SILVER TANTALATE: A HIGH TEMPERATURE TRIBOLOGICAL INVESTIGATION

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As technology advances, mechanical and electrical systems are subjugated to intense temperature fluctuations through their service life. Designing coatings that operate in extreme temperatures is, therefore, a continuing challenge within the tribology community. Silver tantalate was chosen for investigation at the atomic level, the physical and chemical properties that influence the thermal, mechanical, and tribological behavior for moving assemblies in high temperature tribological applications. By correlating behavior of internal physical processes to the macro tribological behavior, the tribological community will potentially gain improved predicative performance of solid lubricants in future investigations.

Three different approaches were explored for the creation of such materials on Inconel substrates: (1) powders produced using a solid state which were burnished on the surface; (2) monolithic silver tantalate thin films deposited by magnetron sputtering; and, (3) an adaptive tantalum nitride/silver nanocomposite sputter-deposited coating that forms a lubricious silver tantalate oxide on its surface when operated at elevated temperatures. Dry sliding wear tests of the coatings against Si$_3$N$_4$ counterfaces revealed friction coefficients in the 0.06 - 0.15 range at T ~ 750 °C. Reduced friction coefficients were found in nanocomposite materials that contained primarily a AgTaO$_3$ phase with a small amount of segregated Ag phase, as suggested by structural characterization using X-ray diffraction. The presence of nanoparticles of segregated Ag in the thin films further enhanced the performance of these materials by increasing their toughness.
Additional characterization of the AgTaO₃ films at 750 °C under normal loads of 1, 2, 5, or 10 N revealed that the friction monotonically increased as the load was increased. These results were complemented by molecular dynamics simulations, which confirmed the increase of friction with load. Further, the simulations support the hypothesis that this trend can be explained in terms of decreased presence of Ag clusters near the sliding surface and the associated decreased porosity. The results suggest that the relative amount of Ag in a TaN or Ta₂O₅ matrix may be used to tune film performance for a given application.
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CHAPTER 1
INTRODUCTION

Historically, humans have used multiple innovations to reduce the amount of work required to perform a specific task. Rolling logs evolved into the wheel facilitating a cart system. Pulleys enabled a more efficient way to apply force. Regardless of the application, friction has always been the bane of mankind’s efficiency. While this problem continued to manifest itself, only a handful of studies looked at the nature of friction prior to the industrial revolution. These investigations lead to the establishment of some basic relationships of interacting forces between surfaces. Friction, however, is not a fundamental force; it is the combined response of different physical processes which requires empirical data to build from.

With the onset of the Industrial Revolution, machinists were creating industrial tools to run 24/7 to enable optimal production. These machines, however, required an efficient, long-lasting lubrication systems to enable sustained production. Over the next century and a half, factories and machines were increasing in number and size, and the cost of running factories was increasing [1]. Because of this, lubrication specialists were needed to facilitate efficiency. New lubrication and wear reducing schemes were designed that often required complicated systems of pumps, seals, high pressures, etc. Lubrication schemes, however, remained a secondary, independent consideration and design flaws continually led to a loss of productivity.

In 1964, the increasing costs associated with the failure rates of industrial plants at an international scale due to wear and associated causes gained the attention of the scientific community [1]. An 18 month study was commissioned by the United
Kingdom’s Department of Education and Science to establish how prevalent, pervasive and detrimental the costs of breakage, corrosion, and wear were to industry. The findings suggested the implementation of preventive methods to increase continued efficiency in the factory setting [2]. This report (now known as the Jost Report after the chairman leading the study) calculated a direct 2-5% loss of the gross domestic product (GDP) among industrialized nations at the time. Some estimates upwards of 10% were suggested when secondary/indirect costs are considered from the lack of good tribological implementation. Currently, in 2009, conservative estimates put $100 billion lost to tribology in the US alone [3]. The recommendation of the report was to treat tribology as a multi-disciplinary field, improved education, and the creation of a comprehensive reference handbook for the industrial community [4, 5]. Through the incorporation, numerous fields including mechanical engineering, material science, chemistry and physics, substantial advancements have been made in the understanding of tribological phenomena [4].

While friction, adhesion, lubrication and wear correspond to physically different characteristics, a holistic approach was created because they are ultimately inseparable. Before motion occurs between contacting surfaces, static friction and adhesion are the dominant physical mechanisms at work. Microadhesion between two surfaces significantly contributes to the friction of the system and, if the adhesion between parts is drastic enough, cold welding can occur [5]. Breaking this weld can tear material from the contact surfaces producing wear and, in extreme cases, cause catastrophic failure of the component. Adhesive tearing, surface deformation, lubricant removal (plowing) of material, and contamination will contribute to abrasive wear of the
components [6]. If enough wear occurs, frictional coefficients increase due to hertzian stresses at the surface [7]. While lubricants are applied to reduce friction, adhesion, and wear, some friction is required for mechanical motion. The intercalation of a third body commonly works by allowing easy shearing of the third body in reference to the other surfaces. Lubrication regimes are usually divided into fluid film lubrication and solid film lubrication.

Historically, most lubrication schemes have used liquid lubricants for friction reduction. Liquid lubricants are useful in industry because they are easy to procure, produce low coefficients of friction, and insure little to no wear and adhesion [8]. There are, however, limitations to their use. Greases and oils are viscous at low temperatures but fail at high temperature due to oxidation, decomposition, and vaporization. Liquid lubricants are also susceptible to low pressure vaporization and radiation degradation. Therefore, they lose functionality and contaminate the surroundings in these diverse conditions [8]. Not only are solid lubricants more resistant to the aforementioned issues, but also simplify system and component design while reducing weight. These properties are desirable in the aeronautical industry because of decreased fuel consumption and environmental impact. Solid lubricants also lend to an increase in productivity due to reduced service maintenance time and material sustainability leading to higher mission success [8].

Solid lubricants are used to reduce friction and wear between rubbing surfaces when service environments are extreme [9]. It is well established that high temperature working environments are still a major challenge for the tribology community. As technology advances, mechanical and electrical systems are subjugated to intense
temperature fluctuations through their service life. Designing coatings that operate in extreme temperatures is, therefore, a continuing challenge within the tribology community. To improve future coating designs, this research investigates at the atomic level, the physical and chemical properties that influence the thermal, mechanical, and tribological behavior of ternary oxides. By understanding the mechanisms that enhance the lubricity of these materials at these temperatures, improved predictive performance of solid lubricants in future investigations is possible.

For the purpose of this study, silver tantalate (AgTaO$_3$) was selected as a lubricious material for moving assemblies at high temperature. Three methods were used to create silver tantalate surfaces in the current work. Firstly, silver tantalate powders were produced using solid state synthesis [10]. These powders were subsequently burnished on a flat substrate and their structural, morphological, and chemical properties of the modified surfaces were thoroughly characterized using a variety of techniques. Powders could also be used to reduce friction when applied on textured surfaces as was shown for silver vanadate powders [11]. Additionally, the powders were used to generate reference Raman data to help analyze future thin film coatings.

Secondly, silver tantalate coatings were manufactured by reactive magnetron sputtering in an oxygen environment using silver and tantalum as source materials. The deposition conditions were optimized to produce AgTaO$_3$ coatings, to compare stoichiometric coatings through wear testing as a function of temperature. Single phase AgTaO$_3$ coatings were also produced to further examine their tribological behavior as a function of temperature and load. Surface, bulk, and cross sectional characterization
was also performed to establish morphological responses to heating and wear testing. These results were then compared to molecular dynamic (MD) simulations to better understand the mechanisms that lead to enhanced lubricity. Coatings of tantalum oxide with silver inclusions were then produced to further inspect the morphological response of the constituent materials of the AgTaO₃ coating. The properties of these coatings were also compared to MD simulations to further characterize the coatings. The MD simulation analysis of AgTaO₃ with the supporting experimentation, can possibly help predict coatings behaviors before experimentation begins.

