TRIBOLOGICAL BEHAVIOR OF SPARK PLASMA SINTERED TiC/GRAPHITE/NICKEL COMPOSITES AND COBALT ALLOYS

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Thesis Prepared for the Degree of

MASTER OF SCIENCE

UNIVERSITY OF NORTH TEXAS

December 2013

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Monolithic composites are needed that combine low friction and wear, high mechanical hardness, and high fracture toughness. Thin films and coatings are often unable to meet this engineering challenge as they can delaminate and fracture during operation ceasing to provide beneficial properties during service life. Two material systems were synthesized by spark plasma sintering (SPS) and were studied for their ability to meet these criteria. A dual hybrid composite was fabricated and consisted of a nickel matrix for fracture toughness, TiC for hardness and graphite for solid/self-lubrication. An in-situ reaction during processing resulted in the formation of TiC from elemental Ti and C powders. The composition was varied to determine its effects on tribological behavior. Stellite 21, a cobalt-chrome-molybdenum alloy, was also produced by SPS. Stellite 21 has low stacking fault energy and a hexagonal phase which forms during sliding that both contribute to low interfacial shear and friction.

Samples were investigated by x-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDS), and electron back-scattered diffraction (EBSD). Tribological properties were characterized by pin on disc tribometry and wear rates were determined by profilometry and abrasion testing. Solid/self-lubrication in the TiC/C/Ni system was investigated by Raman and Auger mapping. A tribofilm, which undergoes a stress-induced phase transformation from polycrystalline graphite to amorphous carbon, was formed during sliding in the TiC/C/Ni system that is responsible for low friction and wear. TiC additions help to further decrease wear. Stellite 21 was also found to exhibit acceptably low
friction and wear properties arising from the presence of Cr$_{23}$C$_6$ in the matrix and work hardening of the cobalt and chromium during sliding.
ACKNOWLEDGEMENTS

I gratefully acknowledge the help and opportunities given to me by Dr. Thomas Scharf. He showed me just how vast the field of material science is by introducing me to tribology and the challenges it presents to us as scientist and engineers. I wish to thank him for all the opportunities he made available to me in both funding and equipment. Discussing my research with him always led me to a new or deeper understanding of a topic.

I thank my lab mates who have always been helpful in showing me how things about the lab work, lending their expertise in performing invaluable experiments to assist my own research, or to helping me with issues I encountered, to also helping me think through problems I encountered during my research.

I also wish to thank my family and friends who were a huge source of support to me during my time here. They not only pushed me to pursue this degree but supported me throughout this effort. I thank my close friends Ankit Sirvastavan, Kyle Roget, Jon-Erik Mogonye, Graciella Penso, Niraj Gupta and Jessica Rimsza.
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CHAPTER 1

INTRODUCTION

1.1 Basics of Spark Plasma Sintering (SPS)

SPS is a powder processing method that utilizes a pulsed direct current to generate heat via resistive heating-Joule heating-of the die assembly and a uniaxial pressing force to aid densification during sintering. SPS produces bulk monolithic parts. SPS is also known as pulsed electric current sintering (PECS) [1], and field assisted sintering technique (FAST)[1][1][1][1]. It shall be referred to as SPS throughout this thesis. SPS is similar to hot isostatic pressing (HIP) in that both methods utilize a uniaxial pressing force that operates during the sintering of the sample. However SPS differs from HIP in how the heat is generated, SPS uses Joule heating of the powder while HIP uses radiative heating. SPS is notable due to its very rapid heating rates. Rates of up to 1000°C/min have been reported in the literature [2]. This ability to rapidly heat allows SPS to reach the processing temperature very rapidly and therefore minimizes processing time. This along with other attributes of the SPS process helps to retain very fine grained microstructures [3]. Because of its rapid heating rates and short processing times SPS is an environmentally friendly technique, minimizing the energy requirements to produce a sample compared to other production methods.

Spark plasma sintering is able to produce fully dense samples in a very short time scale (on the order of minutes) in part thanks to its rapid heating rates. SPS has been demonstrated to be able to process metals, ceramics, and composites [1]. SPS can work with both electrically conductive and insulating materials. In the case of insulating powders the Joule heating effect
comes from the graphite die. SPS is capable of producing fully dense parts of even traditionally
difficult to sinter materials like WC [4,5], or it can produce materials with a controlled porosity
through carefully selected processing conditions. [6]

Reported SPS processing temperatures are several hundred degrees less than reported
by other processing methods [2,7]. It has been suggested that the SPS process may have a
unique phenomenon that improves densification and reduces the temperature requirement to
produce a fully dense part [1,8,9]. Other analysis of the SPS process show that since reported
temperatures are measured from the exterior of the die assembly by thermocouple or optical
pyrometer the sample is actually experiencing temperatures similar to those reported in other
techniques such as HIP. [8][8][8]The difference in temperature is related to the thermal
conductivity of the die. Samples produced by SPS experience a temperature inhomogeneity
along the sample’s radial axis. This heat distribution across the sample’s radius can result in
differing grain size between the edge and center of the sample with the hotter center seeing
more grain growth occurring during sintering. [7]

SPS, shown in Fig. 1, uses a low voltage and pulsed direct current to generate heat via
joule heating of the die. Voltages do not exceed 10 volts and are typically around 3 volts during
operation [1,7]. The amount of current during operation depends upon the die geometry and
the processing temperature, with higher temperatures and faster heating rates requiring
greater currents. Larger dies also require greater currents to produce a similar temperature
compared to a smaller die. The pulsed direct current signal can have its “on” and “off” pulse
pattern modified. Each pulse period lasts 3.3 milliseconds [1]. The Thermal Technologies 10-30
SPS system, used in the present study, is capable of 10 tons of pressing force, 3000 amps, and
10 volts. The pulse DC signal in the standard recipe is 30 ms “on” and 2 ms “off”, giving a 93.8% “on” time where power is being delivered.

**Fig. 1** Diagram of SPS showing electrodes and current flow (die not shown). Temperature is the most significant SPS variable relating to successful consolidation.

Sufficiently high temperatures are required to begin the formation of necking between particles, shown in Fig. 1, and allow for diffusion in order to form a suitable sample. The pressing force has the next greatest effect on consolidation followed by the length of the holding time at the sintering temperature (also known as a soak). The pressing force helps to compact the green body and rearrange the particles, bringing them into contact and allowing for necking to occur. Longer hold times at sintering temperatures provide sufficient time for diffusional consolidation to occur. The pulse pattern has been found to have only a slight effect on densification behavior [1].

SPS can be performed in low vacuum, with an inert atmosphere such as argon or helium, or a gas of choice—for example nitrogen. The die assembly is made of high purity graphite, however tungsten dies are offered for extremely high processing pressures. The assembly consists of two Inconel steel rams which provide the uniaxial pressing force as well as act as the electrodes for the current. Next is a graphite foil to ensure good electrical contact.
between the rams and the rest of the assembly. The graphite ram spacer is next followed by the
die plungers. Between the die and powder sample is another layer of graphite foil.

No plasma spark generation has been shown to occur during the operation of the SPS.
[10]For this reason some prefer to call the processing method by other names such as FAST or
PECS.

1.2 Metal Matrix Composites (MMCs)

Metal matrix composites or MMCs are a class of composites that consist of a metal
matrix and often a second phase for reinforcement with high hardness and wear resistance,
which is often a ceramic material. Carbide materials are often selected due to their high
hardness and low wear rate values. MMCs have many applications in energy, aviation, and
structural applications. MMCs can consist of several composite arrangements. Particulate
composites are the most common, other reinforcement methods include fibers, or lamellar
structures. MMCs are important structural materials due to their high hardness, elastic
modulus, wear resistance, strength, thermal resistance and fatigue resistance. [11]

The volume fraction of the secondary components in MMCs is the most critical
parameter for the tailoring of MMCs properties. Previous work with MMCs with graphite as the
secondary constituent has shown that above 20vol% graphite the coefficient of friction stops
decreasing. It can be concluded that above 20vol% graphite in an MMC is of no practical benefit
to decreasing CoF and instead starts to impact the mechanical properties of the MMC adversely
with no benefit. [12-18]

MMCs have been produced through many production techniques. Methods used
include casting, forging, powder metallurgy, including; laser melting, microwave sintering, HIP,
hot pressing, and SPS. [11] Aluminum based MMCs have been investigated for their mechanical properties due to the low cost of aluminum. Copper MMCs have also seen a large body of work, primarily for various electronic applications in industry. Work by Kovacik et. Al. [14] and also Chandrakanth et [18] who fabricated a C-TiC-Cu hybrid composite via microwave sintering. TiC as a reinforcement phase in MMCs has been studied by Dogan et. al. [19].

