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Fabrication and tribological properties of hard thin films with solid lubricant microreservoirs

John H. Zimmerman

University of New Hampshire, Durham

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Fabrication and tribological properties of hard thin films with solid lubricant microreservoirs

Abstract
Hard coatings containing micron-sized reservoirs have been fabricated and investigated to evaluate their tribological properties. These composite coatings have the potential to reduce friction and extend the life of wear surfaces through the use of a structural matrix embedded with microreservoirs containing solid lubricants. In this thesis, methods of using polymer or silica microspheres as templates for reservoirs in wear resistant coatings were examined. Magnetron rf-sputtered TiN and TiCN films and magnetron rf reactively sputtered TiN films were investigated for use as hard films containing these microreservoirs. The reservoir size as a function of microsphere size and film thickness was measured. Wear tests of the microreservoir thin films with MoS2 and graphite lubricants have been used to examine the performance of the coatings and determine the optimum microreservoir percentage. The coatings with microreservoirs and lubricant showed friction reduction compared to similar coatings without microreservoirs. The maximum coverage achieved using direct spray techniques was about 12 percent. Increased levels of microreservoir coverage percent showed increased levels of friction reduction, with 28% friction reduction at maximum coverage.

Keywords
Engineering, Materials Science

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FABRICATION AND TRIBOLOGICAL PROPERTIES OF HARD THIN FILMS WITH SOLID LUBRICANT MICRORESERVOIRS

by

JOHN H. ZIMMERMAN

BS
University of New Hampshire
1978

MBA
Southern New Hampshire University
1988

THESIS

Submitted to the University of New Hampshire in Partial Fulfillment of the Requirements for the degree of

Master of Science in Materials Science

December 2006
This thesis has been examined and approved.

Thesis Director, James E. Krzanowski,
Professor of Materials Science and Mechanical Engineering

James Harper, Professor of Materials Science and Physics

Karsten Pohl, Assistant Professor of Materials Science and Physics

DECEMBER 12, 2006
Date
DEDICATION

I dedicate this thesis, the work and time that went into it to my family, my wife, Patty, and kids Zach and Jacquie. Their understanding made it much easier.
ACKNOWLEDGEMENTS

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Hard coatings containing micron-sized reservoirs have been fabricated and investigated to evaluate their tribological properties. These composite coatings have the potential to reduce friction and extend the life of wear surfaces through the use of a structural matrix embedded with microreservoirs containing solid lubricants. In this thesis, methods of using polymer or silica microspheres as templates for reservoirs in wear resistant coatings were examined. Magnetron rf-sputtered TiN and TiCN films and magnetron rf reactively sputtered TiN films were investigated for use as hard films containing these microreservoirs. The reservoir size as a function of microsphere size and film thickness was measured. Wear tests of the microreservoir thin films with MoS₂ and graphite lubricants have been used to examine the performance of the coatings and determine the optimum microreservoir percentage. The coatings with microreservoirs and lubricant showed friction reduction compared to similar
coatings without microreservoirs. The maximum coverage achieved using direct spray techniques was about 12 percent. Increased levels of microreservoir coverage percent showed increased levels of friction reduction, with 28% friction reduction at maximum coverage.
INTRODUCTION

Composite coating materials that will extend the life and enhance the tribological performance of existing coatings used in cutting and wear applications are the subject of much current research and development. Existing tool coatings often require the use of liquid lubricants that have environmental issues including worker exposure and proper disposal of used fluids. Much progress has been made moving from petroleum to water based lubricants in many applications, but complete elimination of these lubricants is a much sought after goal. The research conducted for this thesis involves taking a hard thin film, often used to enhance the life of tool bits, and adding microreservoirs to hold solid lubricant. These microreservoirs are fabricated using polymer or ceramic beads as templates. The beads are sprayed on a substrate, after which a hard coat is sputter deposited over the substrate and microspheres. The beads are then removed by ultrasonic agitation, and the resulting microreservoirs are filled with a solid lubricant. These composite films are then tested in a tribometer, (a pin and disk tester) for wear resistance and frictional behavior. Tests comparing friction for films with and without microreservoirs, and with and without solid lubricant, indicate that microreservoirs with solid lubricant reduce friction. Tests to quantify the density of microreservoir coverage that provides the greatest improvement in friction behavior indicate that greater microreservoir density
provides more friction reduction. The techniques developed and used in this study result in a limitation in the microreservoir coverage that is possible without excessive microsphere agglomeration, and additional research based on this work will be necessary to obtain greater microreservoir density. Significant friction reduction was achieved using solid lubricant filled microreservoirs.
CHAPTER I

LITERATURE REVIEW

This literature review begins with examples of embedded solid lubricants in common bulk materials, then reviews material property enhancement through thin films, and ends with efforts in recent research to combine solid lubricants and thin films.

Some commonly used alloys exhibit embedded phase separation during material synthesis, and alloys which contain a combination of a hard matrix and embedded lubricant phases have found extensive use over time. Cast iron, which contains graphitic carbon within a primarily iron matrix, is an example of a material that has reduced friction and is more wear resistant than the base alloy alone. Brasses that contain lead for easier machining are another example of a commonly used metal matrix with an embedded lubricant. (1)

Deposition of thin hard films is a common method for enhancing the performance of bulk alloys. TiN coatings are found on tool bits in common use today, and reactive deposition of TiN is the technique of choice for this coating. Hibbs et al (2) investigated how reactive rf sputtering creates denser, more homogeneous and harder TiN films than dc magnetron sputtering. These characteristics make reactive sputtering appropriate for longer wearing TiN hard thin films. Sundgren et al. (3, 4) established that at a deposition temperature of
500 C, above $10^{-4}$ torr partial pressure nitrogen, the nitrogen atomic ratio would be about 50%, as long as the mole percent of nitrogen in the sputtering gas is above 3 percent. This leads to titanium nitride that will form under a wide range of pressure and flow conditions, and widespread adoption of it as a hard thin film.

Enhancements to hard coatings are the subject of ongoing research. Voevodin et al. (5) investigated simultaneous deposition of a hard film of yttria-stabilized zirconia and solid lubricants MoS$_2$, Au, and amorphous DLC for enhanced friction and wear properties. Endrino et al. (6-8) investigated TiC, WC, HfC, and SiC hard films deposited by pulsed laser while simultaneously depositing Ag by sputtering (MSPLD). This system demonstrated phase separation during deposition and enhanced frictional properties at optimal Ag ratios. Separation of Ag and the hard film into bilayers, rather than spherical particles embedded in TiC, was also observed, a potentially significant problem for this approach. These and other naturally occurring separations of hard and lubricant phases have limits based on materials and processes available. Additionally, Krzanowski (9) illustrated how sputtering from multiple targets can result in phases that are more thermodynamically favorable than the phases sputtered, and on limits of the separation of materials that could be obtained during processing.

These thermodynamic and kinetic limits on separating hard and lubricant phases suggest that other methods of achieving this separation are desirable. Another technique for fabricating potentially useful combinations of materials with
hard matrix and imbedded lubricant phases is to prepare a hard matrix with embedded reservoirs and fill the reservoirs with solid lubricant. This greatly increases the possibilities of material combinations by removing the restraint of needing materials that phase separate under deposition conditions. Voevodin et al (10) laser processed hard surfaces to form grooves. A TiC and DLC hard surface with MoS₂ had better tribological performance than the hard coat alone or a hard coat with lubrication and no grooves. Voevodin et al (11) later extended this work with a TiCN hard coat and laser drilled 10μm and 20μm diameter holes filled with MoS₂ and other powder lubricants, resulting in improved frictional performance and an optimum spacing of .05 mm. This represents lubricant microreservoir percent coverage between 12 percent and 50 percent. However, concerns about diminished mechanical strength will arise as the coverage percentages increase.