Finally, two-phase TaN/Ag adaptive coatings were deposited by magnetron sputtering in a N₂ environment as a “chameleon” coating to expand the coatings’ working conditions to reduce friction in a wider temperature range [12]. These adaptive coatings are a class of smart materials that adjust their surface chemical composition and structure as a function of changes in the working environment to minimize friction coefficient and wear between contact surfaces.
CHAPTER 2
SOLID LUBRICANTS, OXIDES AND SILVER TANTALATE

Solid lubricants that have been reported in the literature as well as used in industry when the temperature exceeds ~ 300 °C include noble metals, alkaline halides, Magnéli phases, and ternary oxides (also termed binary metal oxides) [13]. Solid lubricants that are commonly used at room temperature (graphite and molybdenum disulfide) cannot be used in open air at elevated temperatures (> ~ 400°C). Oxidation of these solid lubricants, has hampered their use at elevated [14].

Ternary oxides were recently shown to exhibit extremely low friction coefficients (0.1 - 0.3) when tested at T > 400 °C [15-19]. Examples of ternary oxides that have been recently investigated include silver and copper molybdates [6-8], silver vanadates [9], and silver niobates [10]. These oxides thoroughly examined due to their production from tribo-chemical interactions that occurred from the temperature dependent wear testing that occurred of composite coatings. These studies led to the premise that silver tantalate should have good tribological behavior at increased temperature and should be addressed.

2.1 Solid Lubricants

Like oils and greases, solid lubricants provide friction reduction by shearing at the interface [20]. The friction reducing properties of graphite and molybdenum disulfide (MoS₂) have been known for centuries [21]. The intrinsic or extrinsic properties leading to shearing of the materials, however, was not discovered until the past century [22].
and other characteristics accommodate shearing [23].

Crystal structure considerations when exploring solid lubricants focuses on bond strengths and anisotropic unit cells [23]. Prime examples of this are the crystal structure of molybdenum disulfide and graphite which have a hexagonal-layered lattice crystal structure. This specific crystal structure possesses Van der Waals bonds between basal planes. These bonds are much weaker than the covalent bonds within the layers (Figure 2.1) [24, 25]. The breaking of the Van der Waals bonds allows the slipping of the layers across each other. MoS2, graphite, and other transitional-metal dichalcogenides are excellent room temperature to mid-temperature (300 °C) solid lubricants because of this lamellar crystal structure [20]. Their soft nature, however, lends to quick wear and their relatively low oxidation temperatures (T<350 °C) reduces stability [24]. High temperature operations of machines are of a major concern for tribologists as these traditional lubricants do not deliver the required performance for these systems.

*Figure. 2.1:* The crystal structure of MoS2 and graphite showing the weaker Van der Waals bonds within the layered structure [26, 27].
2.2 Soft Metals

Mechanically soft coatings are metals (Ag, Au, Cu, Pb, In, Ni) which intrinsically have low shear strengths because of their ductile, soft nature. Soft metals also have high thermal conductivity and are chemically relatively inert [28-31]. The high thermal conductivity improves tribological behavior by allowing heat dispersion at the interface. Chemical inertness provides a stable lubricant with limited environmental interaction and, therefore, is highly corrosive resistant [30].

One of the early developmental concerns with metallic coatings was adhesion. Delamination of the coating was common [32]. It was found that if the coating was too thick, micro-cutting occurs and the coating has a high wear rate [33]. When the coating is thin, breaking through the coating only takes a few cycles [34]. Soft metal coatings have been vastly improved by: (1) new methods of deposition (ion-plating, magnetron sputtering, plasma laser deposition, etc.), (2) using different adhesion layers between the coating, (3) varying coating thickness, and (4) the type the substrate used [29]. All of the parameters are different for each soft metal coating.

Lead and silver are two tribological soft metals. Silver coatings are better at producing a transfer film at the mating interface which provides lower friction by producing a silver against silver contact [30]. Lead coatings, on the other hand, have a low melting temperature (327 °C) compared to other soft metals used in tribology and undergoes surface oxidation [29]. PbO has the same lamellar crystal structure as graphite and the transitional-metal dichalcogenides yielding improved tribological behavior [20]. However, current solid lubricant materials considered so far possess an upper functional temperature limit of 1000 °C due to their low melting point [35].
2.3 Halides

Fluorides (CaF$_2$, BaF$_2$, and LiF) are good functional lubricants in the 450-700 °C temperature range [36, 37]. The main mechanism responsible for their good tribological properties at these temperatures is surpassing the brittle to ductile transition temperature, which causes a softening of the material. However, the temperature limit (above which they degrade rapidly) of these types of materials is typically on the order of 600 to 700 °C and upon cooling they usually become glassy and brittle thus no longer functional [36, 37].

2.4 Hard Coatings

Oxides, nitrides, and carbides are commonly used single and multi-phase hard coatings [38]. These coatings have high Vicker hardness (15-38 GPa) compared to steel (1-3 GPa). Because of this they also have a lower toughness than steel [28, 38]. They resist permanent deformation because of the rigidity of the crystal structure [39], but the low toughness associated with these coatings also allows for micro-fracturing which lowers their wear resistance [28].

Superhard coatings have a Vicker hardness greater than 40 GPa [40]. The most commonly known superhard materials are diamond and cubic boron nitride (c-BN) [38]. These materials are excellent for coating cutting tools. Diamond against diamond wear tests have shown a frictional coefficient of 0.02-0.05 under ambient conditions but increases under vacuum or at higher temperatures [41]. Diamond like carbon (DLC) is a commonly explored hard, tribological coating. It is coveted for its high hardness (30-50 GPa), low friction in vacuum, high elasticity, and chemical inertness [42]. While the
friction and wear behavior of c-BN was relatively unknown prior to 1995 because of its poor adhesion to substrates [43], boron nitride has been found to have a hardness second only to DLC and diamond while exhibiting high thermal conductivity and low thermal expansion [44].

2.5 Nanocomposites

Nanocomposites are isotropic unions of distinctly different components. They consist of nano-crystallites that are usually either embedded in an amorphous matrix (Figure 2.2) or two different crystallites that are in contact with each other [45, 46]. These nanocomposites derive their higher strength from grain boundaries which can “control dislocation formation and the elastic modulus mismatch between components ... (which can) be used to inhibit dislocation mobility” [47]. This is different from alloying where the addition of another element is introduced to harden and strengthen the original material. This fortification is due to the replacement of the atoms within the crystal structure (if the introduced atoms are approximately the same size) or the inclusion of additional atoms within interstitial sites between the host atoms in the crystal (if the additional materials atoms are small relative to the host) [48]. This causes distortions in the crystal system thereby decreasing slippage in the crystal lattice [46].

In addition to producing a nanocomposite to increase toughness and hardness, the inclusion of solid lubricants in the matrix can reduce friction at the interface by revealing pockets of fresh solid lubricants as the surface is worn. Nanocomposites consisting of nitrides and carbides within an amorphous carbon matrix have been extensively studied and were found to be effective friction and wear reducing materials
2.6 Chameleon Coatings

Chameleon coatings are nanocomposites that change their surface chemistry and structure to provide an advantageous coating for the environment encountered (usually through tribochemistry) [18]. First proposed by Donley and Zabinski in 1992 [50], chameleon coatings incorporate multiple phases where tribological interactions between each other and the environment produce lubricious coatings that operate in a variety of conditions [47]. Chameleon coatings are not limited to being a subset of nanocomposites. Nanocomposites are, however, the most widely studied variety.