A hybrid composite consisting of a nickel matrix, titanium carbide for its high hardness, and amorphous graphite for solid lubrication has been investigated by Gopagoni [20,21]. This composite combines the two most common types of MMCs for wear applications, a hard ceramic type and a graphite solid lubricant type. Hybrid composites using graphite for its solid state lubricity have been investigated by others in different material systems as well [16,22]. These hybrid composites offers low friction, low wear rates, and still retain the strength and temperature stability of the nickel metal matrix. Each of the secondary components complements the weaknesses of the other with the hard ceramic increasing wear resistance of the system and the graphite decreases friction in sliding applications.

An in-situ reaction of titanium and carbon elemental powders leads to the formation of TiC during processing[21,23]. Excess carbon is observed to take the form of distinct graphite regions in the matrix [24]. The benefits of using an in-situ reaction in the processing of the MMC include a lowered cost, good coherency and adhesion between phases, and a homogenous particle distribution for TiC.
1.3 Powder Metallurgy and Sintering

Powder processing and solid state sintering are important to understand in order to produce fully dense parts. Powder size, morphology, and physical properties should be understood to develop a processing schedule that will give the best possible result.

Solid state sintering consists of three stages. In the initial stage neck growth between adjacent particles occurs. During this stage only 3-5% of densification occurs to a green body bringing density to ~65%. During the intermediate stage a continuous network of pores located between grains shrink. The intermediate stage dominates during sintering and gives an additional 25% densification, the intermediate stage is valid up to a relative density of 90%. The final stage of sintering sees the pore network close off, resulting in isolated pores. These isolated pores shrink as densification progresses and eventually are eliminated from the microstructure.

In the production of dense homogeneous MMCs, powder metallurgy is far and away the most utilized method of production. This stems not only from the low cost associated with fabrication of composite parts via powder metallurgy but also from the homogeneous distribution of secondary phases which is lacking in casting or other processing techniques associated with MMCs. Powder metallurgy also allows for compositions to be easily varied and to be tailored to a specific application.

Typically to produce a fully dense part, while retaining a fine microstructure with powder metallurgy, melting of the powder during processing is required. Casting, laser melting, laser cladding, electron beam deposition, etc. are just some of the powder metallurgy techniques taking advantage of melting to form a sample. For solid state methods, a HIP, SHS,
SPS, or a traditional furnace sintering schedule can be used to try to densify the part after pressing the powder and forming a green body. [11]

1.4 Stellite Cobalt Alloys

The Stellite family of alloys refers to a family of cobalt base alloys. Stellite 21 is an alloy comprised of cobalt, chrome, molybdenum, nickel, and carbon. It is known for its high hardness, good wear resistance, and low friction. The molybdenum in Stellite 21 gives beneficial corrosive resistance properties to the metal as well, taking the place of tungsten which is used in other Stellite metals. [25,26]

Stellites have been used in aerospace, nuclear, automotive and other industrial applications. It is often used as a bearing material or for hardfacing applications where the ability to withstand mechanical and corrosive attack at high temperature is important [26-28]. The hardness, temperature resistance, and wear resistance of Stellite allow it to perform very well in these applications.

Stellite 21 has been produced for years from a variety of methods. Casting, laser cladding [29], laser melting, plasma alloying [27], spray drying, powder metallurgy among other techniques have all seen use. Stellites have also been produced as films or coatings to improve wear behavior of other materials. [29]

Low friction in Stellite 21 is a result of low stacking fault energy in the γ (FCC) cobalt phase. The γ to ε (FCC to HCP) transformation of cobalt during cooling is slow as the chemical driving force for this change is low resulting in metastable γ phase. Both molybdenum and chromium decrease the stacking fault energy and can also help to stabilize the hexagonal phase [26]. Low wear is due to small carbides (typically M₂₃C₆ with the M being chromium [25]) that
precipitate in the sample during processing. A strain induced transformation where a FCC phase transition to HCP also has a positive effect on wear resistance as well. HCP (0001) planes orient parallel to the surface and easily shear under sliding. [30]
2.1 Preparation of Powders and Samples

Samples for the Ni-Ti-C system were batched from three elemental powders: a -325 mesh size nickel metal powder (99.5% pure), a -325 mesh size titanium metal powder (99.5% pure), and a -325 mesh size graphite powder (99.9995% pure). All powders were sourced from Alpha Aesar. Batches were stoichiometrically mixed and then dry ball milled for a period of 16-18 hours with spherical tungsten milling media. A rotating speed of ~300 rpm was used with the rotary miller. Several compositions were batched consisting of 100g each; their compositions are listed in Table I.

<table>
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<th>Batch</th>
<th>At% Ni</th>
<th>At% Ti</th>
<th>At% Co</th>
<th>At% Cr</th>
<th>At% Mo</th>
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<td>62.66</td>
<td>30.4</td>
<td>3.29</td>
<td>1.2</td>
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</table>

Stellite 21 powders were batched from elemental cobalt (-100+325 mesh 99.8% purity, chromium (-325 mesh 99% purity), molybdenum (2-4µm 99.9% purity), nickel (-325mesh 99.8% purity), and carbon (-325 mesh 99.9995% purity). All powders were supplied by Alfa Aesar. Stellite 21 initial composition can be found in Table I. A batch of 100g was prepared. The
powders were dry ball milled for 24 hours with spherical tungsten milling media and a rotating speed of \(~300 \text{ rpm}\) was used.

The batched and mixed via balling milling powder was then measured out using an Ohaus Adventurer scale. The powder was then poured into the die assembly after placing the graphite foil and disc spacers between the die wall and plungers and the powder. The upper plunger was then inserted by hand. The die assembly was then placed inside the SPS and the die’s black body hole and the pyrometer were aligned. The SPS ram was then lowered and preloaded the die to 5 MPa. The alignment of the pyrometer was checked again. Next the chamber was sealed and pumped to vacuum of \(2.0 \times 10^{-2}\) torr. The power system was turned on and inert gas was allowed to flow into the chamber. Finally the SPS executed the processing parameters that were input by program dictating the pressure, temperatures, and rates for each. Processing parameters can be found in Table 1 for TiC/graphite/Ni and Table 2 for Stellite 21. Once the programmed hold time was completed, the sample was allowed to cool radiatively, a controlled cooling rate was not used.
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<td>200</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1000</td>
<td>20</td>
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<tr>
<td>3</td>
<td>1000</td>
<td>20</td>
<td>12</td>
<td>200</td>
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<tr>
<td>Ni</td>
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<td>1</td>
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<td>2</td>
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</tbody>
</table>

Once the sample had sufficiently cooled the chamber was opened and the die assembly removed. The sample was removed by hand from the die. The anode and cathode ends of the sample were noted. For the TiC/C/Ni system the sample was then mechanically polished at 600,
800, and 1200 grit. Polishing with anything below 600 grit for TiC/C/Ni samples was found to eject surface graphite during polishing. Stellite 21 was polished using 120, 240, 400, 600, 800, and then 1200 grit pads consisting of a SiC abrasive. This was to remove the graphite and carbide layers that formed as a result of the graphite foil used in the die. Samples were polished to a fine metallographic finish and had their final polish using 0.05μm colloidal silica. The sample was then washed in an ultra-sonicator using first an acetone rinse and then an ethanol rinse for 15 minutes each, respectively.

**Table III. Processing conditions for Stellite 21.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp (°C)</th>
<th>Pressure (MPa)</th>
<th>Hold Time (min)</th>
<th>Ramp Rate (°C/min)</th>
<th>Powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1200</td>
<td>60</td>
<td>5</td>
<td>200</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>1000</td>
<td>30</td>
<td>5</td>
<td>200</td>
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<td>3</td>
<td>1000</td>
<td>60</td>
<td>5</td>
<td>200</td>
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</table>

Some samples were sectioned using a diamond saw wafering blade. After sectioning the sample was polished according to the same methods used for samples that were not sectioned. This was to investigate possible variations in microstructure or chemistry across the sample thickness.

Many compositions of the MMC were investigated. In each case nickel was the excess phase and acted as the matrix material. Varying titanium and carbon amounts was an attempt to influence the amount of TiC formation and friction properties of the MMC.
2.2 Characterization

Scanning electron microscopy (SEM) was used to observe the microstructure of the MMC and Stellite 21 alloy. A FEI Nova nanoSEM with a field emission electron source was used for SEM imaging. Both secondary and backscattered imaging modes were used. SEM uses a focused electron beam and a detector, either an Evanheart-Thornly detector or a backscattered electron detector to interpret the signal and produce an image.

With EDS (energy-dispersive x-ray spectroscopy), by analyzing K and L- bands from an x-ray signal data generated by an electron beam basic, compositional analysis of a sample is possible. However EDS provides an accuracy of only ±5 at% making precise quantification difficult.