Another approach to fabricating hard matrix and lubricating reservoirs was explored by Krzanowski et al. (12) using photolithography methods. Semiconductor patterning methods were applies to silicon substrates to create arrays of wear resistant hills and valleys of lubricant. Although promising results were obtained, the cost, processing time, and questionable application to metallic surfaces were significant hurdles to widespread application of those techniques.

A new method involving the use of sputtered coatings with lubricant microreservoirs patterned by polymer and ceramic microspheres was examined by Krzanowski and Zimmerman. (13) This method is the subject of this thesis.
CHAPTER II

EXPERIMENTAL METHODOLOGY

This chapter describes the equipment, systems and techniques used to prepare and analyze samples for this research. It begins with a description of the magnetron sputter system used to deposit thin hard films over ceramic beads and the substrate. A list of significant other equipment used to analyze the samples is found on section 2.2. Section 2.3 discusses software used to determine the percent of the surface that is covered with microreservoirs. Equipment and methods of determining tribological properties are detailed in section 2.4. Methods for applying microspheres including parameters governing usable deposits of microspheres on substrates follow in section 2.5. Finally, the methods used to fabricate composite coatings, including deposition of thin films over microspheres, are the subject of section 2.6

2.1. Deposition System

Magnetron sputtering, with or without a reactive gas, was chosen as the deposition system for this work. It was chosen as a suitable method because deposition of a 1-2 μm coating can be carried out in a reasonable deposition time
(between one half hour and 2 hours for this work) with quick turn around and new depositions possible daily. Magnetron sputtering is compatible with a wide range of elements and compounds common in the materials industry and research community. Targets for sputtering are available on a commercial basis. A schematic of the deposition system, with its major components can be seen in Figure 2.1.

![Sputtering Deposition Schematic](image)

Figure 2.1 Magnetron sputtering schematic
Magnetron sputtering uses argon ions to dislodge atoms from target and onto the substrate to build a film. Reactive gas, in this case nitrogen, that combines with the sputtered material to form compounds on the substrate may be used as well. Pressure in the vacuum chamber prior to sputtering is in $10^{-6}$ to $10^{-7}$ torr range. Pressure is controlled with the admission of argon, with or without nitrogen, and the gas is in the 5 to 8 milli-torr range during sputtering.

Figure 2.2 includes images of the magnetron sputtering system, with labels for some of the key pieces of equipment in the deposition system. The system uses two Advanced Energy RFX 600 Rf Power supplies with ATX 600 auto tuners. The DC sputtering power supply is an Advanced Energy MDX 500. The substrate Bias power supply is an Advanced Energy MDX 1000. Vacuum is obtained with a Varian SD 20 mechanical pump and a Leybold 151 turbo-molecular pump with a Turbotronik NT 150/360 controller. MKS Instruments mass flow controllers and readout are used for argon and nitrogen gas monitoring and flow control. The deposition rate monitor is a Sycon Instruments STM-100/MF.
2.2. Additional Facilities

These systems were used to characterize materials used in this research, including synthesis and tribological testing.

- X-ray Photoelectron Spectroscopy: Material's elemental analysis was performed on UNH's X-ray photoelectron spectroscopy system, a Kratos Axis HS XPS using an Mg Kα X-ray source. Figure 2.3 is a screen image
of the XPS display showing the elemental analysis and binding energy peaks for sample S150, a reactively deposited TiN thin film on silicon.

| Peak | Position BE (eV) | Raw Area (CPS) | Raw Area Raw Area RSF Atonic Mass Conc % Atonic Mass Conc % |
|------|------------------|----------------|----------------|------------------|
| Ti 2p | 454.400 | 8.709 | 722 9 | 2.001 | 47.878 | 54.95 | 80.51 |
| N 1s | 396.400 | 3.881 | 134.1 | 0.477 | 14.007 | 42.83 | 18.77 |
| O 1s | 529.600 | 1.919 | 11.7 | 0.780 | 15.999 | 8.28 | 1.12 |

Figure 2.3 X-ray Photoelectron Spectroscopy screen image with elemental analysis and binding energy spectrum for TiN thin film.

- X-ray Diffraction: Two x-ray diffraction systems were used: 1) A Rigaku D/Max B x-ray diffractometer system with Cu kα radiation and Jade software and 2) an AXS Bruker area x-ray system with Cu kα radiation and Bruker GADDS (General Area Detector Diffraction System) software. Figure 2.4 was developed on the AXS Bruker system and software and shows the measured XRD peaks, including the silicon substrate, in black and the reference Powder Diffraction File, PDF # 38-1420, peaks for TiN.
FCC, in red. The difference in peak heights between the PDF and sample indicates the sample has texture.

Titanium Nitride XRD Peaks

Figure 2.4 Image from AXS Bruker system and software and showing the measured XRD peaks, including the silicon substrate, in black and the reference PDF peaks for TiN, FCC, in red.

- Scanning Electron Microscope: An Amray 3300FE field emission SEM with PGT Imix-PC microanalysis system with electron beam voltage of 7 kV was used to image both surface and cross-sections of prepared samples.
2.3. Microreservoir Percent Coverage

Determining how much of the thin hard film on the surface of a sample is covered by microreservoirs, as a percentage of the total area is key to knowing the optimum level of microreservoirs. National Instrument's Vision software is a mechanism of image processing to identify microreservoirs and characterize the percentage of the surface they represent. Figure 2.3 is a processed binary image identifying each white pixel as part of a microreservoir. Vision identifies each item, in this case each hole, and calculates the size in pixels and/or measured dimensions, percentage coverage, and the size. The image of sample 244b in figure 2.5 has 8.6% microreservoir coverage.

Figure 2.5 Processed binary image of microreservoirs for sample S244b showing 8.6% microreservoir coverage.
2.4. Tribological Testing

Frictional properties of samples were determined with a tribometer. A type of tribometer known as a pin on disk apparatus (Figure 2.6) applies a known load, typically 1 N to 10 N, normal to the surface being tested and measures the force exerted parallel to the surface as the sample spins. Rotational speeds range up to 200 rpm, the most common speed used in this study. A load cell measures the frictional force and voltmeter interfaced with Protek 506 data collecting software.

![Figure 2.6 Pin on disk tribometer used to measure friction values of test specimens prepared for this study.](Image URL)
2.5. Microsphere Application Methods

Microspheres were placed onto substrates using techniques described in this section.

Microspheres randomly arranged on a substrate can act as placeholders and provide a template for the lubricant microreservoirs. Relatively uniform but randomly distributed microspheres can assure the availability of lubricant reservoirs to the counterface at all times. To process a coating using microspheres, a hard film is deposited over the microspheres/substrate, the microspheres removed, and a solid lubricant deposited on the hard coating and into the microreservoirs. It is expected that hard coatings that are less than half the microsphere height will most readily facilitate microsphere removal, although deeper reservoirs may be more effective as lubricant reservoirs. Since the deposited coatings are typically 1-2 μm thick, the ideal microsphere diameters should be on that order, however availability of microspheres in this range is limited. Microspheres are available in powder and as suspensions in liquid, and in the present work we have obtained polymer, copolymer, and silica microspheres in aqueous suspensions. Suspensions used were: a 10% w/w 9.6 μm copolymer suspension (Duke Scientific 7510A), a 10% w/w 3.0 μm polymer latex microsphere suspension (Duke Scientific 5300A), and a 5% w/w 3.0 μm silica suspension (G. Kisker GbR PSI 3.0 Silica Particles). The suspension containing silica particles was chosen to allow deposition of the hard coating at elevated temperatures.
To prepare more dilute suspensions these suspensions were diluted with water, ethyl alcohol, or acetone. Suspensions of ethyl alcohol were found to be the most favorable for creating uniform deposition of microspheres on the substrate; water evaporated too slowly and acetone evaporated too quickly. Sprayed surfaces that were excessively wet resulted in agglomeration of particles during drying and sprays that evaporated before reaching the surface left most microspheres in the air, not on the substrate. Dilution ratios were critical in achieving the desired density of microspheres on substrates. The level of microspheres agglomeration and uniformity was also found to be a function of dilution ratio. Dilution ratios for TiN Reactive samples prepared by manually spraying microspheres were 200:1 or 600:1 by weight and spray passes ranged from 1 to 7.