Multi-compositional overlayers during examination can suffer and/or benefit from tribochemical, tribomechanical, oxidation, diffusion or thermally driven chemical reactions when subjugated to fluctuating environment [47, 51, 52]. These interactions and reactions can be very complex and difficult to separate. Oxidation and chemical reactions, however, are of great interest as they can provide a new component in the
coating at high temperatures potentially providing a beneficial phase. At temperatures in the 500-1000 °C range, oxidation is almost unavoidable. Therefore, the formation of a lubricious oxide seems to be the simplest approach to extending the service temperature range. One example of a chameleon coating that has shown excellent results is WC/DLC/WS₂ [53, 54]. This nanocomposite was successfully cycled between humid and dry nitrogen multiple times. While this composite was not designed to work in environments that require fluctuating temperatures, experimental results show an expansion of the working range compared to conventional solid lubricants.

However, there remains limitations to the range of environments these materials are suited for as most conventional solid lubricants will oxidize at temperatures above 350 °C [24]. Solid lubricant composites were first studied to find temperature dependent, synergistic interactions between the compounds for adaptive coatings [47]. Donley and Zabinski’s study of PbO-MoS₂ showed that an increase in temperature causes an oxidation reaction producing lubricious phases (PbMoO₄ and MoO₃) for the higher temperature range [47, 55, 56].

Coatings that consist of silver and molybdenum disulfide lubricious phases in addition to hard phases (Mo₂N, yttria-stabilized zirconia (YSZ), etc.), have been previously studied to expand the temperature range of traditional tribological materials [15, 17-19]. The Mo₂N/MoS₂/Ag chameleon coating, for example, displayed a coefficient of friction (CoF) of 0.3 at 350 °C and 0.1 at 600 °C compared to a much higher CoF by a Mo₂N hard coating [18, 19]. This drop in CoF as the temperature increases is attributed to lubrication provided by silver and MoO₃ in mid-range temperatures (300-500°C) and to a chemical reaction between silver, molybdenum, and oxygen to produce
silver molybdates as temperature reaches 500°C. Additionally, the Mo₂N/MoS₂/Ag system maintained a CoF of 0.1 for 300,000 cycles at 600°C without failure of the coating [18]. The silver molybdates generated at the surface possess crystalline layered structures similar to that of MoS₂ and graphite [18]. Also, the melting temperatures of the silver molybdates are around 500°C [57-59], which is consistent with possible oxide softening [17, 60].

2.7 Tribochemistry

Tribochemistry is simply the creation or suppression of chemical interactions that occur due to the tribological processes and the materials at the interface. Because of friction between two surfaces, the temperature at the interface can be greater than the surroundings and can provide thermal energy. The reduction of a hard phase into an amorphous phase by the mechanical energy being dissipated by the breaking of the bonds in the surface material is an example of a tribochemical process. The heat and pressure at the tribological contact can be higher than the working temperature and cross the energy of formation boundary. This process produces species different from those in the bulk material [61]. Another chemical interaction can occur when atmospheric oxygen (or an oxygen donor species) and surface materials react producing an oxide [47, 61]. Oxidation of materials is unavoidable when high temperatures cause oxidation of the lubricious phases and subsequently increase the coefficient of friction. Some oxides, however, are lubricious at these higher temperatures and, as such, tribo-oxidation is one of the bases of the research being presented.
2.8 Oxides

Oxides exhibit an unparalleled spectrum of physical properties, which gives them the potential to be incorporated into next-generation devices used in optics, magnetism, and electronics [62]. These oxides may be used as effective solid lubricants that are applied between sliding surfaces that operate under extreme conditions [9]. Oxides are generally considered abrasive when studied at ambient temperatures. The work of Peterson and Magnéli, however, provided insight into the behavior of specific types of oxides at high temperatures [63]. Following the work of Peterson and Magnéli in the 1950s [64-66], investigations into oxides as high temperature solid lubricants were gaining interest in the early 90s. At the peak in interest of oxides as friction reducing agents, the need to study hard and ultra-hard transitional metal coatings for machining parts being used at high temperatures arose. At increased temperatures, these coatings had a reduced CoF due to tribo-oxidation [67].

Magnéli’s research into the structure of compounds of molybdenum and tungsten oxide found that there are structural defects associated with these compounds when they are substoichiometric. Magnéli phases have periodic defects of planar lattice faults and are usually found in compounds with formulas of the type $\text{Me}_n\text{O}_{2n-1}$, $\text{Me}_n\text{O}_{3n-1}$, or $\text{Me}_n\text{O}_{3n-2}$. Magnéli phase oxides exhibit shearing due to these defects which have reduced binding strength [68, 69]. Peterson performed a large scale survey of binary and ternary oxides against an Inconel alloy surface. In his studies, MoO$_3$ was found to provide a CoF $\approx$0.2 at 750 °C. He also found that oxides of VO$_x$, WO$_x$, and others similarly possessed low CoF at high temperatures [64-66]. Additionally, WO$_3$ has more than 11 different structures reported [52, 70].
In an attempt to explain the behavior of binary oxides, Erdemir’s crystal chemical model was developed [71]. Oxides can possess covalent, ionic or mixed bonding. Erdemir’s model shows a relation between ionic potential (the ratio of the cation-anion radius) where higher ionic potentials correlate to a decrease in melting temperature and a decrease in the CoF of these materials. From Figure 2.3 we can see that Re$_2$O$_7$, for example, is reported to have an ionic potential of 13.46 with a CoF of <0.2 while MgO has an ionic potential of 2.8 and a CoF at elevated temperatures of >0.7. The underlying mechanism responsible for this physical phenomenon/properties is that the greater ionic potential, the greater the screening of the cation by the surrounding anions [51, 71].

![Figure 2.3: Relationship between ionic potentials and average friction coefficients of various oxides [71].](image)

Recently, ad initio calculations were performed by Reeswinkel et al. [72, 73] to correlate Magnéli phase compositions to their mechanical properties. In addition to the many mechanical properties that they were able to predict, they found that Magnéli phases that possess distorted metal-oxygen octahedral structures resulted in larger
inter layer distances. These interlayers have weaker coupling as the distance increases and allow for easier plastic deformation [52].

Other non-exclusive mechanisms have also been reported to account for oxides’ ability to reduce friction. They are (1) oxide softening due to the working temperature being between 0.4 and 0.7 of the absolute melting temperature ($T_m$), which is the brittle-to-ductile transition for most oxides [57, 60], (2) melting of the oxide by exceeding $T_m$ [19], and (3) shearing in textured nanocrystalline grains due to dislocation glide resulting in intercrystalline slip [74, 75] [51, 63]. These hypotheses have yet to be rigorously tested and there has been very little discussion of the fundamental mechanisms that enable high temperature lubricity.

Ternary oxides are showing some promising results as an alternative to Magnéli phases for lubrication [18, 52]. Similar to how tribo-oxidation in ultra-hard coatings caused a renewed interest in binary oxides, ternary oxides became a research focus as adaptive coatings to extend the environmental range beyond that of monolithic coatings being investigated. Most early composite coatings mixed a binary oxide with a low temperature solid lubricant based upon the work of Zabinski et al. His preliminary work on PbO-MoS$_2$, which was found to produce PbMoO$_4$, extended the coatings performance to 1000 °C [55]. This range was further extended by others when ZnO-MoS$_2$ and –WS$_2$ were combined to produce ZnMoO$_4$ and ZnWO$_4$ which were also associated with reduced friction at higher temperatures [52, 76].
Ternary oxides were also formed from composites consisting of a soft metal and a transition metal nitride. A number of studies have been performed utilizing different combinations to investigate the performance of these composites. Most notably to this research, is the transition metal nitrides that are combined with silver. “Silver has several desirable properties: (1) it is a soft metal with an easy shear which can effectively lubricate at moderate temperatures (300-500 °C)…; (2) Ag-O bonds are relatively weak, as compared to transitional metal oxides, and when incorporated in a ternary oxide crystal structure enhance shearing of crystal planes and lowering melting point of the original binary metal oxide; (3) elemental Ag does not oxidize readily and would significantly enhance tribological properties of the surrounding oxide phases by providing ductility and enhanced toughness; and (4) Ag is environmentally benign for coating manufacturing.” [52].