Electron back scatter diffraction (EBSD) matches Kikuchi diffraction lines generated by an electron beam in the SEM against known possible reflections based off crystal structures and possible planar spacings related to the compound. EBSD allows for composition, structural, and orientation data to be elucidated from a sample.

X-ray Diffraction (XRD) utilizes x-rays and their characteristic diffraction patterns to provide information regarding what compounds and crystal structures are present in the sample. By using a monochromator, the x-ray radiation can be reduced to a single wavelength which then reflects off a sample surface as the emitter and detector rotate around the sample via a goniometer. Through the use of Bragg’s Law, the interplanar and interatomic spacings can be determined. Additionally, a level of quantification of phases is also possible.

Auger electron spectroscopy (AES) relies upon the Auger effect to determine elemental constituents that are present on a sample. Precise chemical identification is possible due to the
release of an x-ray photon of a specific energy when the electron beam collides and ejects an
electron from an inner atomic orbital which is then filled by another electron from an outer
orbital which emits the x-ray photon. AES is very useful due to its high lateral resolution of >20
nm and high precision, accurate $10^{-3}$. The Auger signal generated by an electron beam comes
from the very top portion, ~2 nm, of the interaction volume and it is considered a surface
technique.

Raman spectroscopy is another method which allows for identification of both
chemistry and structure. Raman can also provide additional information described by the peaks
that are present. A wavelength of 542nm was used for Raman mapping with a step size of 5
µm x 5 µm for each acquisition point of the map for a total of 55x45 points. A dwell of 11
seconds was used and the laser was cut back to 10% power via a filter wheel.

Vickers Hardness used a diamond tip indenter with 300 gram force (2.9 N) load and a 10
second dwell. Indents were spaced 100µm apart. Indent diameter was determined using the
measurement system on the Shimadzu Vickers Hardness tester. The Shimadzu also calculated
Vickers Hardness numbers for the load and indent diameters.

For coefficient of friction measurements a pin on disc (PoD) tribometer was used. This
PoD is a Falex ISC-200 tribometer. A Si$_3$N$_4$ ball of 0.25 in. diameter was used. Sliding conditions
were with a sliding speed of ~2.1-2.2 cm/sec, the hanging weight was either 100g (1 N) or 200g
(2 N). Initial hertzian contact stresses for the TiC/Graphite/Ni composite are estimated to be
~890 MPa at 1 N. For Stellite 21 initial hertzian contact stresses are estimated to be ~970 MPa
for 1 N and 1221 MPa for 2 N applied loads. Friction testing was performed in dry sliding
conditions exposed to ambient air.
Wear rates were either calculated by profilometry of the wear track to determine wear depth and cross section or by abrasion testing. For abrasion testing, a Taber 5130 rotary abraser was used with CS-10 abrasion wheel. 500g weight was used and the samples were abraded for 5000 cycles, being weighed every 1000 cycles to determine weight loss.
3.1 Sample Structure (X-ray Diffraction)

Fig. 2 XRD spectrum for Ti/graphite/Ni A) Ni-10Ti-10C and B) Ni-3Ti-20C.
After processing via SPS, X-ray Diffraction (XRD) in Fig. 2 A shows the titanium and graphite has undergone an in-situ reaction forming TiC. The in situ reaction has completely consumed all the carbon as no graphite reflections are observed for the Ni-10Ti-10C. Reflections for FCC nickel and rocksalt TiC are observed for Ni-10Ti-10C. Peaks for nickel, TiC and graphite are present in the processed Ni-3Ti-20C sample Fig. 2 B. Graphite (002), nickel (111), and TiC (111) peaks, the primary peaks for each phase, are observed in the composite material after processing. Subsequent peaks corresponding to additional reflections are also indicated in Fig. 2. Graphite has hexagonal (P6\_3/mmc) crystal structure, TiC has rocksalt (Fm-3m) structure, and nickel has face center cubic (Fm-3m) crystal structure.

3.2 SPS Process

Fig. 3 Temperature and power over time.
For pyrometer operation (in contrast to operation using a thermocouple to record processing temperatures), the SPS system heats at a rate of 150°C/min and then does a short hold of 10 seconds at 600°C to ensure that temperature readings are accurate. The temperature line in Fig. 3 shows the ramp rate of 200°C/min and the final temperature of 1100°C that was used for the sintering period. After the hold time has been completed, the temperature ramps down at 1000°/min and amps and volts go to zero. We see the process variable shows an exponential decay as the die cools by radiative methods. Cooling is equivalent to 150°C/min initially and the cooling rate decreases over time. Amps and volts vary significantly during operation (Fig. 3) most significantly during the ramp up to the sintering temperature at 200°C. Power also fluctuates once the sintering temperature is reached as the system attempts to maintain the sintering temperature.

Fig. 4 Pressure and ram position over time.
The initial stage of compaction of the green body is seen in the position loop as the applied pressure is increased from 5 MPa to 35 MPa, shown in Fig. 4. Before the process run was started, the powder has been pressed with a force of 5 MPa, this compacts the powder into a green body inside the die assembly. Pressure matches very closely with the setpoint throughout the run. A ramp rate of 40 MPa/min is used during both loading and unloading. A peak pressure of 35 MPa was selected for compaction during the process run. Once the die began to heat, there is another compaction occurring.

Small fluctuations observed in the ram position are indicative of thermal expansion in both the graphite die and ram assembly but also from the composite sample. The SPS system continuously monitors the process parameter for the pressure loop and adjusts applied force accordingly.
3.3 Sample Morphology (SEM Imaging)

3.3.1 Pure Nickel

![Image of pure nickel sample](image)

**Fig. 5 Microstructure of pure nickel sample #1.**

Nickel sample #1 in Fig. 5 shows that nickel grains are visible and the extent of porosity present in the sample can be observed. The material is polycrystalline and shows pores of a single size distribution throughout.

Grains are distinct and show twinning in Fig. 5. The nickel has pores present both intergranularly and at grain boundaries. Intergranular pores are unlikely to be removed from the microstructure by increasing hold time. The pores are of a uniform size and singular distribution, averaging roughly 1-5μm in size.

3.3.2 Nickel-10Ti-10C

Composite materials comprised of a nickel matrix and elemental titanium and graphite form an in-situ carbide phase during processing. The titanium and graphite have almost completely converted to TiC during processing as observed from the XRD spectrum (Fig. 2 A).
Fig. 6 Ni-10Ti-10C sample #2 microstructure.  
This overview of sample #2 in Fig. 6 shows composite TiC/nickel particles in the matrix as their own discrete regions. The 10at% elemental titanium and graphite powder has almost completely converted into TiC via an in situ reaction during processing. A few areas show unreacted particles that have not been fully incorporated-suggesting that temperatures may have been too low for good sintering. Pores or possible graphite regions are also observed in this image. Overall the TiC is distributed homogeneously throughout the sample.
Fig. 7 Ni-10Ti-10C sample #2 TiC clusters.
A higher magnification of sample #2 in Fig. 7 shows more detail of the TiC/nickel composite regions. Some unreacted graphite is seen to surround these composite regions. The composite TiC/nickel regions consist of small micron sized TiC particles and nickel. The size of the composite TiC/nickel regions is roughly that of the starting powders, 44µm in diameter. Increasing hold time in SPS processing did not further coarsen the TiC grains.

3.3.3 Nickel-3Ti-20C

The in situ reaction between Ti and C forming TiC leaves excess graphite (C) for this composition. The graphite and TiC form a dual hybrid composite morphology and should offer improved friction and wear compared to Ni-10Ti-10C.
Fig. 8 Ni-3Ti-20C sample #2 microstructure.
Sample #2 in Fig. 8 shows graphite regions on the surface, which are homogeneously distributed across the sample. Graphite regions are acicular and are the higher volume fraction secondary phase compared against composite TiC/nickel regions, and appear darker in the SEM image in Fig. 8. Graphite diameter is similar to that of the starting powder, 44µm. In comparison composite TiC/nickel regions are much more circular in geometry having a diameter similar to that of starting elemental powders. Some of the graphite regions border adjacent composite particle regions since TiC forms near the graphite source due to excess carbon availability in this composition. As the TiC forms as a result of an in situ carbon and titanium reaction this is not surprising to see. In the upper right quadrant voids that have formed likely from the ejection of graphite during polishing are visible. Line charging from the electron beam makes these pores evident. TiC is also present and is distributed equally throughout the area.
Fig. 9 Ni-3Ti-20C sample #3 TiC and graphite clusters.
Sample #3 in Fig. 9 shows graphite bordering a composite TiC/nickel region. TiC borders this region which is comprised of nickel and TiC grains only a few microns in diameter. Despite a longer hold time, sample #3 does not exhibit TiC grains of a much larger size than other samples from the Ni-3Ti-20C system.
Fig. 10 Ni-3Ti-20C sample #4 microstructure A) at center and B) edge of sample. Sample #4 in Fig. 10 also shows low area fraction of carbon, likely due to surface ejection of graphite during polishing. The second image shows the edge of the sample and the difference orientation of the particles as a result. This different orientation at the edges of the samples is likely an effect arising from friction with the die wall during consolidation of the sample leading to a rearrangement of the grains at this interface with the die.
Sample #5 in Figure 11 shows a good view of the hybrid composite where regions of graphite and composite TiC/nickel regions spread fairly uniformly throughout the material. Nickel grains are also apparent in the image, and show good interfaces between the material and particles in the composite. Starting powders for sample #5 consist of much coarser nickel and titanium powders. As a result, the composite TiC/nickel and graphite zones are of a larger size than other samples from the Ni-3Ti-20C system presented before.