The polymer and silica microspheres were deposited on silicon or 440C stainless substrates using a compressed air driven spray system, or a manually driven spray system. Multiple passes were made over the substrates until the desired microsphere density was achieved. The microsphere distribution uniformity was a function of the number of spray passes with additional passes increasing agglomeration and limiting the reservoir density achievable with this technique. Substrate temperature, air supply pressure, and spray distance also influenced microsphere distribution uniformity and density. A more uniform distribution was achieved with ceramic microspheres in comparison to polymer microspheres. However, because the width of the wear track is significantly
greater than the diameter of the microreservoirs, a perfectly uniform distribution may not be necessary, or even desired, especially with smaller microspheres.

2.6. Coating Fabrication

Multiple steps, including microsphere deposition detailed in the previous section, are required to fabricate a coating prior to tribological testing.

Fabrication of coatings for this work were carried out using the following general procedure, as shown in figure (2.7): cleaning of substrates followed by a) placement of microspheres on the substrate surface; b) deposition of a hard coating layer of TiN or TiCN using direct or reactive rf magnetron sputter Deposition to a thickness of $\sim$ 0.5-1.5 $\mu$m including deposition of a bond layer (titanium, $\sim$ 30 nm thick) using dc or rf magnetron sputter deposition, and; c) removal of the microspheres by sonication; and d) application of a solid lubricant coating by either sputter deposition of MoS$_2$ or by dispersal a graphite-containing ethanol suspension on to the surface, followed by air drying.
Figure 2.7 Overview of process steps for fabricating hard coating and lubricant microreservoirs.

Substrates of both 440C steel and Si wafers were used for this study. The Si wafers were used for the purpose of allowing SEM cross-section images to be obtained by fracturing the Si and viewing edge-on in the SEM. The substrates were first cleaned using a degreasing agent, followed by rinsing in distilled water, then ethanol, and drying with a heated air blower. The microspheres were applied by diluting the microsphere suspension and spraying this solution on the substrates using compressed air driven spray gun or manual sprayer. After the
solvent dried, the samples were placed in the vacuum chamber for deposition of the hard layer.

Deposition was carried out in a high vacuum chamber, described in section 2.1, which was back-filled with high-purity argon to a pressure of 4 to 8 mTorr for sputter deposition. The Ti bond layer was deposited first using dc or rf sputtering from a Ti target. Immediately after this layer was deposited, a hard coating was deposited of either TiN or TiCN. The TiN was deposited using rf sputter deposition from a TiN target or reactively sputter deposited from two Ti targets with nitrogen gas. The TiCN film was deposited by simultaneously sputtering from two targets, one TiN and a TiC target. These coatings were deposited from room temperature up to 500C.

After hard coat deposition the microspheres were removed to create the lubricant reservoirs. This was accomplished by placing the substrates in an ultrasonic cleaner in deionized water or ethanol for as little as 1 second up to 2 minutes. Examining the substrates in an optical microscope after this treatment showed that essentially all of the microspheres were removed.

The final part of the sample preparation was to fill the lubricant micro reservoirs. Ideally, only the reservoirs need to be filled with the solid lubricant, however, in practice this is not possible. Instead, the lubricant reservoir structure is created in-situ during the wear process. To allow this to occur, the solid lubricant needs to be placed on the hard coating surface, which can be done using number of methods, i.e., deposition of a blanket coating or by applying a
suspension the lubricant on to the surface. In this study, two methods were examined: deposition of MoS$_2$ by sputter deposition, and brushing or spraying a suspension of a graphite powder on the surface. The MoS$_2$ was deposited by sputter deposition using an rf power source at room temperature and at an Ar pressure of 8 mTorr. The thickness of the coatings was varied relative to the hard coating thickness. The effect of the reservoirs may be minimal if the MoS$_2$ is significantly thicker than the hard coating and reservoir depth because of the tenacious nature of sputtered MoS$_2$. Alternatively, if the thickness is much less, there may be insufficient material to fill the reservoirs. In this study, we examined MoS$_2$ thickness levels equal to, as well as one-third of, the hard coating layer thickness. Graphite lubricant was applied by brushing or spraying a thin layer of 2% by weight suspension of graphite in ethanol on the hard coating surface. Graphite was then available for movement into the microreservoirs during the wear process.
CHAPTER III

RESULTS AND DISCUSSION

3.1. Microsphere Application Results

Methods for applying microspheres were detailed in section 2.4, and in this section specific samples of microspheres on substrates resulting from those techniques are found.

Figures 3.1 and 3.2 show 9.6 μm copolymer microspheres diluted to 1% by weight with ethyl alcohol and applied to a titanium coated silicon substrate. (Sputtered titanium thin films were used in preliminary bead deposition tests, prior to use of harder TiN and TiCN coats.) The microspheres exhibit agglomeration with some agglomerated particles reaching 100 μm across. This application of microspheres was not used further due to excessive agglomeration. Significant agglomeration can be seen in Figure 3.3, an SEM image of 3μm silica beads on silicon substrate, Figure 3.4 shows 3.0 μm silica microspheres diluted to 0.1 % by weight with ethyl alcohol and applied to a 440C substrate. The level of microsphere agglomeration is much less than Figures 3.1, 3.2, and 3.3 and is suitable as a template for lubricant microreservoir creation.
Better dispersion of the beads resulted from switching to ceramic beads from polymer beads and to improved spray techniques. In each of these cases, the microspheres could be successfully removed after hard coating deposition by placing the film face downward in deionized water or ethanol and applying 1 second up to two minutes sonication, followed by washing in ethanol and drying.

Figure 3.1 Optical micrograph of 9.6 μm copolymer microspheres on a Ti-coated Si substrate, showing insufficient microsphere distribution.
Figure 3.2 Detail from 3.1

Figure 3.3 SEM image of 3µm ceramic microspheres on Titanium Carbo Nitride hard coating showing agglomeration and partial removal.
3.2. Hard Coat Method: TiN Reactive Sputtered

Having obtained a suitable method for placement of microspheres on the substrate surface, the next step was to select a suitable hard coating deposition method. Section 2.5 described how hard films could be rf sputtered directly from commercially available targets of titanium nitride by itself or combined with titanium carbide. This section will describe reactive deposition techniques using two titanium targets simultaneously with argon for sputtering and nitrogen gas to react with titanium to form titanium nitride on the substrate. (14) One limitation
with direct rf magnetron sputtering titanium nitride or other nitride containing targets is a lower rate of deposition than with a pure metal. Pure metal targets are also more readily available and reactive sputtering can be faster when no nitrogen or carbon needs to be sputtered off the targets. Reactive sputtering can also produce higher purity films than direct sputtering. (14) Nitrogen can diffuse into the target under some conditions, as evidenced by gold titanium nitride on the silvery titanium target that was occasionally visible.