*Figure 2.4: Crystal structure of Ag₃VO₄.*

Composite tribological coatings of silver and nitrides of the transition metals from column VB and VIB were tested as composites to work as a chameleon coating. The hypothesis was that, at elevated temperatures, a ternary oxide would be tribochemically produced on the surface. Most of these compounds produce more than one oxide and investigation into which are beneficial or detrimental was done. Previous studies on VN/Ag and NbN/Ag produced the ternary oxides of Ag₃VO₄, AgVO₃, and AgNbO₃ [11, 35, 63, 77]. Understanding the mechanisms that cause friction reduction by these
materials is paramount to creating coatings for high temperature friction reduction. The VN/Ag system produced a CoF at 750 °C of 0.1 which was attributed to the formation of Ag3VO4 and the suppression of AgVO3 in the wear track. This was determined by in situ Raman wear testing, temperature dependent XRD, and EDX. Raman spectroscopy revealed the formation of AgVO3 from Ag3VO4 in the wear track during heating. The formation of AgVO3, however, is speculated to be suppressed by the wear process. Only the Ag3VO4 and VO2 phases remained in the wear track. The Ag3VO4 is attributed with the reduced friction at high temperatures due to its melting temperature and its crystal structure (Figure 2.4). The speculated segregation of the coating above 450 °C cannot be confirmed by in situ Raman due to silver not being Raman active. Peaks of silver vanadate were also not apparent until cooling of the VN/Ag coating after being heated to 900 °C in the in situ XRD scan [63]. Ag3VO4 has a melting temperature of 450 °C. Therefore, its high temperature behavior is not conducive to application into systems running at 1000 °C [11, 35, 63, 78].

For the NbN/Ag coating, XRD after wear testing at 750 °C confirmed the formation of AgNbO3 in the coating. The NbN/Ag coating had an average CoF at RT of 0.35 with a successive decrease to 0.30 and 0.27 at 350 °C and 750 °C, respectively. A slight increase in the CoF occurred when the coating was wear-tested at 1000°C. The NbN/Ag coating, however, also produced AgO3 and Nb2O5 and in situ Raman confirms the creation of silver niobate and niobium oxides. AgO3 was also not apparent in the Raman spectroscopy for the niobium coating. The presence of Nb2O5 is speculated to be suppressed in the wear track due to sliding for the NbN/Ag coating or increased formation of AgNbO3 [63].
Ternary oxides formed from Mo$_2$N/MoS$_2$/Ag and WN/WS$_2$/Ag that produce Ag$_2$Mo$_2$O$_7$ and Ag$_2$WO$_4$ were also studied. Coatings of MoN and WN with the inclusion of silver [15, 17-19] were tested at 600 °C. They had different tribological responses and the coating with MoN had a better CoF than WN. These coatings produced Ag$_2$Mo$_2$O$_7$ and Ag$_2$WO$_4$ respectively. Evaluation of these oxides by wear testing showed that the oxides behaved the same as their composite equivalent. MD modeling attributed the difference in behavior to silver molybdate dynamically evolving to form Ag clusters at 527 °C while silver tungstate did not have any phase transformations of the crystal structure. This was confirmed by temperature dependent XRD and Raman analysis [58].

Ab initio molecular dynamics (AIMD), *in situ* XRD, *in situ* Raman, and tribological testing were used to explore the reasons for the superior tribological behavior of Ag$_2$Mo$_2$O$_7$ compared to Ag$_2$WO$_4$. Both oxides were chosen because they are the

*Figure 2.5: Crystal structure of Ag$_2$Mo$_2$O$_7$.*
tribochemical product of coatings consisting of group 6 transition metal nitrides with silver inclusions. The two oxides have different crystal structures. It was also found they have different melting temperatures and tribological performance.

The crystal structure of Ag$_2$WO$_4$ is tetrahedral WO$_4^{+2}$ with oxygen atoms linked to the surrounding Ag atoms. Alternatively, Ag$_2$Mo$_2$O$_7$ (Figure 2.5) consists of planar frame structures (Mo$_4$O$_{14}^{-4}$) consisting of four five-coordinated Mo (MoO$_5^{-}$) which are perpendicularly linked by -O-Ag-O- and -O-Ag-Ag-O-. The Ag$_2$Mo$_2$O$_7$, therefore, has a lamellar crystal structure similar to that of graphite and MoS$_2$. The melting temperature of Ag$_2$Mo$_2$O$_7$ (509 ± 1 °C) is also lower than Ag$_2$WO$_4$ (>600 °C) which is likely due to the weaker crystalline bonds in Ag$_2$Mo$_2$O$_7$ compared to Ag$_2$WO$_4$. In situ Raman and in situ XRD results agree with the phase transformation temperatures for Ag$_2$Mo$_2$O$_7$ and Ag$_2$WO$_4$. The AIMD calculations show that, unlike Ag$_2$WO$_4$ (which does not go through a phase change at 527 °C), Ag$_2$Mo$_2$O$_7$ will segregate into silver and MoO$_3$ which are both previously studied SLs [79, 80].

It was found that both Ag$_2$Mo$_2$O$_7$ and Ag$_2$WO$_4$ exhibit a decrease in friction from RT to 600 °C. However, the CoF of Ag$_2$Mo$_2$O$_7$ was lower at every temperature compared to Ag$_2$WO$_4$ and the total drop in the CoF for Ag$_2$Mo$_2$O$_7$ (0.25) was greater than that for Ag$_2$WO$_4$ (0.13). The largest drop in the frictional coefficient for Ag$_2$Mo$_2$O$_7$ was going from 450 to 600 °C (0.13) which straddles the phase transformation temperature. The CoF for Ag$_2$Mo$_2$O$_7$ was lower at high temperatures than those recorded for both Ag [80] and MoO$_3$ [79] suggesting that Ag and MoO$_3$ alone do not account for the performance of the Ag$_2$Mo$_2$O$_7$ coating. This study suggests that the drastic drop in friction from 450 to 600 °C was attributed to the segregation of silver.
molybdate into silver and molybdenum oxide. No such phase transformation was observed for silver tungstate.

Figure 2.6: Crystal structure of cubic perovskite, also representation of high temperature structure of AgTaO$_3$.

2.9 Perovskites

Discovered in 1839 by Gustav Rose, perovskites are a class of crystal structures with ABO$_3$ chemistry [62] which have largely been overlooked by the tribological community to date. The perovskite structure can accommodate by substitution some 30 elements on the A site and over half the periodic table on the B site [62]. Perovskites not only have a layered crystal system, but also have the ability to allow for alternating crystal layers and doping of the oxide. Materials in this crystal family can also have different melting temperatures, which can facilitate researching of their softening and melting temperatures. Collectively, the flexibility of the perovskite structural skeleton offers a great opportunity to create new materials with a variety of designed functionalities. Perovskite materials exhibit many interesting and useful properties that have received a great deal of attention from researchers in a variety of different topic areas. They are now commonly used as functional materials in laser technologies, integrated optics, telecommunication signal processing and others [81-83].
2.10 Silver Tantalate

Silver tantalate is a perovskite that has a relatively high melting temperature (1172 °C [10]) and it is a ternary oxide [79]. Silver tantalate undergoes a series of 5 structural phase transitions until 485°C where it hits the cubic phase which is stable until it’s melting point [10]. Its temperature-dependent material properties, including its mechanical and tribological response to sliding, are integrally related to these structural changes. Since it is known to preserve a cubic phase above 507 °C, it is ideal for modeling in high temperature simulations up to its melting temperature [84].