An intermetallic NiTi phase can also be seen in several regions where a TiC band exists around the intermetallic phase. This intermetallic structure can be seen to exist in circular regions separate from composite TiC/nickel regions.
Fig. 12 Ni-3Ti-20C sample #5 TiC particles imbedded in NiTi intermetallic lamellar structure. Fig. 12 shows higher magnification images of TiC and NiTi intermetallics. These intermetallic regions also have a composite morphology like the composite TiC/nickel particles in other TiC/graphite/nickel samples. Closer examination of the intermetallic phases shows that it is actually two different intermetallics which have phase separated. Hexagonal Ni$_3$Ti and cubic NiTi are present. TiC grains are also inter-dispersed inside this intermetallic region. The TiC grains are apparent in the backscattered electron images in Fig. 12 showing z-contrast. The TiC grains are very blocky and cuboidal. The NiTi intermetallics were found to only form in samples that used coarser starting powders.
Fig. 13 Ni-3Ti-20C sample #6 A) microstructure and B) close-up of TiC region.
Sample #6 in Fig. 13 was also produced with coarser starting powders and additionally contained nickel coated graphite. The size of the secondary phases (graphite and TiC) is larger.
than other samples. However the size is similar to sample #5 which also was produced from coarser powder. Fig. 13 shows a mix of cuboidal TiC near the periphery and more needlelike TiC grains towards the center of the composite TiC/nickel region. Graphite is seen to border the TiC/nickel composite region in the bottom corner of the image.

![Fig. 14 Ni-3Ti-20C sample #7 microstructure. Sample #7 in Fig. 14 was held for 15 minutes like samples #5 and #6 (Fig. 11 and Fig. 13). However all starting powders were the finer -325 mesh. As a result the secondary phases are much smaller in size. Graphite and TiC are dispersed homogeneously throughout the microstructure.](image-url)
Fig. 15 Ni-3Ti-20C sample #8 microstructure.

Fig. 15 shows the edge of Sample #8. There is no noticeable size difference of the nickel, graphite, or composite TiC/nickel grains compared to the center of the sample. It can be concluded that the variation in temperature across the sample radius does not have a significant effect on grain size for this composite material. Composite TiC/nickel and graphite regions are fairly equally spread out across the sample area.

Overall morphology of the Ni-3Ti-20C samples was not observed to vary drastically with changes in SPS processing temperature, pressure, or hold time. Starting particle size had the greatest effect on microstructure, changing the diameter but not the volume fraction of the secondary phases.
3.3.4 Nickel-5Ti-35C

Ni-5Ti-35C was batched in order to investigate the friction and wear behavior when high volume fractions of graphite are present. The in situ Ti+C reaction forms 5at% TiC assuming the reaction runs to completion and exhausts all the titanium.

Fig. 16 Ni-5Ti-35C sample #6 microstructure.

Fig. 16 shows that a slightly higher area fraction of TiC is observed in the Ni-5Ti-35C samples compared to the Ni-3Ti-20C. As in previous samples, composite TiC/nickel regions have a mostly circular appearance and have fine grains a few microns in size dispersed with nickel in-between. Graphite and TiC border each other in some areas, with the localized graphite having helped form the TiC by an in situ solid state reaction. Spacing between the secondary phases is good and fairly homogenous distribution of the particles is observed.
Fig. 17 Ni-STi-35C sample #7 A) microstructure and B) cross section view of microstructure. Sample #7 in Fig. 17 shows the overall microstructure and a cross section view, sample axis are superimposed upon each image. The uniaxial pressing force exerted during sintering was along the x-axis of Fig. 17. In the micrograph, composite TiC/nickel particles appear to be quite circular. Graphite grains however have deformed greatly from the applied pressure during the sintering process. This deformation has made the graphite very acicular in appearance. Graphite has deformed as it has the lowest mechanical property values amongst the composites constituents. TiC and graphite zones are homogeneously distributed.
3.4 Sample Chemistry (EDS Scans)

**Fig. 18 EDS spectrum of Ni-3Ti-20C sample #5 TiC ring surrounding TiC region.**

TiC ring shown in Fig. 18 is present around all composite TiC/nickel regions. A point scan in Fig. 18 determined atomic percents of 48.62% C and 49.39% Ti, and 1.99% Ni. This TiC ring is observed around all composite TiC/nickel regions regardless of composition, temperature, pressure, or hold time. The TiC ring may likely form first during the in-situ reaction and further TiC forms once carbon diffuses through this exterior TiC ring, like a cored particle growth model.
Fig. 19 EDS spectrum of Ni-3Ti-20C sample #6 TiC region showing A) TiC and B) nickel. Blocky primary TiC grains and TiC needlelike grains are present in Fig. 19 images.

Quantification of the EDS spectrum indicated in Fig. 19 A, for the TiC grain determined the composition to be 41.12 at% carbon, 2.11 at% Ni, and 56.77 at% Ti. The point scan from Fig. 19 B shows that nickel is present. Quantification for B was 70.38 at% Ni, 7.67 at% Ti, and 21.95 at%...
carbon. This region likely does not possess as much carbon as reported, but is an error of the EDS system and the respective interaction volume produced by the electron beam.

Fig. 20 EDS spectrum of Ni-3Ti-20C sample #5 NiTi intermetallics A) NiTi and B) Ni$_3$Ti. Cubic NiTi, the grey phase represented in the micrographs in Fig. 20, is detected by EDS in Fig. 20 A. EDS spectrum chemical quantification reports 45.24 at% Ti, 52.09 at% Ni, and 2.68
at% carbon. Hexagonal Ni$_3$Ti, the lighter grey phase in the micrographs is detected by an EDS points scan in Fig. 20 B. EDS quantification reports 25.18 at% Ti, 74.03 at% Ni, and 0.79 at% carbon. The black phase in Fig. 20 corresponds to TiC grains and has been identified by EDS in Fig. 19.

3.5 Sample Grain Orientation (EBSD Maps)

![Fig. 21 EBSD of pure nickel Sample #1.](image)

Pure nickel in Fig. 21 shows polycrystalline grains having a random orientation and also a large amount of twinning inside the nickel grains. Despite evidence of porosity in the matrix (Fig. 5), no pores are observed in this EBSD scan.
Fig. 22 EBSD Ni-3Ti-20C sample #5 microstructure.

Fig. 22 shows an intermetallic region in the upper left and a composite TiC/nickel particle region in the lower right. Twining of the nickel matrix is visible. Graphite regions are at locations represented as black and were unable to be indexed properly, likely some disorder or uneven surface of the graphite zones is responsible for the difficulties in indexing by EBSD. The intermetallic region consists of two different NiTi compounds that have phase separated with Ni$_3$Ti (hexagonal) and NiTi (cubic) which have been indexed by EBSD. TiC having a rocksalt structure is also present as angular primary TiC particles.
Fig. 23 EBSD Ni-3Ti-20C sample #6.

Fig. 23 shows TiC region in the left quadrant and NiTi/Ni$_3$Ti intermetallic zone, similar to that observed in Fig. 22, to the right. The intermetallic region also has TiC grains present inside it in various orientations. The nickel matrix shows a high degree of twinning. Graphite regions proved difficult to index and are at the black regions. TiC grains are inter-dispersed with nickel in the TiC/nickel composite particles. TiC grains are only a few microns in size.
Fig. 24 Selected NiTi/Ni$_3$Ti region from Ni-3Ti-20C #6 A) EBSD of selected grains B) Ni$_3$Ti pole figures C) NiTi pole figures.

Fig. 25 Selected NiTi/Ni$_3$Ti region 2 from Ni-3Ti-20C #6 A) EBSD of selected grains B) Ni$_3$Ti pole figures C) NiTi pole figures.
The NiTi and Ni$_3$Ti phases orientation relationship was investigated from EBSD data. Neighboring grains of the two phases were selected from sample #6 (Fig. 23) and pole Fig.s were generated. A relationship between two different sets of NiTi and Ni$_3$Ti grains are shown in Fig. 24 and Fig. 25.

