of primary C.
Table 2. 
Area fraction and average area of precipitates in Ni-3Ti-20C

<table>
<thead>
<tr>
<th>Phases</th>
<th>Area fraction</th>
<th>Average Area (µm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>All Precipitates</td>
<td>18.2</td>
<td>0.56</td>
</tr>
<tr>
<td>Primary C</td>
<td>8.3</td>
<td>6.57</td>
</tr>
</tbody>
</table>

3.3 Vickers Micro-Hardness

The inclusion of the hard TiC phase within the composite contributed to a substantial increase in Vickers hardness (HV) over that of the pure Ni whose values are shown in Table 3 with their measured standard deviation. This increase in hardness is an indicator that the tribological properties of the material will be improved due to an increase in matrix stiffness and thus reduced area of contact under a given load as well as reduction in wear rate.

Table 3.
Vickers hardness (HV) of Ni-3Ti-2-C and pure Ni

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hardness (HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-3Ti-20C</td>
<td>240 ± 6</td>
</tr>
<tr>
<td>Pure Ni</td>
<td>165 ± 6</td>
</tr>
</tbody>
</table>

3.4 Tribology

POD friction and wear tests conducted for a total sliding distance of 140m are shown in Figure 11 and show a clear improvement of CoF for the Ni-3Ti-20C composite compared to pure nickel. The results for pure Ni show a slow increase in run in friction to a steady state coefficient of approximately 0.75. This is likely due to the existence of a nascent oxide on the surface with a higher hardness than the bulk that initially would reduce the contact area between the Si₃N₄ ball and lower friction until it is worn away. After the oxide layer is removed the expected behavior of a pure metal with high adhesion leads to higher observed CoF. For the Ni-3Ti-20C
composite in both the 1.11 GPa and 1.50 GPa $P_{\text{max}}$ tests the CoF showed a steady state value of approximately 0.1. Both of these tests showed a short run in distance to the steady state value which is likely due to the exposed graphite on the sample surface acting as a solid lubricant and the increased hardness of the matrix due to the TiC phases that reduces contact area. Interestingly the tribological behavior during the 1.11 $P_{\text{max}}$ test resulted in high friction at the onset of testing which could be due to the lower contact stress not being able to provide C to the surface, will be shown in subsequent analysis.

![Graph](image.png)

**Figure 11.** Coefficient of friction versus sliding distance for Ni-3Ti-20C and pure Ni.

The wear characteristics of the Ni-3Ti-20C composite are given by the wear rate calculation method described in section 3.4.4. The resultant wear rate for the Ni-3Ti-20C composite tested at 1.11 GPa $P_{\text{max}}$ was $1.38 \times 10^{-6}$ mm$^3$/Nm, which is in the low wear regime.
3.5 Auger Electron Spectroscopy (AES)

AES was used to map both the worn and unworn surfaces of the Ni-3Ti-20C composite to analyze the distribution of elemental species within the microstructure and on the worn area. Figure 12 shows the results of the AES mapping of the unworn composite. The Ti map and the overlay map including Magenta representing Ti+C clearly shows that the cuboidal structure and acicular structures shown in the previous SEM images are the TiC phase identified by XRD. Also the rounded more spherical structures are composed of nearly all C and are the graphite phase identified by XRD.

![Figure 12](image1.png)

Figure 12. AES SEM image and elemental maps of unworn Ni-3Ti-20C.

The worn area AES map shown in Figure 13 is the wear track from the 1.11 GPa $P_{\text{max}}$ POD test after the full 140 m of testing. The blue in the figure corresponding to C shows a much
higher density within the track indicating that a carbonaceous tribofilm was formed during friction testing. This film is the primary candidate for the reduction in friction over pure Ni likely by reduction of interfacial shear strength ($\tau$) between the Si$_3$N$_4$ pin and sample surface.

![AES SEM image and elemental map of worn Ni-3Ti-20C.](image1)

3.6 FIB/SEM Serial Sectioning

Two sets of serial sectioned data were collected on the 1.05 GPa $P_{\text{max}}$ wear track to analyze the subsurface structural changes as a result of tribologically-induced stress. Both data sets were sectioned by 50 nm slices to ensure capturing multiple images of each precipitate in the matrix.