Silver tantalate can be produced by a solid state synthesis method similar to silver niobate from a mixture of Ag₂O and Ta₂O₅ or Nb₂O₅, respectively. However the formation Kinematics of silver tantalate is much slower than that of silver niobate. For the formation of these ternary oxides, the decomposition of Ag₂O into elemental silver before the final formation is required. Niobate can absorb elemental oxygen into the crystal structure through diffusion while tantalate does not have these oxygen transport channels. After decomposition of the Ag₂O in the process, 45% of the oxygen is trapped in the Nb₂O₅ bulk whereas the Ta₂O₅ showed no oxygen trapping. This suggests the possibility that upon decomposition of AgTaO₃, oxygen is not confined to the bulk. Elemental silver, therefore, will be produced instead of being trapped in the Nb₂O₅ lattice and be available for oxidation during wear tests [10].

Silver tantalate has not been widely investigated. Historically, this has been due to difficulties with its synthesis as a stoichiometric single-phase system and the relatively high cost of tantalum [85]. More recently, however, simple processing routes have been developed that involve conventional solid-state reaction and sintering [84].
Furthermore, while tantalum remains a relatively expensive material, its market price has decreased in recent years due to competition from other materials (ceramics, aluminum, niobium, etc.). Device miniaturization has also led to the need for less material in its most common applications [85]. The removal of these barriers encourages further research into the promising material properties and potential applications of silver tantalate.
EXPERIMENTAL PROCEDURE AND METHODOLOGY

Silver tantalate powders were synthesized using a solid state synthesis technique. In this technique, oxides of Ta$_2$O$_5$ and Ag$_2$O (Alfa Aesar, purity 99.993 and 99.995, respectively) were dried in a furnace for 2 h at 200 °C. Stoichiometric ratios were homogenized by mortar and pestle in denatured ethanol for 1.5 h then calcinated at 1050 °C and 1000 °C for 16 h in a quartz crucible to produce AgTaO$_3$ and Ag$_2$Ta$_4$O$_{11}$, respectively. The powders were then burnished on Inconel 718 substrates.

Oxide thin film coatings of silver tantalates were deposited on mechanically polished Inconel 718 substrates using an ATC 1500 unbalanced magnetron sputtering apparatus (AJA international, North Scituate, MA). The substrates were cleaned ultrasonically in acetone and methanol for 15 min, rinsed in nanopure deionized water, and dried using compressed nitrogen prior to insertion into the vacuum chamber. The system was evacuated to a base pressure below 10^{-4} Pa. Elemental targets (Ø = 5 cm) of Ta (99.98%), and Ag (99.997% purity) were acquired from Plasmaterials, Inc. (Livermore, CA) and used as the source material. Growth of the thin films was executed in a mixed atmosphere of Ar (99.999%) and O$_2$ (99.99%). The substrates were subsequently heated to a temperature of 550°C and held at a bias potential of -120 V while being rotated about their polar axis at a speed of 50 rpm. All depositions were carried out for 90 min. A thin Ta layer was deposited for the initial 5 min to enhance adhesion of the coating to the substrate. Average coating thicknesses (1.7 to 3.0 μm for

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$^1$ Part of this chapter was reproduced from: Stone DS: Tribological Investigation of Nanocomposite Thin Films of Transitional Metal Nitrides with Silver Inclusions. Carbondale: Southern Illinois University, Carbondale; 2011.
all samples) were measured using a Micro Photonics Inc. optical profilometer and corroborated by later measurements done by TEM. Other deposition conditions are listed in Table 3.1.

Composite coatings of tantalum oxide with 14 at.% Ag content were created employing the same elemental targets of Ta and Ag (power settings of 200 and 10 W, respectively), with a mixed atmosphere of Ar and O₂ (partial pressure 5.0 and 2.3 mTorr, respectively) for deposition. TaN/Ag coatings were fabricated using the same elemental targets of Ta and Ag described above. Growth of the thin films was executed in a mixed atmosphere of Ar (99.999%) and N₂ (99.99%) with a ratio of 5.0:0.5 mTorr for all coatings. The substrates were subsequently heated to a temperature of 300°C and held at a bias potential of -60 V while being rotated about their polar axis at a speed of 50 rpm. During deposition, the Ta target was kept at a fixed power of Pₜₐₐ = 200 W while the power to the Ag target (Pₐ₉) was varied to produce coatings with different stoichiometry. All depositions were carried out for 90 min. The films of AgTaO₃ and TaN/Ag were produced using different temperature parameters due to the difference in temperature of formation for the lubricious phases of silver tantalate and the formation of TaN phases.

Table 3.1 Power to the Ta (Pₜₐ) and Ag (Pₐ₉) sources, oxygen partial pressure, and elemental composition for selected tantalum oxide (S1) and silver tantalate (S2, S3, and S4) samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pₜₐ (W)</th>
<th>Pₐ₉ (W)</th>
<th>O₂ (mTorr)</th>
<th>Ag (at.%</th>
<th>Ta (at.%</th>
<th>O₂ (at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>60</td>
<td>0</td>
<td>1.0</td>
<td>0</td>
<td>30</td>
<td>70</td>
</tr>
<tr>
<td>S2</td>
<td>60</td>
<td>10</td>
<td>0.7</td>
<td>20</td>
<td>30</td>
<td>50</td>
</tr>
<tr>
<td>S3</td>
<td>60</td>
<td>18</td>
<td>1.5</td>
<td>20</td>
<td>20</td>
<td>58</td>
</tr>
<tr>
<td>S4</td>
<td>60</td>
<td>25</td>
<td>1.5</td>
<td>24</td>
<td>18</td>
<td>58</td>
</tr>
</tbody>
</table>
Friction and wear tribotesting of the materials was carried out using a Nanovea ball on disk tribotester (Micro Photonics Inc., Irving, CA). Wear tests at temperatures in the 25 to 750 °C range were performed in humid air (relative humidity of 60 ± 5%), and as a function of load of 1, 2, 5, 10 N (Under these conditions, the corresponding initial mean Hertzian contact stresses were 0.5, 0.6, 0.8, and 1.0 GPa, respectively,) at the 750 °C. All tests were performed at 3.33 Hz for 10,000 cycles, sliding speed of 0.11 m/s and a total sliding distance of 10 m unless otherwise noted. 6 mm diameter Si$_3$N$_4$ was selected as the counterface material since it is the material of choice in high temperature hybrid bearing assemblies [19].

The elemental and phase compositions for as deposited and after tribotesting inside and outside the wear track was determined using a Leybold Max 200 X-ray photoelectron spectroscopy (XPS) and using a Model 670xi scanning Auger nanoprobe (SAN). XRD patterns before and after tribotesting were acquired using a GBC MMA diffractometer equipped with a Cu Kα radiation source. XRD only measures the bulk material and therefore phase identification inside and outside of the wear tracks was evaluated using a Renishaw SPM micro-Raman system phase identification and a Thermo Scientific Nicolet Almega XR Raman spectrometer both utilizing 532 nm laser excitation. In addition, site selective cross-sectional transmission electron microscopy (TEM) studies inside wear tracks were performed with high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM), bright field TEM (BFTEM), energy dispersive X-ray spectroscopy (EDS), and selected area electron diffraction (SAED) using an FEI Tecnai G2 F20 S-twin TEM operated at 200 keV. Finally, site selective specimens compatible with 3D atom probe tomography (APT) were analyzed.
using a Cameca LEAP 3000X-HR™, operating at a specimen base temperature of 35 K
and equipped with a 10ps 532nm pulsed laser with a pulse frequency of 160kHz and a
pulse energy of 0.2-0.3 nJ. Site specific TEM and APT specimens were prepared using
a FEI Nova 200 NanoLab dual-beam focused ion beam (FIB) / scanning electron
microscope (SEM).

3.1 Solid State Synthesis

Solid state synthesis although possesses a diverse plethora of methods (melt, solution, oven and gas methods) for this research the method of choice has been a thermal method. The starting materials constituents are used in their solid state, no catalyst is applied, and thermal energy is the added to the materials causing a chemical reaction. This reaction requires a close and intimate contact is needed between the materials therefore grinding of the material together before thermal reactions takes place is needed. Usually for this method diffusion of the material into each other takes place before the final reaction producing the product of interest occurs.