Variables that primarily influence the properties of rf directly sputtered compounds include rf power, substrate bias and temperature, target to substrate distance, vacuum chamber base pressure, and argon pressure and flow rate. Variables controlling the formation of reactive compounds additionally include nitrogen pressure and feed rate, and nitrogen to argon ratio. Many parameters that produced directly sputtered films are not applicable when depositing reactive films. In this study, reactive deposition substrate temperatures ranged from room temperature to 500°C. Total pressures during sputtering were 3.8 mTorr to 8.6 mTorr. Sputtering power varied from 100 W to 180W and sputtered targets were 2 inches in diameter. Argon flow was 20 or 35 sccm. Nitrogen flow ranged from 3 sccm to 8 sccm. A substrate temperature of 300°C was determined to be the optimal temperature for forming reactive TiN films. Figure 3.5 indicates how, at 300°C, the film oxygen content was found to decrease with increasing substrate bias, reaching 2% at 150V. Another temperature with enough data points to look for trends, 350°C, did not exhibit the same bias related trend, as shown in figure
3.6. Deposition parameters were tuned until acceptable TiN film quality was achieved. Film quality was determined by noting color, film adhesion, resistance to scratching, and elemental content via XPS and XRD. Appendix A lists many samples that preceded usable TiN. Table 3.1 compares parameters that resulted in acceptable films from direct sputtering and reactive sputtering. Key changes include increasing substrate temperature from room temperature to 300°C and increasing substrate bias from 25 to 150 volts.

![Percent Oxygen vs. Bias Voltage](image)

**Figure 3.5** Oxygen content and substrate for TiN reactively sputtered film at 300°C.
Figure 3.6 Oxygen content and substrate bias voltage for TiN reactive deposition at 260 C to 500 C.

Reactive and Direct rf Sputtering Comparison

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Direct Sputtering</th>
<th>Reactive Sputtering</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bead Type</td>
<td>Polymer</td>
<td>Ceramic</td>
</tr>
<tr>
<td>rf power (watts)</td>
<td>190</td>
<td>180</td>
</tr>
<tr>
<td>Substrate Bias (Volts)</td>
<td>25</td>
<td>150</td>
</tr>
<tr>
<td>Substrate Temperature (C)</td>
<td>Room Temperature</td>
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</tr>
<tr>
<td>Pressure (miliTorr)</td>
<td>3.8</td>
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<tr>
<td>Argon Feed Rate (sccm)</td>
<td>Not Controlled</td>
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</tr>
<tr>
<td>Nitrogen Feed Rate (sccm)</td>
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</tr>
<tr>
<td>Target to Substrate (cm)</td>
<td>6.4</td>
<td>9.5</td>
</tr>
</tbody>
</table>

Table 3.1 TiN hard films with direct and reactive rf magnetron sputtering parameters resulting in acceptable films.

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3.3. Samples Prepared Using Direct Sputtered TiN and TiCN

Samples of lubricant microreservoirs in rf magnetron sputtered titanium nitride and titanium carbonitride hard coatings were prepared to develop fabrication methods, examine the resulting material and structures, and to test for friction and wear resistance. Samples shown here all used the direct-sputtered hard coatings; samples using reactive TiN are discussed in the next section, section 3.4. Polymer microspheres of 3 μm and 9 μm diameters and ceramic (silica) microspheres of 3 μm diameters acted as lubricant microreservoir templates. A complete table of these coatings can be found in appendices B and C. Images and discussion of selected samples follows.

Figure 3.7 shows SEM images a magnetron-sputter deposited TiN coating deposited at room temperature over 9.6 μm copolymer microspheres after microsphere removal, on a silicon substrate. The microspheres are PSDVB, a polystyrene polymer, cross-linked with 4 to 8% divinylbenzene, from a 10% w/w 9.6 μm copolymer suspension (Duke Scientific 7510A). The TiN hard coat remaining after bead removal exhibits evidence of possible melting and/or deformation of the polymer sphere, or possible bonding with the film. Although the substrate was at room temperature at the start of deposition, higher temperatures are realized at the surface as deposition proceeds.
Figure 3.7 SEM Image of a room temperature magnetron sputtered TiN thin film showing a lubricant microreservoir after 9.6 μm copolymer microsphere removal.

Figure 3.8 is an SEM image of magnetron sputtered 0.5 μm thick TiCN, deposition at 500°C, over ceramic microspheres on a silicon substrate, again followed by microsphere removal. While the polymer microspheres resulted in a jagged edged hole, the silica microspheres yielded a smooth edged hole. Both holes have a difference in texture adjacent to the hole when compared to the flat film surface.
Figure 3.8 SEM Image of a 500°C magnetron sputtered TiCN thin film showing a lubricant microreservoir after 3.0 µm silica microsphere removal.

Figure 3.9 shows a cross section of a 1.85 µm thick TiCN layer, deposited at 500 C on a silicon substrate with 3 µm microspheres, without any lubricant applied. This cross section was obtained by fracturing the silicon substrate and TiCN hard layer. It is unlikely that the fracture would go exactly through the centerline of the hole and thus the images may not show the part of the hole continuous to the substrate. The chance that the fracture will go through the centerline of the hole is low because of the way the fracture is created. (Scoring the back side of the silicon substrate, and manually bending it until it breaks creates the fracture line.) The score has no relationship to the holes in the thin film and therefore it is most likely that the fracture will miss any particular
hole, and when it does go through a hole, every chord through the hole has an equal chance of being the fracture line. Nonetheless, a clearly defined microreservoir can be seen that is suitable for filling with a solid lubricant.

Figure 3.9 SEM cross-section showing micro-lubricant reservoir formed from a 3 \( \mu \text{m} \) silica microsphere. The thin film is 1.85 \( \mu \text{m} \) thick TiCN on a silicon substrate, magnetron sputter deposited at 500°C. Spherical outlines drawn showing 2 \( \mu \text{m} \) reservoir diameter and 4 \( \mu \text{m} \) diameter if extended to silicon substrate.

A solid lubricant component was added after microsphere removal, either via magnetron sputtering for MoS\(_2\) or direct application of the graphite suspension. Figure 3.10 shows a SEM cross-section of a microreservoir that has the dual lobed shape of agglomerated microspheres, placed in a 1.72 \( \mu \text{m} \) thick
TiCN thin film. The upper layer of a 2.2 μm thick MoS₂ film closely conforms to the contours of the TiCN surface. Figure 3.11 shows an example of a microreservoir from the edge of a wear track, where disturbed MoS₂ remains in the indentation.

Figure 3.10 SEM cross-section of 2.2 μm thick MoS₂ layer on 1.72 μm thick TiCN thin film on a silicon substrate. 3.0 μm silica microspheres were the reservoir template for the agglomerated reservoir in an unworn area of substrate.
Figure 3.11 SEM of single microreservoir of the same cross section as Figure 4 with disturbed MoS$_2$ on surface and in the microreservoir, on edge of wear track.

Figures 3.12 and 3.13 show optical micrographs of a TiCN thin film on a 440C substrate with microreservoirs based on 3 $\mu$m silica microspheres. The reservoirs contain graphite from a 2% graphite ethanol suspension applied to the surface. Microreservoirs are visible on and outside the track. Graphite-filled reservoirs are visible in the wear track. This indicates that graphite was pushed into the reservoirs and was available for friction reduction as the run progressed, but after graphite was worn away from the surface outside of the lubricant reservoirs.
Figure 3.12 Optical micrographs of TiCN thin film with 3.0 μm nominal microreservoirs, and 2% graphite suspension as lubricant coating, showing microreservoirs in and around track.

Figure 3.13 Optical micrographs of TiCN thin film with 3.0 μm nominal microreservoirs and 2% graphite suspension as lubricant coating with wear track and graphite filled microreservoirs.
Figure 3.14 is an optical micrograph of a wear track on TiCN thin film with nominal 3 μm microreservoirs with graphite in lubricant microreservoirs in the wear track and no graphite in reservoirs outside the wear track.
3.4. **Samples Prepared Using Reactively Sputtered TiN Films with Microreservoirs**

This section describes the results obtained using reactively deposited TiN thin films with 3 μm silica beads as templates for lubricant microreservoirs. It includes a list of the samples and images showing the samples with microreservoirs and graphite.