![SEM image of serial sectioned lift-out in the direction of sliding.](image2)
The first data set was collected from the center of the wear track at the location of maximum contact stress and sectioned in the direction of sliding as indicated by the white lines shown in Figure 14. The block lift-out analyzed was 2x3x14 \( \mu \text{m} \). The green measurement bar in Figure 14 indicates the wear track width. Figure 15 shows four selected images from the data set collected in the direction of sliding. Figure 15 (a-d) as well as the entire data set showed evidence of the C tribofilm in varying thickness on the order of 50-250 nm. Also shown in Figure 15 (a-d) and the rest of the data set is a heavily deformed mechanically mixed region with varying thickness on the order of 100-600 nm. In Figure 15 (b-d) the mechanically mixed region is observed to delve deeper into the subsurface in the presence of TiC precipitates. This morphological evolution is likely due to localization of stress in the matrix near the harder TiC precipitate and is analyzed in subsequent sections using FEA.

![Figure 15. Selected images from serial sectioned data set collected in the direction of sliding. Field of view is 3x2 \( \mu \text{m} \).](image)

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The second data set was collected from the same wear track but sectioned normally to the direction of sliding. Figure 16 shows the location of the lift-out with white lines indicating the direction of sectioning. The block lift-out analyzed was 3x4x18 µm. Figure 17 shows four selected images from the data set that captured deformed graphite particles. The graphite particles are deformed and sheared at an angle in the direction of sliding and are being extruded to the surface of the composite. Figure 17 (a-b) shows evidence of intergranular separation of the refined Ni grains at the front of the aciculary shaped graphite particle. This deformation mode provides the pathway for deformed subsurface graphite to the surface as shown in Figure 17 (c-d). This observed deformation mechanism gives direct evidence that the C tribofilm is not purely generated by smearing of graphite particles already exposed to the free surface but is also being fed C by deformed subsurface graphite, thus shows a novel solid lubrication mechanism in this, and perhaps other, MMCs.

Figure 16. SEM image of serial sectioned lift-out in the direction normal to sliding.

Throughout both data sets, the Ni matrix was observed to retain its interface with TiC precipitates without any formation of void nucleation and subsurface cracking. This is likely due
to the strong cube on cube grain orientation relationship for LENS deposited Ni-TiC composites shown by Gopagoni et al.[37].

Figure 17. Selected images from serial sectioned data set collected in the direction normal to sliding. Field of view is 4x3 µm.

3.7 High Resolution TEM

A FIB/SEM prepared lift-out specimen of Ni-3Ti-20C was taken from the center of the 1.50 GPa $P_{\text{max}}$ wear track in the direction of sliding similar to the lift-out location shown in Figure 14. Bright field HRTEM micrographs which reveal atomic mass contrast of higher intensity for low mass elements and lower intensity for greater mass elements were taken near the surface of the specimen. Figure 18 shows a micrograph which reveals four distinct zones of plastic deformation at and below the sliding surface.

To identify the concentration of elements present in each zone an EDS line scan from the surface through zone 4 was performed. The area scanned and the relative intensities are shown in Figure 19. Zone 1 is predominantly C with little contribution from other elements while zone
2 is predominantly Ni with a transition of decreasing C. In zone 3 the relative counts of Ni-L and Ni-K both drop indicating a presence of other elements in this region then increase again in zone 4 as the scan progresses into the bulk.

Figure 18. Bright field HRTEM micrograph of Ni-3Ti-20C worn subsurface.