3.2 Physical Vapor Deposition

Un-balanced magnetron sputtering is a physical vapor deposition technique by which pure material are used as a source, physically removed by a plasma to produce a gas of the removed materials which are then deposited on the substrate, either as is or after it has reacted with a gaseous species to form a secondary compound before attachment. Magnetron sputtering is a common method of deposition of tribological coatings because it allows for the production of mono coatings, nitrides, carbides,
oxides, layered, and nano-composites [86]. Compared to other methods of coating productions, it permits source material that cannot be thermally evaporated. Although magnetron sputtering is a line of sight process it creates even, scalable coatings while atomic layer deposition does have a high aspect ratio allowing for conformal coatings on complex three dimensional shapes, it is limited to small parts, coating are generally kept thin to due to time requirements and the starting material and after processing waste can be quite toxic. Pulsed Laser Deposition has difficulties with even coatings due to droplet formation from the high kinetic rate of deposition [87], while electroplating is cost effective, it suffers from limit to the materials available for deposit and toxicity of the solutions.

Magnetron sputtering is a multi-parameter, multi-step process that allows control of the growth of coatings. Initially, the system is evacuated to a base pressure of <10⁻⁴ Pa to void the processing chamber of any gaseous impurities to reduce contamination of the product. Once a high vacuum state is attained, high purity Ar gas is introduced to the system, and a potential difference (bias) between the top and bottom of the system is applied to ionize the Ar. The Ar is maintained at a pressure of 0.2 to 4.0 Pa depending on the processing parameters desired, whilst the bias is increased or decreased to control ion energies. For etching the substrate, higher pressures and higher bias are used to provide more ions to the system to increase sputtering yield, while during deposition lower pressures and lower bias are used. The sputtered material yield is decreased due to less ion bombardment, but the amount of material transferred to the substrate is greater due to lower incident collisions with the Ar gas with the target. Application of a negative RF or DC voltage (300-500 V) [depending on the targets’
conductivity] to the target surface initiates positive ion bombardment causing sputtering (Figure 3.1 (a)). The substrate is RF biased to (1) use the stripped electrons to sustain the plasma by ionizing the neutral sputtering atoms, and (2) to control the deposition conditions at the substrate (Figure 3.1(b)).

During this process, the ions in the plasma are accelerated towards the target. If there is more kinetic energy than the binding energy at the lattice site, a “collision cascade” can occur where energy is distributed to the nearest neighbors in the target [86]. These collisions can redirect some of the momentum back to a surface atom. If there is enough energy, an ejection of the atom will occur (i.e. sputter) as represented in Figure 3.1(a). The accelerated ions striking the target also produce secondary electron ejections which further ionizes the gas through electron-atom collisions [89].

With a standard DC diode sputtering configuration, too many secondary electrons are accelerated away from the cathode thereby reducing ionization near the target. To increase the yield of ions for sputtering, a magnetic field can be applied around the cathode to redirect the electrons to the target surface and create plasma
confinement [88]. This field, however, hinders the use of the plasma for surface modification at the substrate. Unbalanced magnetron sputtering changes the geometry of the magnetic field lines to create a stronger magnetic field on the outside edge relative to the center. This process extends the plasma outwards from the target, as seen in Figure 3.1(b). The sputtered atoms are focalized in this configuration and rotation of the substrate is necessary to obtain a consistent coating over the entire substrate surface.

Reactive sputtering is the introduction of a gas, such as oxygen or nitrogen during coating processing. This allows for a reaction with the sputtered material as it travels towards the substrate. In turn, this method produces a compound species for deposition on the substrate [90].

3.3 Wear Testing

Testing the frictional behavior of a coating is done by applying a load (P) normal to the surface film while sliding the load tangentially and measuring the resultant tangential force (F) on the stationary counterface. The ratio F/P gives the frictional coefficient constant for the material being tested.
Figure 3.2: Nanovea ball-on-disk wear tester.

The Nanovea tribotester is a ball on disk configuration (Figure 3.2), that consists of a plate that rotates relative to a ball which is held by an arm with an internal capacitor (load sensor). As the sample moves, a deflection in the arm occurs. The arm deflection (recorded in voltage) is indicative of the tangential force: Higher voltages correspond to larger friction coefficients. This ball on disk configuration is, for experimental testing of coatings, the most common method for wear testing.

3.4 X-Ray Diffraction Measurements

X-ray diffraction (XRD) is a non-destructive method for measuring structure in bulk materials and can also provide information about the preferred crystalline orientation and grain size. Since different compounds will have different XRD patterns, a database of XRD patterns can be utilized to identify different species in the coating. This testing method is very useful as over 300,000 characterizations have been classified to date (see International Centre for Diffraction Data). This database was utilized in all classifications of our coatings.
XRD probes the samples crystal structure by constraining a beam of monochromatic X-rays at the surface and measuring the angle of incident in relation to the angle of the scattered X-rays. If the atoms’ repeat spacing (lattice spacing) is of the same order of magnitude as the incident beam wavelength, then constructive interference will occur (Figure 3.3). Since the spacing between the planes has to be an integral number of the wavelength for the requirements for construction interference to be met, the use of Bragg’s law:

\[ n\lambda = 2d_{hkl}\sin\theta_{hkl} \]  

allows for the calculation of the interplaner spacing. Here, \( n \) is an integer, \( \lambda \) is the wavelength of the incident wave, \( d_{hkl} \) is the interplaner spacing, and \( \theta_{hkl} \) is the Bragg angle [91]. The interplanar spacing and the Bragg angle are a function of the Miller indices (h k l) of the crystal lattice.

\[ g = k\lambda (\beta \cos \Theta)^{-1} \]  

where \( \lambda \) is the incident wavelength of the X-ray and \( \Theta \) is the Bragg angle. The value of \( k \)

Figure 3.3: X-ray diffraction.
are usually taken to be 0.9-1 and are dependent on the shape of the grains, $\beta$ is the half-width, half-Maximum (HWHM) value of the strongest, low angle peak in the diffraction pattern, and $g$ is the grain size. The broader the peak, the smaller the grain size. This is due to coherent scattering of the incident ray from the size of the domains (the boundary between the crystallites where the crystal lattice starts and stops), thereby broadening the peak [92]. However, $k$ are based on the crystallographic indices of the plane being observed, the beam size, and the shape of the grains. These values usually are between 0.9-1.0, 0.94 is most commonly used modeling a spherical particle, cubic symmetry and a Gaussian distribution of the peak, however they can range from 0.7 and 1.7 when dealing with real particles, therefore the accuracy of the formula should be used as only an approximation.

3.5 Raman Spectroscopy

Raman spectroscopy can provide information on the bonding structure and the elemental composition of the material under investigation. If previous Raman scattering measurements have been performed of a known substance, then it’s Raman signature can be used to identify the composition of an unknown substance [93]. Unlike XRD which measures the bulk of the material, Raman spectroscopy measures the coating’s surface composition. Raman is limited, however, as the largest database available for characterization contains only 11,000 entries from Sigma-Aldrich.

A laser with a wavelength between 400 and 1000 nm is focused at a substance and the scattered light is collected. The collected light is passed through a monochromator and then filtered (removing the Rayleigh scattering). The remaining
light is received by a sensor system comprised of either an interferometer and a FT program or a dispersive spectrometer and a charged coupled device detector. 