Table 3.2 lists parameters important to preparation of 440C substrates with reactively deposited TiN thin films and microreservoir templates by sprayed ceramic microspheres. Substrates were sprayed in batches as needed over the course of the study, and substrates sprayed at the same time belong to the same spray group. Substrates without any microspheres are identified as spray group zero.

As noted in a previous section of this thesis, silica microspheres were purchased as 5% by weight suspensions in water. These suspensions were mostly diluted directly with ethyl alcohol, although spray group 24 was dried to completely remove water prior to dilution with ethanol. Suspension concentration indicates how much the original suspensions were diluted, for example the original 5% solution, although not listed here, would be shown as 20:1. Achieving uniform microsphere distribution with higher ratios of microreservoir to total area required a balance between suspension concentration and number of spray passes. Spray concentrations that were too high used excessive amounts of the original microsphere suspension and could also result in excessive
agglomeration on the substrates. Lower suspension concentrations would require more spray passes to achieve the desired reservoir percent coverage, but each additional spray pass increased the odds of excessive agglomeration. A spray pass is defined as one manual squirt of the spray bottle, with the spray as close to perpendicular to the substrate surface as practicable. Higher reservoir density without agglomeration depends on several factors. Manual agitation, followed by sonication of the microsphere suspension was considered essential to reducing microsphere agglomeration on the substrate surface. Microspheres were sprayed with 2 oz Mist Sprayer (#1151, Paris Presents Inc, Gurnee, Illinois 60031); In 200:1 or 600:1 concentrations with from 0 to 7 spray passes. 200:1 suspensions were 10% water, with the balance ethyl alcohol. 600:1 suspensions have 3.3% water with the balance ethyl alcohol. The 24 series were prepared with 100% ethyl alcohol. Substrates were placed in a triangular arrangement on the deposition heater/platform with 1 indicating the rear position, 2 – front left, and 3 - front right.
## TiN Reactive Deposition Sample Preparation

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Microsphere Spray Group</th>
<th>Microsphere Suspension Concentration</th>
<th>Spray Group</th>
<th>Deposition Group</th>
<th>Substrate Deposition Position</th>
<th>Reservoir Coverage Percent</th>
<th>Average Reservoir Size $\text{um}^2$</th>
<th>Spray Group Implied Density %</th>
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<tr>
<td>S194CE</td>
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<td>G</td>
<td>3</td>
<td>8.81</td>
<td>35.6</td>
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</tbody>
</table>

1 - 440C Substrates  
2 - 2 oz Mist Sprayer #1151, Paris Presents Inc, Gurnee, Illinois 60031  
3 - Substrate Deposition Position: 1 - Rear, 2 - Front Left, 3 - Front Right

### Deposition Conditions
- Sputter Guns Power: 180 W  
- Substrate Bias: 150 V  
- Deposition Temp: 300°C  
- Ar Flow Rate: 20 sccms  
- N₂ Flow Rate: 5 sccms  
- Pressure: 3.5 - 4.0 mTorr

Table 3.2 Samples prepared by reactive deposition of titanium nitride.

Spraying microsphere suspensions containing both water and ethanol has the potential to concentrate and agglomerate the microspheres because of the slower drying time of water when compared to ethanol. While many factors affect the amount of agglomeration, the ratio of water to ethanol in the suspension did
not seem to be a controlling factor. Even with the removal of water from the suspension in spray group 24, it was noted that areas of the substrate dried at different rates, indicating the presence of water in the suspension as it dried on the surface of the substrate. This water was probably absorbed into the ethanol from the air during spraying and drying.

Reservoir percent coverage was determined with National Instrument's Vision software, as described in section 2.3, as was average reservoir size. Spray group implied density was developed from an observation that the measured density and the number of spray passes seemed to be only moderately related. Spray group 21, 600:1 dilution with 2 passes was assigned implied density 2% and the same spray group with the same dilution and 7 passes was assigned 7% with all other densities calculated relative to these. Spray group implied density seemed to show better correlation with friction indicators than measured density, as will be seen in following sections of this thesis. Spray group 23 showed greater agglomeration, figure 3.15, than other spray groups as shown by average reservoir size. This agglomeration did not affect the friction results in any meaningful way, as is detailed in the tribological results section.
Figure 3.15 Optical image of spray group 23 with average reservoir size 121 μm² showing distributed graphite in wear track.
Figure 3.16 shows a cross-section image SEM image of a titanium nitride film on silicon substrate with a lubricant microreservoir in a 1.53 μm thick film formed using nominal 3 μm silica microspheres. The film was deposited by reactive rf magnetron sputtering of titanium with nitrogen gas at a substrate temperature of 300°C.
Figure 3.17 is an agglomerated microreservoir in reactive titanium nitride on another part of the sample shown in figure 3.18. A thin layer of graphite is present, apparently flattened by the wear process.

Figure 3.17 SEM image of another part of sample in figure 3 showing graphite lying in agglomerated microreservoir.
Figure 3.18 is an SEM image of a 3um nominal microsphere with reactively deposited TiN that was not dislodged by 2 minutes sonication in ethanol. Virtually all microspheres were removed by sonication, leaving only a few still covered.

Figure 3.18 SEM image of 3um nominal microsphere with reactively deposited TiN that was not dislodged by 2 minutes sonication in ethanol.
Figure 3.19 is an SEM image of graphite partially removed from a microreservoir in reactive TiN on silicon, apparently dragged out by the counterface during the pin on disk test.
3.5. **Tribological Testing: TiCN Coatings with MoS$_2$ and Graphite**

Pin on disk tests were conducted to investigate the effectiveness of the microreservoirs and lubricant behavior on TiCN films with lubricant microreservoirs. Two lubricants were used, MoS$_2$ and graphite.

3.5.1. MoS$_2$ Lubricant

The tests of MoS$_2$ were carried out at a speed of 200 rpm with 1 N load, 25% humidity, and a WC counterface 6.25 mm in diameter.

Pin on disk tests were first conducted on the hard coating alone and then against the same coating with empty 3 μm nominal microreservoirs. These results showed greater average friction coefficient with the empty microreservoirs compared to the same thin film without microreservoirs. Over the first 1500 cycles coatings with empty microreservoirs resulted in an increase from 0.33 to 0.56 in average friction for TiCN deposited at 500°C and from 0.55 to 0.61 in average friction for TiCN deposited at ambient temperature. Left unfilled, the holes in the film may contribute to weakening the mechanical strength of the coating and cause film fracture.

Pin on disk tests of sputtered MoS$_2$ on TiCN deposited at ambient temperature and tested at 25% relative humidity compared the friction factors of coatings with and without microreservoir holes present in the films. It was found that in the first 2000 cycles, the friction factor averaged 0.19 without
microreservoirs and 0.28 with microreservoirs (constituting 15.5% of the surface). For the last 2000 cycles of the test, the friction factor remained at 0.19 without microreservoirs and dropped to 0.24 with microreservoirs. The poor performance of these coatings was attributed to poor mechanical properties of ambient-temperature deposited TiCN, so in the subsequent films, the TiCN was deposited at 500°C.

Samples were prepared to also determine the effect on friction caused by completely vs. partially filling microreservoirs with lubricant. Two samples were deposited to examine this concept: one with a 1.44 µm thick TiCN hard coat with microreservoirs covering 3.5% of the surface and a 0.461 µm thick MoS₂ lubricant coating; and the other with a 1.72 µm thick TiCN coating, with microreservoirs also covering 3.5% of the surface, but with a 2.2 µm thick MoS₂ lubricant coating. Pin-on-disk conditions were 50% humidity, 200 rpm, 1 N load, and the WC counterface. The hard thin film was TiCN deposited at 500°C, with microreservoirs resulting from 3 µm silica microspheres. Friction for the partially filled microreservoirs was 0.43 and 0.29 for the completely filled microreservoirs 33% lower for the filled lubricant microreservoirs. While some improvement was noted here, the friction was not substantially better then TiCN with empty microreservoirs (0.33-0.56 as indicated above). The effective use of MoS₂ in this application is impacted by its humidity sensitivity and tendency to oxidize during wear. Understanding this behavior and its integration with a microreservoir-containing coating will require significant further study. For this reason,
subsequent investigations were conducted using graphite, which is less humidity sensitive in ambient atmospheres.