A closer examination of the structure of the top three zones through bright field HRTEM micrographs are shown in Figure 20. Figure 20 (a) of zone 1 corresponds to the C tribofilm and shows no long range order. This indicates that the C tribofilm consists of predominantly amorphous C that was transformed by tribological stress from the graphitic phase of the unworn composite. This is a novel result, since it has been assumed that graphite is on the surface of the worn composite providing lubrication through basal plane slip. Figure 20 (b) and Figure 18 show nano-crystalline Ni atop elongated, refined Ni grains that has a similar structure reported by Prasad et. al. in nano-crystalline Ni films that have undergone sliding wear [38]. Figure 20
(c) shows nano-crystalline Ni surrounded by a matrix of amorphous C. Zone 4 in Figure 18 exhibited a gradual transition of reduced grain refinement to the bulk of the subsurface. The elongated Ni grains in zone 2 are possibly a result of stress assisted grain growth and reorientation at a point of high subsurface shear stress. Another more likely possibility is these refined Ni grains (dislocation cell boundaries) were originally formed during sliding without the presence of protective carbon on the surface, and were subsequently mixed with carbon further along in the sliding wear process. Observation of these refined Ni grains having developed in the absence of protective carbon are shown in Figure 21 for a specimen Ni-3Ti-20C that underwent 140 m of sliding wear at 1.11 GPa $P_{\text{max}}$.

![Figure 19. Scanning TEM micrograph and EDS line scan of Ni-3Ti-20C worn subsurface.](image)
Figure 22 shows a progression of increasing magnification of bright field HRTEM images below the surface of the worn composite. Figure 22 (a) shows a deformed region of C within the heavily refined Ni matrix. Figure 22 (b) shows a higher magnification from (a) and a slight intensity gradient between two regions of C. Figure 22 (c) shows a higher magnification of (b). In this figure it can be seen that the slight intensity gradient is due to a change in structure. The lower half of the figure shows evidence of crystallographic C planes while the upper half shows no long range order and consists of amorphous C. This image shows the transformation from graphitic to amorphous C and occurs at a depth from the surface of approximately 600nm.

Figure 20. Bright field HRTEM micrographs of subsurface deform zones. (a) Zone 1. (b) Zone 2. (c) Zone 3.
Zones 1 and 3 are both structures likely contributing to the observed reduction in CoF in the Ni-3Ti-20C composite. Zone 1 being comprised of amorphous C has no restrictions of crystallographic slip and can easily shear under imposed surface tractions and thus lower the interfacial shear strength and CoF. Zone 3 can also provide easy shear mechanisms due to the
crystalline Ni being on the order of 5-10 nm while being suspended in an amorphous carbon matrix.

3.8 Finite Element Analysis (FEA)

The five precipitate configurations outlined in section 3.5 are shown with their initial positions and final shape and positions after three frictional sliding contacts in the positive X direction in Figure 23. In each case the precipitates translated in the direction of sliding by more than three times their initial size. This translation is likely due to the Ni matrix being modeled as perfectly plastic and thus work hardening not being incorporated to impose an increasing yield strength for the regions of high deformation. Graphite in each case showed an elongation towards the surface and in the direction of sliding at an angle of ~45º. TiC also exhibited a rotation as well as translation and showed little to no plastic deformation.

Figure 23. Initial and final positions of precipitates after three frictional sliding contacts. Green is graphite, red is TiC.

Figure 24 shows plastic equivalent strain contour plots for each precipitate configuration. In each configuration a localization of plastic strain accumulated at the surface of the matrix and
in the presence of graphite it was shifted towards the direction of sliding. The lowest accumulation of plastic strain was seen for the case of TiC at the surface directly above the precipitate. The presence of the lower yield strength graphite precipitate in each other case showed more than double the accumulated plastic strain in the model. This large and highly localized plastic strain in the presence of graphite even without the assistance of nearby TiC confirms that the tribological stress drives the graphite towards the surface.

Figure 24. Plastic equivalent strain contour plots after three frictional sliding contacts.