NiTi is cubic and has a CsCl prototype with crystal structure Pm-3m. Ni$_3$Ti is hexagonal and has the structure P6$_3$/mmc. It is apparent from the pole Fig.s that there is a direct relation between the (0001)||{110} and also <11-20>||<111> directions. Coincident points are indicated on the pole Fig.s by a small circle of the same color indicating the relationship. This relation follows a Burgers orientation relationship. The points show an agreement of within 1° between each other.
Fig. 26 EBSD Ni-3Ti-20C sample #7.
Sample #7 shown in Fig. 26 consisted of much finer (-325mesh) starting powders than Samples #5 and #6, Fig. 22 and Fig. 23, respectively. Twinning is present in the nickel, likely a result of stress induced twinning from compaction via the rams during the SPS run. Composite TiC and nickel regions are visible and show small micron sized TiC grains. No NiTi intermetallics were formed in this sample as it was batched from the fine (-325 mesh) powder.
3.6 Friction Behavior

**Fig. 27 Friction plot for pure nickel sample #1.**
Pure metallic nickel shows an average coefficient of friction (CoF) of ~0.7 shown in Fig. 27. The friction value of 0.7 is the steady state value and dominates early on after initial run in of the wear track. This coefficient of friction value agrees with previous work performed on pure nickel with these sliding conditions [21,24]. As expected, nickel has no beneficial low friction properties and exhibits adhesive behavior under sliding conditions.
Friction data in Fig. 28 for Ni-3Ti-20C shows that additions of graphite to the nickel matrix results in lower average CoFs compared to pure nickel. For volume fraction of 20% graphite expected CoF values should be from 0.1-0.2. Samples 1-4 do not show values that are in this low range. Instead they increase in their CoF over time at a constant rate. This non-steady state behavior could be due to poor adhesion between the phases resulting in the ejection of surface graphite giving high friction values. Another explanation is that the acicular morphology of graphite, seen from a cross section view of the sample (Fig. 17), results in subsurface graphite not being easily extruded to the surface and forming a tribofilm. The volume fraction of graphite is important; however, another critical factor is how it is dispersed through the material. If distances between graphite regions are high, low friction will not be
achieved. Samples #5-8 have achieved low friction during the entire run and are examined in more detail in Fig. 29.

Fig. 29 Friction plot for Ni-3Ti-20C composition with low friction values.
Samples 5-8 show very low CoF values of ~0.1 for the entire 200 m of sliding distance. Sample #6 CoF values do not increase greatly over the test but they are much more varied than the other samples having lower CoF values. This may have to do with the nickel-coated graphite present in this sample having an effect of the phase transformation from crystalline to amorphous carbon at the surface, which was determined previously [21]. Average friction values are 0.084 for #5, 0.119 for sample #6, 0.076 for sample #7, and 0.132 for sample #8. This low friction is made possible by the formation of an amorphous carbon tribofilm during sliding.
However, Ni-5Ti-35C does not show CoF values as low as Ni-3Ti-20C (Fig. 28). Increasing graphite content beyond 20vol% was unable to achieve predicted friction values of ~0.1. Sample #2 friction behavior is erratic, suggesting that the formation of the tribofilm is intermittent and friction behavior is dominated more by adhesive friction mechanisms as in sliding on metals. Sample #4 showed an unusual behavior, increasing in friction throughout the run until 150m where a new steady state friction value of ~0.1 is observed.
3.7 Wear Tracks

**Fig. 31 PoD wear track with 100g load on pure nickel sample #1.**
Wear track from pure nickel #1 is shown in Fig. 31. The wear track shows a mixture of abrasive and adhesive wear. Pores in the pure nickel matrix have ruptured and coalesced in the wear track. No wear debris is observed outside the wear track.

**Fig. 32 PoD wear track with 100g load on Ni-3Ti-20C sample #5.**
Sample 3-20 #5 in Fig. 32 shows some smearing of carbon in the wear track. Both composite TiC/nickel particles and graphite clusters are present in the wear track. The
amorphous carbon tribofilm is extruded from both surface graphite grains and subsurface graphite, as determined previously for similar LENS deposited Ni-Ti-C composites [21]. No wear particles are observed inside or outside of the wear track.

Fig. 33 PoD wear track with 100g load of Ni3-Ti-20C sample #6
Sample #6 in Fig. 33 shows that wear debris are visible on the exterior of the wear track edges. This debris was likely generated by abrasive wear. Amorphous carbon tribofilm is partially visible in the center of the wear track. The self/solid lubrication provided by the amorphous carbon has prevented adhesive wear.
3.8 Unworn and Worn Sample Surface Chemistry (Auger Electron Spectroscopy)

Auger electron spectroscopy (AES) point scans of a composite TiC/nickel region are shown in Fig. 34 for unworn Sample #6. A passive surface oxide layer is present on the surface of the sample. Sputter cleaning was not preformed so as to preserve the structure of unworn and worn surfaces.

Fig. 34 A) Auger spectrums for unworn Ni-3Ti-20C sample #6 and B) AES electron image showing point scan locations.
The composite TiC/nickel particle region, Fig. 34 A point 1, shows the Ti, C, and O peaks. In addition to carbon, the presence of both Ti and O suggest a TiO$_2$ surface layer has developed which is common when polishing, or just native oxidation, of titanium and its compounds. The nickel region, Fig. 34 A point 2, also has carbon and oxygen present as well as what appears to be a small amount of sulfur. Sulfur is a surface contaminant phase and was not detected in the powders via XRD or EDS scans.

Fig. 35 A) Auger spectrums for unworn Ni-3Ti-20C sample #6 intermetallics region and B) AES electron image showing point scan locations.
Auger line scans from the NiTi intermetallic region are shown in Fig. 35. Ni$_3$Ti (point 1) and NiTi (point 2) are both detected as well as TiC (point 3). The surface oxide film greatly impacts the precisions of the elemental quantification for these points. Sulfur is again detected at trace levels for all three points. The intermetallics identified by AES agree with EDS and EBSD results and stoichiometry.

![Auger concentration map of Ni-3Ti-20C sample #6 unworn surface for Ti, Ni, C, and O.](image)

**Fig. 36 Auger concentration map of Ni-3Ti-20C sample #6 unworn surface for Ti, Ni, C, and O.** AES mapping of an unworn surface of sample #6 Ni-3Ti-20C is shown in Fig. 36. Auger point scans shown in Fig. 34 and Fig. 35 were taken within the same area that was mapped by AES in Fig. 36. A nickel matrix is seen to surround both graphite and TiC/nickel composite regions. Some nickel is also detected in the graphite region, this is because the graphite for this sample was nickel coated. The TiC/nickel composite region also is inter-dispersed with nickel.
Titanium is also observed to be present in the matrix, it is not just segregated to the TiC and NiTi intermetallics.

Fig. 37 Auger concentration map of Ni-3Ti-20C sample #6 wear track 1 for Ti, Ni, C, and O. Fig. 37 shows AES inside wear track from sample #6. Carbon, as mentioned before to be amorphous, and nickel are readily apparent. Titanium and carbon are present throughout the material. Carbon regions also have small amounts of nickel in them, a result of the carbon powder being nickel coated. In the lower corner a layer of carbon is seen on top of what is a composite TiC/nickel particle region. This carbon layer is a tribologically induced feature and likely consists of carbon that has transformed from crystalline graphite to amorphous carbon. However AES is unable to determine if this tribofilm is amorphous. NiTi intermetallic is seen in the top left and a TiC/Ni region in the bottom right.
3.9 Unworn and Worn Sample Surface Structure (Raman Spectroscopy)

![Raman map and spectrum of unworn surface from Ni-3Ti-20C sample #6.](image)

Raman spectroscopy point scan and area map of an unworn surface of sample # 6 is shown in Fig. 38. Carbon is known to be Raman active and its Raman peaks were observed during this scan. The observed peaks are very sharp and distinct, a characteristic of crystalline materials. The graphite spectra show both D- (1360 cm\(^{-1}\)) and G- (1580 cm\(^{-1}\)) peaks. These peaks correspond to bond stretching in the rings and chains of all sp\(^2\) atoms, and what is referred to as the breathing mode of the sp\(^2\) atoms present in the graphite rings. D’ peak represents deformation along the c-axis of the graphite structure [31,32]. This brings the graphite basal
planes closer together than reference distances. This change in spacing is probably a result of the pressure from the SPS machine during sintering.

![Raman map and spectrum of wear track from Ni-3Ti-20C #6.](image)

Fig. 39 Raman map and spectrum of wear track from Ni-3Ti-20C #6.

The Raman point scan taken from the map in Fig. 39 was acquired after sliding on the wear track of sample #6. The same G and D peaks are observed inside the wear track. The G and D peaks are still present but G peak has increased from ~1580 to 1610 cm\(^{-1}\). The D' peak is not observed, which is an expected behavior of the Raman signature for amorphous carbon. These results support a sliding wear-induced formation of a low interfacial shear strength carbon film. This film has increased structural disorder/modification due to shift in G-peak to
higher Raman shift and increased broadening suggesting the graphite to amorphous carbon transformation occurred during sliding.