3.5.2. Graphite Lubricant

A 2% by weight suspension of graphite, (Alpha Aesar graphite powder, microcrystal grade, APS 2-15 micron) in ethyl alcohol was prepared. While the size of the graphite particles cover a range larger than the microreservoir diameter, counterface movement may further reduce the particle size and move smaller particles into the microreservoirs. Figure 3.13 in section 3.3 of this thesis shows graphite present in microreservoirs, providing some evidence for this effect.

Pin on disk tests on a TiCN coating were first conducted without microreservoirs, with and without the 2% graphite suspension. Pin and disk conditions were WC counterface, 1 N load, 200 rpm, and 25% humidity. The results are shown in Fig. 3.20 a and b. Without microreservoirs, over the initial 1500 cycles, average friction was 0.33 with no lubrication, and 0.29 with graphite lubrication. Between 6500 and 8500 cycles average friction without lubrication was 0.41 and 0.40 with lubrication, indicating the effect of lubrication without microreservoirs is almost gone.

Tests of a TiCN film, with similar test conditions as before, with microreservoirs covering 6% of the surface, without lubrication, showed average friction of 0.32 over the first 1500 cycles. Tests of the same film with a 2%
graphite suspension applied to the surface, showed average friction of 0.24 over the first 1500 cycles. The average friction for the last 2000 cycles was 0.42 without lubrication and 0.37 with lubrication. Figure 3.20 a shows that initially and over time, the TiCN film with microreservoirs and graphite lubrication has lower friction than the other 3 combinations. While an improved behavior was found, further optimization can be realized by adjusting the percentage of microsphere coverage. Work to examine this effect is the subject of subsequent sections of this thesis.

Figure 3.20 a Pin-on-disk test results with and without 3.0 μm nominal microreservoirs covering 6% of the surface and with or without 2% graphite solution lubricant. Four conditions are plotted: NRNL – No Reservoirs, No Lubricant; WRNL – With Reservoirs, No Lubricant; NRWL – No Reservoirs, With Lubricant; WRWL – With Reservoirs, with Lubricant.
Figure 3.20 b displays average values for the data used in figure 3.20 a. This chart shows that both early and late in the pin on disk test the combination of microreservoirs and lubricant has the lowest friction coefficient of the four combinations.

Figure 3.20 b: Average values for figure 3.20 a. Pin-on-disk test results with and without 3.0 \( \mu \text{m} \) nominal microreservoirs covering 6\% of the surface and with or without 2\% graphite solution lubricant. Four conditions are plotted: NRNL – No Reservoirs, No Lubricant; WRNL – With Reservoirs, No Lubricant; NRWL – No Reservoirs, With Lubricant; WRWL – With Reservoirs, with Lubricant.
3.6. Tribological Testing: Reactive TiN Coatings with Graphite

The previous section compared the results of tribological testing of a TiCN film with and without microreservoirs and with and without graphite lubricant, showing that microreservoirs and lubricant had the lowest friction of the four possible combinations. That testing was at 6% microreservoir coverage. This section extends that work to determine the optimum percentages of microreservoir coverage. The thin hard coating was changed from TiCN to reactively deposited TiN.

3.6.1. Friction Tests and Data

Pin on disk wear tests were performed on reactively sputtered TiN thin films coated on 440C substrates. Tests with 440C, WC, and alumina counterfaces indicated that alumina was the preferred counterface. WC and 440C counterfaces would wear off onto the TiN hard film, whereas alumina would cause the film to wear.

Values for tests are found in Table 3.3. Fourteen percent is the maximum value of microreservoir coverage and twelve percent is the maximum value of microreservoir implied density. These were the highest coverage values that could be obtained without excessive agglomeration using the spray techniques that were the basis for this work.
### TiN Reactive Deposition Friction Data

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Reservoir Coverage Percent</th>
<th>Spray Group</th>
<th>Implied Density %</th>
<th>No Lube Failure Style</th>
<th>Max Friction, No Lube</th>
<th>Max Friction, First 1000 Cycles or To Failure</th>
</tr>
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<td>QF</td>
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<td>0.73 0.52 0.18</td>
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**Failure Style:** QF - Quick Failure, LL - Longer Lived

**Deposition Conditions**
- Sputter Guns Power: 180 W
- Substrate Bias: 150 V
- Deposition Temp: 300°C
- Ar Flow Rate: 20 sccms
- N2 Flow Rate: 5 sccms
- Pressure: 3.5 - 4.0 mTorr

**Table 3.3 Measured and calculated values from reactive TiN tribological tests**

Pin on disk tests were conducted using an alumina .25 inch spherical counterface, TiN reactively deposited hard coat deposited at 300°C with nominal 3 µm microreservoirs ranging from zero to 12% of surface area, on 440C substrate, at 200 rpm with a 1 N load and 25% humidity. These tests were conducted to evaluate the enhancement of wear properties with lubricant microreservoirs. In
each case, wear tests were initially run on the hard coat without graphite, and then three sprays of graphite ethanol suspension were added and another test run on the same substrate. Additional pin on disk tests were run on the same sample, if warranted, by removing the graphite with an ethanol wash.

Wear tests patterns fell into two broad categories: quick failure, QF, and long lived, LL, as indicated in Table 3.3. Figure 3.21 has two charts of friction factor curves plotted against cycles. Samples for both charts have no lubricant microreservoirs. Figure 3.21 a shows a quick failure for the non-lubricated hard film, with initial failure around four hundred cycles and resulting the wear track shown in the upper micrograph, a wear track worn through to the substrate. The sample lubricated with graphite shows significant failure through 11,000 cycles, as seen in the lower micrograph. Figure 3.1 b indicates an initial peak less than .3 and a gradual increase in friction factor over the 11,000 cycles of the test. The micrograph of the wear track indicates limited failure. Limited failure is also indicated for the graphite-lubricated sample.

Figure 3.22 is a similar plot of friction factor and cycles for samples that have microreservoirs. These microreservoirs were patterned by nominally 3 μm ceramic beads. The curves for the samples in figure 3.22 are similar to figure 3.21; however the difference between the lubricated and non-lubricated curves is greater with microreservoirs, continuing the pattern shown with TiCN films.
Figure 3.21a No microreservoirs, non-lubricated curve shows quick failure.

Figure 3.21 b No microreservoirs and non-lubricated curve shows long life

Figure 3.21 Charts of Friction Coefficient vs. Cycles curves. Coating is reactively deposited TiN on 440C with alumina ball counterface. Each chart shows no lubrication and graphite lubrication curves. Images on right show wear tracks with non-lubricated on top.
Figure 3.22 a  Non-lubricated curve shows quick failure

Figure 3.22 b  Non-lubricated curve shows long life

Figure 3.22 Both sets of friction curves have microreservoirs. Similar conditions to figure 3.21. Images on right show wear tracks with non-lubricated track on top.
3.6.2. Analysis of Friction Data

Figure 3.23 shows friction factor plotted against microreservoir coverage as a percent of the surface area. It plots non-lubricated and lubricated data points for the percent coverage of a particular sample and separates the data by failure style, in order to evaluate the effectiveness of lubricant microreservoirs. Figure 3.23 demonstrates some expected patterns: No Lubrication data points are generally higher than lubrication values, but not always, especially in the longer lived data. With no lubrication, quick failure data points are higher than long-lived data. Little difference was noted in the pattern among the lubrication data points comparing quick failure to long lived. Some no lubrication QF points have friction factor below .4 for the first 1000 cycles because their friction vs. cycles curves had less slope in the beginning. (See Appendix D for all Friction Vs. Cycles graphs.) No obvious pattern was found relating friction factor to reservoir percent coverage.