Raman works on the principle of inelastic scattering of monochromatic light by the atoms in a molecule. Monochromatic light interacts with the molecule and can either (1) polarize the electron cloud in the molecule or (2) induce nuclear motion. Both interactions create a higher, unstable energy state (Figure 3.4). The re-radiated photon in electron

Figure 3.4: Diagram of Rayleigh and Raman scattering. Stokes scattering (inelastic) involves the absorption of energy from a photon by the nucleus in the molecule. Rayleigh scattering (elastic) is the polarization of the electron cloud by the incident photon, but little to no energy is lost in the interaction. Polarization will have energy values close to the energy of the incident light.[94] This elastic scattering (also known as Rayleigh scattering) is not used in Raman spectroscopy and is removed from data recorded from the vibrational response. Inelastic scattering (also known as Stokes and anti-Stoke scattering) is the result of

34
inducing nuclear motion in the molecule by the transfer of energy from the incident light to the molecule (stokes) or vice versa (anti-stokes). In Stokes scattering, energy transfer from the photon to the molecular bond will cause the scattered photon to have a longer wavelength. The energy difference between the incident and scattered photon is the energy required to activate the normal mode vibrations. This energy is dependent on the size of the atoms and the strength of the bonds [93, 94].

**Figure 3.5:** Diagram of in situ Raman wear tester [95].

### 3.6 Optical Profilometry

Optical profilometry is used to measure the thickness of the coating. Nanovea ST 400 non-contact optical profilometer (Figure 3.6) uses white light and chromatic aberration to measure the distance from the sensor to the surface and has an accuracy of ~10 nanometers. White light is passed through an objective lens with a high degree of chromatic aberration. Depending on the distance from the focal length, a monochromatic wave will refocus due to the confocal configuration. The wavelength of
the monochromatic light will predominately pass through a spatial filter set at the focal point. A diffraction grating splits the light that passes through the spatial filter to a series of charge-coupled devices which measure the location of the greatest intensity in the diffraction pattern. This location is directly related to the divergence of the dominant wavelength and, therefore, directly corresponds to the vertical height position. If several measurements are made across the surface of a sample, a topological map can be created [96, 97]. Film thicknesses for the double-metal oxides (Ag₂Mo₂O₇ and Ag₂WO₄) and the VN/Ag coatings are listed in Tables I and II, respectively [58].

Figure 3.6: Nanovea optical profilometer.

3.7 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) provides information on surface contamination and surface composition. A linear XPS scan can provide a surface profile and, with ion etching between scans, a depth profile can be obtained. XPS identifies the elemental and chemical states by measuring the energy of photoelectrons emitted from the core shells of the atoms on the surface (1-10 nm) by bombarding the surface with X-
ray photons of known energy (Figure 3.7). The photoelectric equation is:

\[
E_{\text{kin}} = h\nu - E_B - \Phi_s
\]

(3)

where \( h\nu \) is the energy of the incident X-ray, \( E_B \) is the binding energy of the electron in the matter, \( \Phi_s \) is the work function of the equipment (not the metal), and \( E_{\text{kin}} \) is the measured energy of the emitted electron. By knowing \( h\nu \) and \( E_{\text{kin}} \), it is easy to calculate \( E_B \) which is a sensitive characteristic of each element [98].

![Photoelectric effect](image)

*Figure 3.7: Photoelectric effect [99].*

Shifts in the elemental binding energy result from changes in the potential due to valence electrons interacting with other nearby atoms. It can also provide information on the bonding. The greater the displacement from the nucleus of the electron charges, the higher the binding energies of the core electrons [100].

3.8 Focus Ion Beam – Scanning Electron Microscopy

Focus ion beam – scanning electron microscopy (FIB-SEM) is a characterization technique that combines the high magnification microscope of the SEM with the milling, ablating nature of Ga ions to image or sputter the surface. The system has two beams
(an electron beam and an Ga ion beam) which are used in tandem to characterize the topography of the sample, while having the capacity to mill cut-outs so that characterization of the cross sectional material can be accomplished. Most FIB-SEM systems are also equipped with an electron dispersive X-ray spectroscopy (EDS) system. This allows for the characterization of the elemental composition of the material by the bombardment of the material by the electrons from the SEM causing an inner core electron excitement to be emitted out of the atom. Then a higher shell electron drops down to fill the inner shell releasing a high energy photon (X-ray) which is measured by a spectrometer.

3.9 Transmission Electron Microscopy

Transmission electron microscopy (TEM) characterizes a sample by using a thin sample (usually produced by FIB-SEM). TEM works by directing a beam of electrons from a gun that are directed at thin (<10nm) sample with a specific energy. The electrons interact with the sample material and generates a diffraction pattern if the material is polycrystalline or crystalline material. Additionally, images of the material can be obtained using bright field TEM (BFTEM). The electrons are transmitted through the sample and interaction with the sample the three dimensional interactions are compressed into a 2 dimensional image. Depending on the elemental composition of the material that the electrons are interacting within the sample, determines how many electrons pass through a given location. Depending on the Z number of the elements, the contrast of the image will change (Z-contrast). Higher Z numbers will have darker areas where as lower Z number elements will produce brighter areas. Z-contrast is used
in conjunction with high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) to capture the elastically scattering electrons. The higher the mass of the interacting atom, the higher the angle that the electron will be scattered at. The characterization technique allows to differentiate the different elements within a thin, cross sectional cut out of the sample.

3.10 Atomic Probe Tomography

Atomic probe tomography (APT) combines either a sharp tip (<100 nm) that a high voltage is applied in a site specific manner between it and the sample, or a laser that is pulsed, thus vaporizing the atoms at that location. The vaporized ions from the surface are then measured by a time-of-flight mass spectrometer. [101, 102] By rastering the laser or using an array of tips, a two dimensional picture of the surface can be created while repetitive application to the same location a depth profile can be created, when combined a 3D image is created. The elemental distribution can be resolved at the atomic scale [101].
CHAPTER 4

RESULTS AND DISCUSSION

4.1 Solid State Synthesized: Powders of AgTaO$_3$ and Ag$_2$Ta$_4$O$_{11}$

To begin our investigation, powders of AgTaO$_3$ and Ag$_2$Ta$_4$O$_{11}$ were synthesized and analyzed to ascertain composition/crystallography data for these materials. Figure 4.1 shows (a) XRD patterns and (b) Raman spectra of the synthesized AgTaO$_3$ and Ag$_2$Ta$_4$O$_{11}$ powders. Graphs (i) and (ii) correspond to powders processed at 1050 °C and 1000 °C with different stoichiometries (conducive to the completed reaction) of the starting materials, respectively. XRD revealed that the powders processed at 1050 °C formed a pure monoclinic AgTaO$_3$ phase (PDF # 22-473) [84, 103-105]. Analysis of the XRD pattern of the powders processed at 1000 °C suggested that they consisted of Ag$_2$Ta$_4$O$_{11}$ (21-1345) and orthorhombic Ta$_2$O$_5$ (54-514, 25-922) phases (space groups Pmm2 (25) and Ibam (72), respectively) with no AgTaO$_3$ peaks. Limited data existed for the Raman response of the materials other than Ta$_2$O$_5$ and low range Raman (up to ~300 cm$^{-1}$) for AgTaO$_3$. Therefore, the materials produced by solid state synthesis were also used as reference for Raman analysis of the thin film coatings produced by

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magnetron sputtering. Burnished coatings for both types of powders were tribotested at different temperatures. Steady-state averaged coefficients of friction (CoFs) as a function of temperature are shown in Figure 4.2. The AgTaO$_3$ powders performed well, especially at high temperatures, with CoFs of 0.43, 0.32, 0.23, and 0.18 at 25, 350, 500, 725 °C.

Figure 4.1: (a) XRD patterns and (b) Raman Spectra for AgTaO$_3$ and Ag$_2$Ta$_4$O$_{11}$ powders processed at (i) 1050 °C and (ii) 1000 °C.

Figure 4.2: Steady state CoF for AgTaO$_3$ and Ag$_2$Ta$_4$O$_{11}$ powders as a function of temperature.
and 750 °C, respectively. The mixed Ag$_2$Ta$_4$O$_{11}$/Ta$_2$O$_5$ phase powders did not perform as well, especially at elevated temperatures, with measured CoFs of 0.76, 0.70, 0.58, and 0.53 at 25, 350, 500, and 750 °C, respectively. Additionally, the burnished powders did not last the entire 10,000 cycles and failed at all temperatures within the first 1500 cycles. No changes were seen in the XRD patterns of the synthesized powders after tribotesting at high temperatures (not shown in Figure 4.1). This suggests that the initial phases were stable. These preliminary results suggested that silver tantalate may be an ideal coating for further investigations as a solid lubricant.