Figure 25 shows Von Mises stress contour plots for each configuration. In the case of just TiC a localization of stress equivalent to the yield strength of Ni is observed directly above
precipitate which agrees with the plastic strain accumulation in Figure 24 and these results together explain the penetration of the heavily deformed zone 3 into the bulk observed in the serial sectioning data in Figure 15 (b-d). For the cases containing graphite precipitates the Von Mises stress is observed to be below the yield strength of Ni directly above and below the graphite and is likely due to the strain energy being accommodated within the graphite precipitate as shown in Figure 24. In each case containing graphite there is also a highly localized region of yielding in the Ni matrix at the apex of the formed acicular precipitate that extends to the surface. This behavior is likely due to the sharp radius of the interface between the deformed graphite and Ni matrix acting as a local stress concentrator. This stress concentration in conjunction with the high density of grain boundaries near the surface could allow for intergranular separation of the Ni matrix to provide the path necessary for graphite to reach the surface as seen in the serial sectioning data shown in Figure 17. Therefore, refined, plastically deformed Ni grain boundaries serve as pathways for extrusion of graphite/amorphous C to flow to the surface.

Figure 26 shows shear stress contour plots near the precipitates as the rigid indenter’s leading edge is directly above during the third frictional sliding contact. In each case there is an observed pile up of deformed Ni at the front of the rigid indenter and localization of shear stress from this location leading to the precipitate. In the configurations that contain graphite there is also a localization of shear stress localized on either side of the precipitate. These shear contours in the Ni matrix surrounding the graphite precipitate will allow for slip in the surrounding grains and are what drive the initial shape of spherical graphite to an acicular shape.
Figure 25. Von Mises stress contour plots after three frictional sliding contacts. Legend units in GPa.
Figure 26. Shear stress contour plots during indenter contact of third frictional contact. Legend units in GPa.
CHAPTER 4

CONCLUSIONS

A metal matrix composite composed of Ni-3Ti-20C was successfully fabricated using the laser engineered net shaping process. This MMC was shown by XRD and SEM to have primary and eutectic FCC TiC as a reinforcing phase that increased the hardness over that of the pure Ni sample as well as primary and eutectic graphite phases that were homogeneously distributed in the matrix. AES mapping and FIB/SEM serial sectioning revealed that unidirectional sliding friction and wear tests resulted in an in-situ formation of a C tribofilm. HRTEM and serial sectioning showed the subsurface deformation zones and microstructure as a result of friction and wear testing. FEA was used to investigate the subsurface stress and strains due to frictional sliding contact near modeled TiC and graphite precipitates. The thesis concludes with the following novel points.

- The observed low steady state CoF is due to the in-situ formation of an amorphous C tribofilm, which has been traditionally thought to be graphitic in structure.
- Tribological stresses in the subsurface push the C towards the surface through intergranular separation of heavily deformed crystalline and nano-crytalline Ni. These plastically deformed Ni grain boundaries serve as pathways for extrusion of graphite/amorphous C to flow to the surface.
- Improved friction at the retained steady state value of ~0.1 is not only from surface carbon, since subsurface compressive stresses feed primary and eutectic graphite into the mechanically mixed layer.
- The transformation from graphitic to amorphous C occurs in the subsurface at a depth of approximately 600nm.
- TiC precipitates increased the depth of heavily deformed and grain refined Ni due to localized stress concentration.

- These composites, processed in-situ in near net shape, offer a good combination of high hardness, fracture toughness and low friction/wear, and, thus are good candidates for surface engineering applications where all three properties are required.
CHAPTER 5

FUTURE WORK

Further study into the Ni/TiC/C MMC can be subdivided into three categories, thorough tribological testing, optimization of volume fractions, and improved system FEA modeling that, each would benefit understanding of solid lubrication mechanisms and possibly yield improvements in both mechanical and tribological properties.

- Thorough tribological testing at various sliding speeds and $P_{\text{max}}$ to determine at which regimes wear characteristics and friction could vary depending on tribofilm formation and thickness or lack thereof as well as varying environments to determine if the friction behavior of the amorphous C tribofilm is sensitive water vapor.

- Optimization of volume fraction of both graphite and TiC particles and their relation to hardness of the matrix and wear and friction behavior.

- Improved system FEA modeling that will incorporate work hardening of the Ni matrix, new mesh surface creation criteria to model and understand the extrusion of graphite through refined Ni, and a full three dimensional microstructure of the real microstructure through reconstruction of FIB/SEM serial sectioning data that can show how the applied contact stress is distributed throughout the monolithic composite.
REFERENCE LIST