In order to compensate for the different friction factor vs. cycle curve styles and the differences in individual sample friction factors, ratios were calculated for the maximum friction in each pair of curves, using maximum lubricated friction, divided by maximum no lubrication friction. A ratio of 1 indicates no difference between the lubricated and unlubricated samples, and a low value of this ratio is
preferred. This is plotted in figure 3.24 and shows some apparent downtrend in the highest values for the data points at each percentage.

![Friction Factor First 1000 Cycles vs. Reservoir Coverage Percent](image)

Figure 3.23 Friction Factor plotted against reservoir coverage percent.
Figure 3.24 Maximum friction ratio plotted against reservoir coverage percent.

Reservoir percent coverage should be a function of microsphere concentration in the spray suspension and the number of sprays of the solution. However, during preparation of samples by spraying ceramic beads, it was observed that measured values of reservoir coverage did not always track the number of sprays. Reservoir implied density was defined in section 3.4 (spray concentration times the number of sprays, then adjusted to match measured reservoir coverage values). Figure 3.25 shows a graph of reservoir coverage percent as measured against reservoir implied density. Ideally this should be a straight line, and the expected trend with significant variation is observed,
Figure 3.25 Reservoir coverage percent plotted against reservoir implied density percent.

The chart of maximum friction ratio to implied density of the microreservoirs (Figure 3.26) shows a downward trend as the reservoir coverage increases, particularly for the highest values observed at each level of coverage. Maximum friction ratio is about 1 at reservoir implied density percent of zero, meaning the lubricant by itself is not reducing friction when microreservoirs are not present. 12 percent implied density has a maximum friction ratio of .72, meaning that the maximum friction ratio has been reduced by 28%. Microreservoirs and lubricant have demonstrated an ability to significantly reduce friction.
Figure 3.26 Maximum friction ratio plotted against reservoir implied density percent

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CHAPTER IV

CONCLUSION

This investigation of the properties of lubricant microreservoirs embedded into hard coat thin films augmented our understanding of techniques for reducing friction for cutting tool applications. As a result, a new method has been developed and tested to fabricate hard coatings containing lubricant microreservoirs. The results of this work have shown:

1) Lubricant reservoirs can be successfully created in hard coatings using microspheres placed on the substrate surface before hard coating deposition. Both polymer and ceramic microspheres were used in this study. The microspheres could be removed after hard coating deposition by ultrasonic agitation.

2) Deposition of MoS₂ films over the microreservoir-containing TiCN coatings showed mixed results due to the humidity sensitivity of MoS₂. This system may be useful but the humidity needs to be kept below 25%. Given the excellent lubricating properties of MoS₂ at lower humidity levels, or in vacuum, it is not clear that the microreservoirs would play an important role unless the coating is subject to high cycles and excessive wear.
3) Use of the microreservoir-containing TiCN and TiN coatings with a graphite lubricant showed friction reduction. Wear tests showed the microreservoirs were filled with graphite during wear, even though the graphite was removed elsewhere on the surface. The coatings with microreservoirs containing graphite showed reduced friction compared to similar coatings without the microreservoirs.

4) Reservoir coverage of about 12 percent was the maximum level achievable, using direct spray techniques, on TiN thin films without excessive agglomeration of the microspheres during spraying of the substrates. Greater friction reduction and higher microreservoir density films may be achievable through techniques using other microsphere deposition techniques and sizes.

5) Microreservoirs filled with graphite in reactively formed TiN thin film coatings showed increased improvement in friction reduction at increasing levels of reservoir coverage. This ranged from no effect with no microreservoirs to 28% reduction at maximum microreservoir coverage, demonstrating that microreservoirs and lubricant significantly reduced friction.
SUGGESTIONS FOR FUTURE RESEARCH

Investigate larger sphere sizes.

The cross-sections of the wear tracks are several times the size of individual microreservoirs, making it possible for larger spheres to be used as templates. Agglomeration may be more of an impediment, or because the level of coverage per microsphere is greater than the 3 μm spheres used in most of this study.

Greater aspect ratios may have an effect on the film microreservoir combination. Current aspect ratios of typically 1 μm thick film with 3 μm nominal spheres give an aspect ratio of 3 to 1 height to width.

Smaller spheres will necessitate films thinner than 1 μm which may compromise durability or strength.

Investigate spheres with separation properties for higher density.

As microsphere coverage approached 12%, agglomeration became a significant problem. Magnetized ceramic spheres may provide a way for
separation to be achieved, although not on magnetic steels. Other methods for achieving greater dispersion need to be identified and investigated.

**Investigate burnished lubricant**

Graphite lubricants were sprayed on the thin films and pushed into the holes by the counterface. It may be possible to achieve greater life by burnishing the graphite to completely fill the holes prior to wear testing.

**Investigate alternatives to ceramic spheres**

Commercial users may not want ceramic spheres, which have the potential to cause unwanted wear, in their deposition systems. Alternatives that can work at high temperatures are needed. There may also be an issue with small pieces of the coating that are on the spheres, for the same reasons.

**Investigate Agglomeration**

Various amounts of agglomeration were seen in this work. What impact does the amount of agglomeration have and how can it be quantified? Determine its importance relative to other factors such as coverage ratio.
REFERENCES


# APPENDIX A: TITANIUM NITROGEN REACTIVE DEPOSITION

Titanium Nitrogen Reactive Deposition

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<th>Samples</th>
<th>Pin on Disk Sample</th>
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<th>Temp/Power</th>
<th>Gas Flow</th>
<th>XPS Results</th>
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# APPENDIX B: POLYMER MICROSPHERES ON 440C, SILICON, AND ALUMINUM BRONZE

## Polymer Microspheres on 440C, Silicon, and Aluminum Bronze

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## APPENDIX C: CERAMIC MICROSPHERES ON 440C, SILICON, AND ALUMINUM BRONZE

Ceramic Microspheres on 440C, Silicon, and Aluminum Bronze

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- **S46 440C Silica 3 Drops 1750 Ti Bead Bed 100 25 10 RT 15.5**
  - **TIN** Hard 190 25 45 RT 1/5/06 Change to 3um silica beads to reduce clustering and average cluster size
  - **MoS2** Lube 150 40 20 RT 1/6/06 TIN delamination at edge with washing

- **S47 Si Silica 3 Drops 1750 Ti Bead Bed 100 25 10 RT 1/5/06**
  - **TIN** Bead Bed 100 25 10 RT 1/8/06 Bead deposition tests, cooling

- **S48 440C None Ti Bead Bed 100 25 10 RT 1/5/06**
  - **TIN** Hard 190 25 45 RT 1/6/06
  - **MoS2** Lube 150 40 20 RT 1/9/06

- **S49 Si Silica 3 Drops 1750 Ti Bead Bed 100 25 10 RT 1/5/06**
  - **Ti** Bead Bed 100 25 10 RT 1/10/06
  - **TICN** Hard 190 25 45 RT 1/11/06
  - **MoS2** Lube 150 40 20 RT 1/12/06

- **S50 440C None Ti Bead Bed 100 25 10 RT 1/10/06**
  - **TICN** Hard 190 25 45 RT 1/11/06
  - **MoS2** Lube 150 40 20 RT 1/12/06

- **S51 440C Silica 3 Drops 1750 Ti Bead Bed 100 25 10 RT 1/10/06**
  - **TICN** Hard 190 25 45 RT 1/11/06
  - **MoS2** Lube 150 40 20 RT 1/12/06