These results agree with sliding on carbon nanotube Ni composites[33]. The map also shows that amorphous carbon is present not only at the pre-worn graphite grains, but also throughout the track, as a tribofilm. The heat map showing the Raman signal indicates where the amorphous carbon tribofilm is thickest. Carbon can be seen to have extruded and smeared from the graphite particle in the wear track in the direction of sliding. The amorphous carbon has likely smeared inside the track and is responsible for the low CoF values that were measured in Fig. 29.
3.10 Sliding Wear Behavior

**Fig. 40 Wear factor of Ni-3Ti-20C determined by profilometry.**
Wear factor for samples #5, 6, and 7 from Ni-3Ti-20C show wear rates on the order of $10^{-6}$ which is in the low wear regime. Standard deviation represented by the error bars is a result of large variations in the width and depth of the wear track at the 6 locations measured by profilometry for each track. Sample #7 which is comprised of finer starting powders shows a lower wear rate, however standard deviation does not clearly show that sample #7 preformed better. The NiTi intermetallics present in samples #5 and 6 did not improve wear resistance more than #7 which only had TiC as a reinforcement phase. It is well known that NiTi intermetallics are brittle and not considered low friction and wear materials. In addition, this may be a result of shorter spacing between TiC grains in the matrix, since finer powders
resulted in closer spacing between phases, which has been shown to protect the matrix
material better.

3.11 Abrasion Testing

![Abrasion Testing Graph]

Fig. 41 shows that the addition of TiC to the nickel has improved abrasion resistance for
all three composites. All composite samples showed less mass loss than pure nickel, which is
expected since the TiC reduces wear. Sample #1 showed slightly lower mass loss of the Ni-10Ti-
10C composites. The rate of mass loss is fairly constant for all samples.
Fig. 42 Abrasion results for Ni-3Ti-20C composition.

Fig. 42 shows the abrasion resistance of Ni-3Ti-20C composites. The results are somewhat ambiguous when compared to the previous sliding friction and wear results. Samples #5 through #8 showed low CoF of \( \sim 0.1 \) and wear rates of \( \sim 5 \times 10^{-6} \text{ mm}^3/\text{N} \cdot \text{m} \). However, the abrasion resistance measured via mass loss is unclear when compared to pure nickel. Samples #6 and #8 exhibit lower mass loss compared to pure nickel and hence better abrasion resistance. However, Samples #5 and #7 show more mass loss compared to pure nickel. More analysis needs to be done to understand why these two samples exhibit poor abrasion resistance. The other Ni-3Ti-20C composites (Samples #1-#4) also exhibit worse abrasion resistance compared to pure nickel. As previously stated, their friction and wear values were also not as good as Samples #5-#8. One observation is that increasing the SPS hold time results...
in decreasing mass loss/improved abrasion resistance. Also, coarser starting powders for Samples #5 and #6 show ambiguous abrasion behavior with the only difference being the Ni coated graphite powder was used in Sample #6 that may account for improved adhesion of graphite to nickel in the composite during SPS resulting in improved abrasion resistance.

Similarly, for the case of fine powder sizes used in processing Samples #7 and #8, the results vary. The rate of mass loss is also constant for these Ni-3Ti-20C composites.

In comparing Ni-3Ti-20C to Ni-10Ti-10C composites, all around better abrasion wear resistance is observed in the Ni-10Ti-10C samples with the exception of Ni-3Ti-20C Samples #6 and #8. Therefore, the addition of graphite to the composite material to improve sliding friction and wear behavior has also led to some improvement in abrasion wear resistance in some composites by reducing mass loss through abrasive and adhesive wear.
Fig. 43 Abrasion results for Ni-5Ti-35C composition.

Fig. 43 shows the abrasion resistance of Ni-5Ti-35C composites. As in the sliding friction results shown in Fig. 30 for these composites, where the CoF values were higher than Ni-3Ti-20C composites, the abrasion resistance is also worse than pure nickel. Sample #1 exhibited the best abrasion resistance of these composites. The overall performance of Ni-5Ti-35C is worse than pure nickel, Ni-3Ti-20C, and Ni-10Ti-10C. In theory, Ni-5Ti-35C should have performed better than Ni-3Ti-20C (Fig. 42) as it has more TiC for reinforcement and wear resistance and more graphite which provides solid/self lubrication and decreases adhesive or abrasive wear by forming an amorphous carbon tribofilm during sliding. In the future, more
analytical and characterization testing need to be performed to better understand the abrasion results for these composites.

**Fig. 44 Micrographs of composite surfaces after abrasion testing.**
Fig. 44 shows SEM images after abrasion testing for pure nickel, Ni-10Ti-10C, and Ni-3Ti-20C composites. Pure nickel shows significant abrasive wear. Ni-10Ti-10C sample #1 shows similar wear to pure nickel in its matrix, however the composite TiC/nickel regions are not
nearly as abraded. TiC particles protect nearby nickel matrix material from abrasive wear. This correlates to the improved abrasion resistance behavior of the mass loss observed in Fig. 41.

Ni-3Ti-20C sample #8 also shows similar wear of the nickel matrix. Overall wear is not as significant as that of pure nickel as shown by lower mass loss in Fig. 42. Likely graphite has been removed from the surface of the material as seen in the upper right and bottom left of the micrograph. As with Ni-10Ti-10C composition, in the composite TiC/nickel regions the TiC protects the nearby nickel matrix from abrasive wear.

To summarize, increasing carbon (graphite) content decreases the CoF and increases the sliding wear resistance of the material by providing solid/self lubrication protecting the matrix from adhesive or abrasive wear. Improved abrasion resistance is also observed in some of the higher graphite composites. However, beyond 20at% C, the abrasion resistance decreases as observed in Ni-5Ti-35C composites (Fig. 43). Increasing TiC content, as in Ni-10Ti-10C composites, increases the abrasion resistance. Abrasion resistance can be further increased by optimizing TiC distribution in the matrix.
Table IV. Vickers hardness for TiC/C/Ni system.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Sample 4</th>
<th>Sample 5</th>
<th>Sample 6</th>
<th>Average±Std Dev</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-10Ti-10C</td>
<td>332</td>
<td>233</td>
<td>305</td>
<td>274</td>
<td>287</td>
<td>297</td>
<td>288±33</td>
</tr>
<tr>
<td>Ni-3Ti-20C</td>
<td>206</td>
<td>238</td>
<td>283</td>
<td>215</td>
<td>120</td>
<td>146</td>
<td>201±60</td>
</tr>
<tr>
<td>Ni-5Ti-35C</td>
<td>104</td>
<td>115</td>
<td>151</td>
<td>138</td>
<td>184</td>
<td>138</td>
<td>138±28</td>
</tr>
</tbody>
</table>

Vickers hardness results are listed in Table IV. A load of 300 grams and a 10 second hold were used to generate these hardness values. The hardness is seen to decrease with increasing graphite concentration, or decreasing TiC content.

Hardness values vary across individual samples. This variance is from the random distribution of hard (carbides) and soft phases (graphite) throughout the composite material. Hold time was not observed to be a significant variable in average hardness values.

Across the composite system the following trends are observed. Adding graphite decreases the hardness. Additions of TiC increased hardness. This is an expected behavior of a hard particle reinforced composite material.
Fig. 45 Micrographs of Vickers indents from Ni-3Ti-20C sample #6. Indents made in (A) nickel, (B) TiC and (C) near graphite.

Fig. 45 shows representative Ni-3Ti-20C sample #6 Vicker’s hardness indents. Indents are present at (A) nickel, (B) composite TiC/nickel region, and (C) near a graphite region. The fracture toughness and ductility of the nickel prevents cracking from the indenter during loading. The nickel indent (A) has a diameter of ~61 µm. The indent in the TiC/nickel composite region (B) has a diameter of ~32 µm, the hardness of the TiC prevents deformation of the matrix from the indenter. The third indent (C) in Fig. 45 has a diameter of ~65µm. It can be concluded that hardness varies across the samples face and depends upon which phases of the particulate composite the indenter interacts with during indentation. These observations support the variation in hardness values in Table IV for each composite.
4.1 Sample Structure (XRD)

Fig. 46 Co-Cr, Mo-Co, Cr-Mo binary phase diagrams. [34]

A cobalt-chromium binary phase diagram is shown in Fig. 46 [34]. HCP cobalt is the stable phase at room temperature. Additions of chromium stabilize the FCC cobalt phase with cobalt forming a limited solid solution with chromium. Selected processing conditions Table III. should yield FCC cobalt. The molybdenum-cobalt diagram shows that molybdenum can form
solid solution with γ-cobalt under the selected processing conditions. The chromium-molybdenum binary phase diagram shows that under the chosen processing conditions mixing of chromium and molybdenum solutions is possible.