- **S52 Si Silica 3 Drops 1750 Ti Bead Bed 100 25 10 RT 1/10/06**
  - **TICN** Hard 190 25 45 RT 1/11/06
  - **MoS2** Lube 150 40 20 RT 1/12/06
<p>| Sample ID | Substrate | Bead Type | Bead Size (um) | Bead Deposition Method | Bead Dilution (to 1) | Coating Material | Coating Type | Power (Watts) | Bias (Volts) | Time (Min) | Temp. (C.) | Thickness | Cover age % | Deposition Date | Comments |
|-----------|-----------|-----------|---------------|------------------------|---------------------|------------------|--------------|--------------|-------------|-------------|------------|-----------|-----------|------------|---------------|----------|
| S54       | Si        | None      | Ti            | Bead Bed              | 100                 | TiCN             | Hard         | 100          | 25          | 10          | RT         |           |           | 1/18/06    | Significant delamination |
| S55       | 440C      | Silica    | 3             | Drops                 | 1750                | TiCN             | Hard         | 190          | 25          | 45          | RT         |           | 1/18/06    | Significant delamination |
| S56       | 440C      | Silica    | 3             | Drops                 | 1750                | TiCN             | Hard         | 190          | 25          | 45          | RT         |           | 1/18/06    | Significant delamination |
| S57       | 440C      | None      | Ti            | Bead Bed              | 100                 | TiCN             | Hard         | 190          | 25          | 45          | RT         |           | 1/18/06    | Significant delamination |
| S58       | Si        | Silica    | 3             | Drops                 | 1750                | TiCN             | Hard         | 190          | 25          | 45          | 500        |           | 1/20/06    | First 500C deposition |
| S59       | 440C      | Silica    | 3             | Drops                 | 1750                | TiCN             | Hard         | 190          | 25          | 45          | 500        |           | 1/20/06    | Tape test, Ti well adhered |
| S60       | 440C      | None      | Ti            | Bead Bed              | 100                 | TiCN             | Hard         | 100          | 25          | 45          | 500        |           | 1/23/06    | Significant delamination |
| S61       | 440C      | Silica    | 3             | Drops                 | 1750                | TiCN             | Hard         | 190          | 25          | 45          | 500        |           | 1/23/06    | Significant delamination |
| S62       | 440C      | None      | Ti            | Bead Bed              | 100                 | TiCN             | Hard         | 100          | 25          | 10          | 500        |           | 1/27/06    | Significant delamination |
| S63       | Si        | None      | Ti            | Bead Bed              | 100                 | TiCN             | Hard         | 100          | 25          | 10          | 500        |           | 1/27/06    | Significant delamination |
| S64       | AIBz      | None      | Ti            | Bead Bed              | 100                 | TiCN             | Hard         | 100          | 25          | 45          | 500        |           | 2/7/06     | SEM         |
| S65       | AIBz      | Silica    | 3             | Drops                 | 1750                | TiCN             | Hard         | 100          | 25          | 45          | 500        |           | 2/7/06     |             |
| S66       | AIBz      | Silica    | 3             | Drops                 | 1750                | TiCN             | Hard         | 100          | 25          | 45          | 500        |           | 2/7/06     |             |
| S67       | Si        | Silica    | 3             | Drops                 | 1750                | TiCN             | Hard         | 100          | 25          | 45          | 500        | 0.514      | 2/7/06     |             |</p>
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<th>Bias (Volts)</th>
<th>Time (Min)</th>
<th>Temp. (°C)</th>
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APPENDIX D: TIN WITH GRAPHITE TRIBOLOGICAL TESTS' CHARTS

S 194 No Reservoirs Alumina Counterfaces, With and Without Graphite
TIN, 180 W, 150 V Bias, 20 sccm Ar, 5.0 sccm N, 300 C, 35% H, 440C Substrate, 200 rpm, 1N

Deposition Group: A
Position: 1
Percent Coverage: None
S 197 3um Nominal Reservoirs, Alumina Counterface, With and Without Graphite

Position: 3
Percent Coverage: 7.9%

Deposition Group: A

Cycles: 0 to 12,000

Graphite

TIN, 180 W, 160 V Bias, 20 sccm Ar, 5.0 sccm N, 300 C, 36%, H, 440C Substrate, 200 rpm, 1N

S197 C No Lube
S 197 D 2% Graphite

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S 212, 3 um Nominal Reservoirs, Alumina Counterface, With and Without Graphite

TiN, 180 W, 150 V Bias, 20 sccm Ar, 5.0 sccm N, 300 C, 35% H, 440C Substrate, 200 rpm, 1N

Deposition Group: C
Position: 1
Percent Coverage: 2.5%
S 213, TiN, 3um Nominal Reservoirs, Alumina Counterface
25% H, 440C Substrate, 200 rpm, 1N

Deposition Group: D
Position: 2
Percent Coverage: 2.5%

-Lubrication
-Graphite Lubrication
S 214, TiN, 3um Nominal Reservoirs, Alumina Counterface
25% H, 440C Substrate, 200 rpm, 1N

Deposition Group: E
Position: 2
Percent Coverage: 6.4%
S 215, TiN, 3um Nominal Reservoirs, Alumina Counterface
35% H, 440C Substrate, 200 rpm, 1N

Deposition Group: C
Position: 2
Percent Coverage: 5.7%

- S215A No Lubrication
- S215B 2% Graphite Lubrication
S 216, TiN, 3um Nominal Reservoirs, Alumina Counterface
25% H, 440C Substrate, 200 rpm, 1N

Deposition Group: E
Position: 3
Percent Coverage: 3.9%
S 217, TiN, 3um Nominal Reservoirs, Alumina Counterface
58% H, 440C Substrate, 200 rpm, 1N

Deposition Group: D
Position: 3
Percent Coverage: 6.1%

Deposition Group: D
Position: 3
Percent Coverage: 6.1%

Deposition Group: D
Position: 3
Percent Coverage: 6.1%
S 220, TiN, No Reservoirs, Alumina Counterface
25% H, 440C Substrate, 200 rpm, 1N

Deposition Group: D
Position: 1
Percent Coverage: None
Deposition Group: F
Position: 1
Percent Coverage: 7.5%

S 232, TiN, 3um Nominal Reservoirs, Alumina Counterface
25% H, 440C Substrate, 200 rpm, 1N

- S232 A No Lubrication
- S232 B 2% Graphite Lubrication
S 233, TiN, 3um Nominal Reservoirs, Alumina Counterface
25% H, 440C Substrate, 200 rpm, 1N

Deposition Group: F
Position: 2
Percent Coverage: 9.8%
S 234, TiN, 3um Nominal Reservoirs, Alumina Counterface
25% H, 440C Substrate, 200 rpm, 1N

Deposition Group: F
Position: 3
Percent Coverage: 14.1%

---

Graph showing cycles vs. lubrication conditions:
- S234 B No Lubrication
- S234 C 2% Graphite Lubrication
S 234, TiN, 3um Nominal Reservoirs, Alumina Counterface
25% H, 440C Substrate, 200 rpm, 1N

Deposition Group: F
Position: 3
Percent Coverage: 14.1%
S 242, No Carrier Water, TiN, 3um Nominal Reservoirs, Alumina Counterface

25% H, 440C Substrate, 200 rpm, 1N

Deposition Group: G
Position: 1
Percent Coverage: 4.1%
S 243, Low Carrier Water, TiN, 3um Nominal Reservoirs, Alumina Counterface
25% H, 440C Substrate, 200 rpm, 1N

Deposition Group: G
Position: 2
Percent Coverage: 5.1%
S 244, Re-lubricated, Low Carrier Water, TiN, 3μm Nominal Reservoirs, Alumina Counterface
25% H, 440C Substrate, 200 rpm, 1N

Deposition Group: G
Position: 3
Percent Coverage: 8.6%