**Fig. 47 XRD spectrum for Stellite 21 powder.**
The XRD scan of the Stellite 21 starting powders, comprised of a mixture of elemental powders, (Fig. 47) shows graphite, molybdenum, chromium, cobalt, and nickel peaks. Both carbon and cobalt are hexagonal lattices and represented by blue text for their miller indices. Cubic lattices are represented by black text. Carbon is present as graphite crystal structure with hexagonal symmetry (space group P6₃/mmc), molybdenum and chromium are BCC metal structure (space group Im-3m), cobalt is HCP metal structure (space group P6₃/mmc), and nickel is FCC metal structure (Fm-3m). Cobalt only has a single peak in the XRD spectrum (Fig.
and this (101) peak is not very intense although it has the highest intensity according to powder diffraction file (PDF #01-089-7094).

**Fig. 48 XRD spectrum of Stellite 21 sample #1.**

XRD scan for sample #1 is shown in Fig. 48. Cobalt (HCP) peaks are observed with no FCC cobalt detected. The highest intensity and most reflections are exhibited by HCP cobalt since the alloy is cobalt based. Hexagonal phases are represented by blue text and cubic phases are represented by black text in Fig. 48. The processing temperature of this sample should allow cobalt to form a stable FCC phase. The FCC phase has not been retained during cooling, or the starting powder may have never transitioned to FCC from HCP during processing. The FCC to HCP transition in cobalt is martensitic and can occur rapidly. Chromium FCC (110) reflection is observed however. No molybdenum, nickel and carbon peaks are seen in the XRD spectrum for sample #1. Many of the peaks for these phases are very close in 2theta values and have some
overlap. A chrome carbide ($\text{Cr}_3\text{C}_6$) phase exists as well that formed in situ during SPS. This is the typical carbide phase for Stellite 21[26].

![XRD spectrum of Stellite 21 sample #2.](image)

**Fig. 49 XRD spectrum of Stellite 21 sample #2.**

XRD scan of Sample #2 in Fig. 49 shows slightly different reflections than #1. Cobalt HCP peaks are also present with no FCC cobalt observed in the XRD scan. FCC chromium (110) and (211) peaks are observed and molybdenum peaks are now discernible in the spectrum.

Molybdenum is present as a BCC crystal structure. Chrome carbide peaks ($\text{Cr}_3\text{C}_6$) are also detected in the XRD scan. No nickel or carbon peaks are observed in the scan.
4.2 Sample Morphology (SEM imaging)

Fig. 50 Stellite 21 Sample #1 microstructure. Cobalt and chromium grains are apparent in Fig. 50, cobalt being the light grey color and chromium the darker grey. Bright spots correspond to regions of molybdenum grains, although no molybdenum was detected in the XRD scan (Fig. 48). Molybdenum has possibly formed a solid solution with cobalt which would explain the lack of reflections in XRD and the low volume percent of molybdenum grains seen in Fig. 50. Stellite 21 is not normally produced via a solid state process like SPS.
Fig. 51 Stellite 21 sample #1 A) microstructure and B) view of small carbides. Fig. 51 A shows a higher magnification image of the microstructure of Stellite 21 again showing the cobalt matrix, chromium grains and Cr$_{23}$C$_6$ precipitates. Fig. 51 B shows small carbides a few microns in diameter which are present throughout the sample. The carbides exist throughout the microstructure and are apparent at both grain boundaries and inside grains. Molybdenum represents only a small area fraction of the sample seen in Fig. 51 A. Molybdenum may have substituted into the M$_{23}$C$_6$ carbides or formed an intermetallic phase with cobalt, i.e. Co$_3$Mo or Co$_7$Mo$_6$. However this is typically observed when higher molybdenum content is used in the alloy. [25].
Unlike sample #1, sample #2 shows a slightly different microstructure. Cobalt is again the primary matrix material and is a grey color. The bright areas represent molybdenum grains, which was detected in the XRD scan (Fig. 49). A much greater volume fraction of molybdenum is seen in sample #2 compared to sample #1 (Fig. 50). Black regions are chromium grains and \( \text{Cr}_2\text{C}_6 \) precipitates. The dispersion of these various phases is homogenous across the sample.
Sample #3 in Fig. 53 shows a somewhat similar microstructure of that of sample #1. Cobalt is the majority constituent of the matrix and has a grey color in Fig. 53. The dark black phase is chrome or $\text{Cr}_2\text{C}_6$. A difference between sample #1 and #3 is that #3 shows a greater area fraction of molybdenum, seen as the bright phase.

Both samples #2 and #3 were processed at the same temperature and show a high volume fraction of molybdenum grains in the microstructure. The presence of molybdenum reflections in the XRD spectrum of sample #2 also support molybdenum existing as its own phase. Contrasted against micrographs (Fig. 50) and XRD spectrum (Fig. 48) of sample #1 it is seen that at lower processing temperatures molybdenum does not form a solid solution with cobalt and exists as its own distinct phase.
4.3 Sample Chemistry (EDS Scans)

**Fig. 54 EDS spectrum of Stellite 21 Sample #3.**

EDS Spectrum of sample #3 (Fig. 54) shows peaks for cobalt, chromium, molybdenum, carbon, and nickel. Quantification of the spectrum determined the atomic% to be the following: cobalt 51.06%, chromium 25.19%, molybdenum 3.5%, carbon 17.48%, and nickel 2.78%. This is close to the batched composition for Stellite 21. Carbon content as reported by EDS is higher than what was batched. EDS is known to have difficulties accurately detecting elements with low Z values. Nickel K-lines are very faint and overshadowed by cobalt K-lines at ~7.5 keV.
EDS Map of Stellite 21 sample #2 For Co, Cr, Mo, and C.

EDS Map from Stellite 21 sample #2 indicates the dispersion of several constituent elements of Stellite 21. Cobalt is the matrix material and appears as a light grey in the SEM image. Chromium appears darker grey in the SEM image. Chromium is known to form a solid solution with cobalt, however the EDS map (Fig. 55) does not indicate very much if any chromium present in the cobalt matrix. The lack of cobalt-chromium solid solution may also explain why a FCC phase is not retained upon cooling after processing (Fig. 48 and Fig. 49).
Molybdenum appears as whitish color in SEM imaging (Fig. 55). Carbon is present throughout the material as indicated by EDS. The greatest abundances of carbon are also where chromium and molybdenum exist. A $\text{Cr}_2\text{C}_6$ carbide is known to form in Stellite 21. Molybdenum carbides can also exist according to literature.

4.4 Sample Grain Orientation (EBSD Maps)

Fig. 56 EBSD of Stellite 21 sample #1.

EBSD scan in Fig. 56 indicates that the Stellite 21 is polycrystalline and shows a random orientation for its grains. EBSD reports that cobalt is present as a HCP phase, showing very little FCC cobalt present. This contradicts the results from the XRD spectrum which indicated that cobalt is present as HCP (Fig. 48). EBSD indexing reports the majority of present phases are FCC cobalt and $\text{Cr}_2\text{C}_6$. 

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For sample #3 (Fig. 56) a lower processing temperature was used compared to sample #1. Grain size does not appear to have been affected by the change in processing temperature. EBSD data indicates that the Stellite 21 is polycrystalline and shows a random orientation for its grains. EBSD reports that cobalt is present as a HCP phase, showing very little FCC cobalt present. XRD, however, shows cobalt present as HCP (Fig. 49). As reported in sample #1 (Fig. 56), the majority of present phases are FCC cobalt and Cr$_{23}$C$_6$. 
4.5 Friction Behavior

Friction behavior for Stellite 21 with a hanging weight of 100g is shown in Fig. 58.

Average friction values were 0.45 for #1, for #2 0.52, and #3 had a value of 0.42. Friction values for #2 are seen to increase throughout the run. Run-in occurs over a similar number of cycles for all three samples, after which they enter their steady state friction regimes.

Friction values of 0.4 have been reported in the literature [30,35] and suggest that cobalt HCP basal planes are not aligning parallel to the surface. Instead FCC cobalt transforms to HCP, mostly consisting of grains in the direction <10-11> for the HCP phase. This transformation is a result of a strain induced transformation. For (0001) basal planes to align near the surface a greater normal pressure during sliding is required.
Fig. 59 Friction data for Stellite 21 at 200g load.
Friction behavior for sample #1 at 200g (Fig. 59) is similar to that at 100g (Fig. 58).

Sample #2 shows a different friction behavior at the higher applied load than what was exhibited at 100g. Average friction values are for #1 0.58 and 0.36 for #2. Sample #3 was not tested at 200g. The CoF decreases after run-in for sample #2. Sample #1 does not show a decrease in friction but maintains a CoF of ~0.55, suggesting that HCP planes may not be aligning as desired and are unable to provide suitable low friction behavior. Literature reports friction values of 0.2 when (0001) basal planes are aligned in the wear track promoting low friction.
Fig. 60 Stellite 21 sample #1 PoD A) wear track 1 B) wear track 2.
Signs of abrasive wear are visible in both wear tracks in Fig. 60. The dark regions are cobalt with silicon also present according to EDS point scans. The presence of silicon in the wear track suggests material transfer from the Si$_3$N$_4$ ball. Wear tracks 1 and 2 have similar wear track width and do show a small amount of wear debris outside the track. These wear tracks appear similar but exhibited slightly different friction values during sliding,

Fig. 61 Stellite 21 sample #2 PoD A) wear track 1 B) wear track 2.
Wear tracks for sample #2 in Fig. 61 have similar features to sample #1 Fig. 60. Abrasive wear is observed in the wear tracks and wear debris are visible outside the track. Wear track 2 (Fig. 61 B) shows a greater amount of wear debris compared to wear track 1. The similarity in wear track feature across samples suggests that similar friction mechanisms are active despite slightly different friction values of 0.45 and 0.52 at 100g. Under a 200g load, friction values of 0.58 for sample #1 and 0.36 for sample #2 were observed (Fig. 58 and Fig. 59).

Fig. 62 PoD wear track 1 for Stellite 21 sample #3.
Sample #3 wear track 1 in Fig. 62 exhibited good friction behavior, achieving a friction value of 0.42. Abrasive wear was apparent in the wear track. Some wear particles are visible outside of the track. Wear debris are visible outside of the wear track, and are likely generated as the surface material spalls off during sliding. [35]
4.6 Hardness Behavior

<table>
<thead>
<tr>
<th>Sample 1</th>
<th>614</th>
<th>595</th>
<th>989</th>
<th>793</th>
<th>391</th>
<th>676.4±225.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 2</td>
<td>408</td>
<td>411</td>
<td>443</td>
<td>474</td>
<td>362</td>
<td>419.6±41.9</td>
</tr>
<tr>
<td>Sample 3</td>
<td>529</td>
<td>443</td>
<td>648</td>
<td>677</td>
<td>314</td>
<td>522.2±149.5</td>
</tr>
</tbody>
</table>

Vickers hardness for Stellite 21 is presented in Table V. Sample #1 has the highest hardness values. The higher processing temperature for sample #1 could lead to this higher hardness by solid solution strengthening as the higher temperature enables molybdenum to form a greater amount of solid solution with cobalt as seen when comparing volume fraction of molybdenum in Fig. 50, Fig. 52 and Fig. 53. Samples #2 and #3 were processed at the same temperature; however, applied pressure was varied between the two. Sample #3 was processed with a 60 MPa pressing force which may work harden the cobalt-chromium solid solution more during processing compared to sample #2 resulting in higher reported average hardness.
Fig. 63 Micrographs of Vickers indents from Stellite 21 sample #2.
Vickers hardness indents preformed with 300 grams and a 10 second dwell. Indent A has a diameter of ~37 µm. The diameter of indent B is ~34 µm, molybdenum can be seen bordering the bottom of the indent. For indent C, the diameter of the indent is 39 µm. Deformation of the cobalt matrix is visible in B and C. Work hardening is an important aspect lending to the high hardness of the Stellite 21 family of cobalt alloys.
4.7 Wear Behavior

Stellite 21 samples show wear rates on the order of $10^{-5}$ to $10^{-6}$, which qualifies as medium to low wear behavior. The large variance for wear rates of sample #1 is a result of widely different values for width and depth in the wear tracks. Sample #2 shows the lowest wear overall, having a wear rate of $2.4 \times 10^{-6} \text{ mm}^3/N \cdot m$ for wear track 2 (WT2). The wear rate for WT1 of all Stellite samples all are close to a value of $\sim 7.0 \times 10^{-6} \text{ mm}^3/N \cdot m$. Processing effects on these samples had no effect on wear resistance at a load of 100g.

Wear track 2 was preformed with a load of 200g. For sample #1 this resulted in more wear than in the case of #2. This difference in wear rate for these samples can be related to the friction values during sliding (Fig. 59). Sample #2 showed much higher friction, which continued to increase with distance traveled. The high friction then is a result of the removal of material from the surface, leading to high wear.
CHAPTER 5

CONCLUSIONS

SPS allows for rapid solidification of highly dense monolithic parts consisting of dissimilar composite materials - comprised of a metal matrix and ceramic secondary phases or metallic alloys. The SPS parts showed a uniform particle distribution and consistent microstructure across the entire sample. SPS processing conditions were varied and appeared to have only a small effect on the tribomechanical properties of the materials, most influential was the SPS hold time. Instead, compositional effects and phase distributions had a greater effect on the tribomechanical properties.

A dual hybrid composite consisting of TiC/graphite/nickel was produced by SPS and took advantage of an in situ reaction between titanium and carbon powders leading to the formation of the reinforcing TiC phase. This predominance of the TiC phase in the Ni-10Ti-10C composite was responsible for increased hardness and improved abrasion wear resistance compared to pure SPS nickel. Increasing carbon (graphite) content in the Ni-3Ti-20C composite resulted in lowering of the coefficient of friction down to ~0.1 and reduced wear rates (~5x10$^{-6}$ mm$^3$/N·m) compared to the other composites and pure nickel. Hardness also increased with the additions of TiC in all composites and NiTi intermetallics. Therefore, the combined improvements in tribomechanical properties provide solid/self lubrication protecting the matrix from sliding adhesive and abrasive wear. The low friction in the Ni-3Ti-20C composite is due to the transformation of crystalline graphite to amorphous carbon which is present as a tribologically-induced tribofilm in the wear track. The presence of this amorphous carbon tribofilm was determined by AES and Raman spectroscopy point scans and area mapping.
Improved abrasion resistance is also observed in some of the higher graphite composites. However, beyond 20 at% graphite starting powder, the abrasion resistance decreased as observed in Ni-5Ti-35C composites. In addition, a cobalt chromium molybdenum alloy known as Stellite 21 was also successfully produced via SPS. A cobalt chromium solid solution acts as the matrix with molybdenum and nickel to stabilize favorable phases and the in situ SPS formed \( \text{Cr}_2\text{C}_6 \) phase to improve hardness. Its friction properties were tested and showed intermediate friction (CoF~0.4), likely due to the HCP cobalt basal planes orientated parallel to the sliding direction. The occurrence of a cobalt FCC to HCP stress-induced phase transformation during sliding is in doubt as no FCC cobalt was originally detected in the as-produced SPS alloy. Further reductions in CoF down to 0.1-0.2 is in doubt likely since there was not complete alignment of (0002) HCP cobalt planes with the surface, and the sliding contact pressure was too low to facilitate this texturing of surface HCP cobalt. Stellite 21 alloy showed good wear resistance with wear rates down to \( \sim 5 \times 10^{-6} \text{ mm}^3/\text{N} \cdot \text{m} \), similar to TiC/graphite/Ni composites. The presence of \( \text{Cr}_2\text{C}_6 \) in the matrix and work hardening of the cobalt and chromium during sliding are responsible for improved wear resistance. Finally, the hardness of Stellite 21 varied depending upon processing conditions - hardness was greatest with higher processing temperatures and pressures.
CHAPTER 6

FUTURE WORK

Several areas need to be addressed to better understand SPS processing parameters and how they could result in further improvements in tribomechanical behavior for both materials systems. In the case of TiC/graphite/nickel composite, shows low friction and wear behavior by the transformation of graphite to amorphous carbon although the tribofilm is not evenly distributed across the entire wear track, as was previously determined in similar LENS composites. This may be due to differences in solid-state SPS processing versus liquid-solid solidification LENS processing and more work needs to be performed to address the mechanisms. In addition, wear resistance could possibly be further improved by optimizing the distribution of TiC throughout the material. Improved milling techniques to disperse the starting powders more thoroughly or altering SPS processing conditions (e.g., pulse pattern and hold time) could potentially facilitate a more dispersed TiC morphology in the composites.

For the SPS Stellite 21 cobalt alloy, relatively low friction and wear are observed, but remain higher than values reported in the literature. For example, further studies on increasing the contact stresses during sliding may be needed to induce the crystallographic changes in cobalt to facilitate low interfacial shear. Also, more variation in the processing conditions should be investigated to determine the viability of SPS to produce low friction and low wear Stellite 21. The presence of FCC or HCP cobalt in the matrix and in the wear track must be resolved and will require the use of transmission electron microscopy (TEM). Additionally the orientation of the HCP planes in the wear track should be investigated by TEM analysis as well to determine solid lubrication mechanisms.
REFERENCES