4.2 Silver Tantalate Coatings

4.2.1 Mixed Phase Coatings

Mixed phase tantalum oxide and silver tantalate coatings were sputtered on Inconel substrates using the growth parameters listed in Table 1. A relatively high substrate temperature (550 °C) was selected to facilitate the formation of the tantalate phases that are hypothesized to be lubricious. Core level XPS spectra were recorded to determine the chemical and phase composition of the four sets of samples. The atomic concentrations of Ag, Ta, and O were estimated using the areas under the Ag3d, Ta4p, and O1s spectra and are summarized in Table 4.1.
Table 4.1 Power to the Ta (PTa) and Ag (PAg) sources, oxygen partial pressure, and elemental composition for selected tantalum oxide (S1) and silver tantalate (S2, S3, and S4) samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>P_{Ta} (W)</th>
<th>P_{Ag} (W)</th>
<th>O$_2$ (mTorr)</th>
<th>Ag (at.%)</th>
<th>Ta (at.%)</th>
<th>O$_2$ (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>60</td>
<td>0</td>
<td>1.0</td>
<td>0</td>
<td>30</td>
<td>70</td>
</tr>
<tr>
<td>S2</td>
<td>60</td>
<td>10</td>
<td>0.7</td>
<td>20</td>
<td>30</td>
<td>50</td>
</tr>
<tr>
<td>S3</td>
<td>60</td>
<td>18</td>
<td>1.5</td>
<td>20</td>
<td>20</td>
<td>58</td>
</tr>
<tr>
<td>S4</td>
<td>60</td>
<td>25</td>
<td>1.5</td>
<td>24</td>
<td>18</td>
<td>58</td>
</tr>
</tbody>
</table>

XRD patterns for coatings S2, S3, and S4 are shown in Figure 4.3. For coating S1 (P$_{Ag}$ = 0 W), the XRD data (not shown) suggested the growth of a pure Ta$_2$O$_5$ phase. The co-deposition of silver (P$_{Ag}$ = 10 W) and tantalum with relatively low oxygen partial pressures resulted in the formation of a three phase system, i.e. AgO, Ag$_2$O, and Ag$_2$Ta$_4$O$_{11}$ (S2). For P$_{Ag}$ = 18 W and with a relative increase in oxygen partial pressure to 1.5 mTorr, a Ag$_2$O/Ta$_2$O$_5$/Ag$_2$Ta$_4$O$_{11}$ three-phase system was formed (S3). Further

![XRD patterns](image.png)

*Figure 4.3: XRD patterns of selected silver tantalate coatings before (bottom) and after tribotesting at 750 °C (top).*
increase in the power to the Ag target ($P_{Ag} = 25\ \text{W}$) resulted in the formation of an Ag/AgTaO$_3$ two-phase system (S4). This S4 coating has a structure that is similar to the burnished AgTaO$_3$ powders that were calcinated at 1050 °C. XRD data recorded after tribotesting at 750 °C revealed that coatings S1 (not shown in Figure 4.3) and S4 did not change significantly as a result of tribotesting. The three phases that formed during the growth of S2 were found to react at high temperatures and form three phases: Ta$_2$O$_5$, Ag, and Ag$_2$Ta$_4$O$_{11}$. After testing at 750 °C, S3 consisted of Ag and AgTaO$_3$, which is similar to the stable phases that formed during the growth of S4.

The CoF of the coatings measured in the 25 to 750 °C range are shown in Figure 4.4. As expected, the CoF of the pure Ta$_2$O$_5$ phase (S1) was high (> 0.8) when tested at 25 °C and decreased to ~ 0.5 when the temperature was increased to 750 °C. A reduction in the CoF of binary oxides with temperature is expected due to softening that
occurs with the heating process [57]. S2 displayed relatively high CoF values, similar to
the ones recorded for S1 even though Ag was added to the recipe. However, S2 was
deposited using a relatively low oxygen partial pressure and a low $P_{Ag}$. A significant
enhancement in the performance of these coatings was observed with higher oxygen
partial pressures and higher silver contents (by increasing the power to the Ag sputter
target). For example, S4 displayed a CoF of 0.06 when tribotested at 750 °C, which is a
very low value at such a high temperature. S3 was also found to be lubricious with a
recorded CoF of 0.13 at 750 °C.

These results confirm that S4 is the most lubricious at 750 °C. We speculate that
the CoF for S4 is lower than that of the pure AgTaO$_3$ powders because of the presence
of segregated Ag in the sputter-deposited coatings. The synthesis of pure AgTaO$_3$ is
challenging among all silver-based perovskites owing to the requirement of high
sintering temperature, which is usually higher than the decomposition temperature of
the compound. Because of its optimal performance and stability, S4 was investigated
further in subsequent investigations.

4.2.2 Silver Tantalate (AgTaO$_3$) Further Characterization

To further understand the high temperature solid lubrication mechanisms of the
S4 coating, additional characterizations were performed and compared to simulations
executed by Professor Martini’s group at UC Merced. Experimentally measured values
were compared to frictional forces predicted in model simulation and graphed as
functions of temperature ranging from 27 to 750 °C in Figure 4.5. Both results coincide
displaying decreases in friction with increases in temperature culminating with minimal friction values at 750 °C. There is a discrepancy in magnitude of the frictional force because of inherent size-scale difference between the two techniques. The contact area in the model is at a nanometer scale while the experimental contact area is on the order of tens to hundreds of microns. Correspondingly, the applied loads also differ significantly between the model and experimental results since Newton-scale loads cannot be applied to a nanometer-scale contact. Similarities in friction trends and tribofilm evolution suggest that the simulation is indeed capturing the dominant mechanisms underlying the temperature-dependent friction of AgTaO₃.

Figure 4.5: Model predicted (black squares; left y-axis) and experimentally measured (red circles; right y-axis) friction force on AgTaO₃. Note that the units of force on the two y-axis differ by several order of magnitude displaying decreases in friction with increases in temperature culminating with minimal friction values at 750 °C. There is a discrepancy in magnitude of the frictional force because of inherent size-scale difference between the two techniques. The contact area in the model is at a nanometer scale while the experimental contact area is on the order of tens to hundreds of microns. Correspondingly, the applied loads also differ significantly between the model and experimental results since Newton-scale loads cannot be applied to a nanometer-scale contact. Similarities in friction trends and tribofilm evolution suggest that the simulation is indeed capturing the dominant mechanisms underlying the temperature-dependent friction of AgTaO₃.

Raman spectra shown in Figure 4.6 were collected inside and outside of the wear track of coating S4 after tribotesting at 750 °C. It is evident that the wear track
contains AgTaO$_3$ and Ta$_2$O$_5$ phases. XRD of the S4 coating in Figure 4.3 did not show any Ta$_2$O$_5$ peaks due to detection size limitations whereas Raman spectroscopy is much more surface sensitive. The absence of Ag peaks in the Raman spectra was expected given that Ag is Raman-inactive. A more careful evaluation of the Raman spectra gathered inside and outside of the wear track revealed that the intensity of AgTaO$_3$ peaks increased with respect to the Ta$_2$O$_5$ peak inside the wear track suggesting that AgTaO$_3$ is contributing more to the decrease in CoF. However, the EDS maps in Figure 4.6 suggested that elemental Ta was more prominent in the wear track than elemental Ag compared to the unworn regions.

Detailed surface and subsurface chemical and structural investigations were carried out using FIB/SEM, BFTEM, and HAADF-STEM with EDS mapping. These characterization techniques were used to determine the cross-sectional elemental and...
phase distributions as well as any structural changes that occurred inside the wear track at 750 °C.

A cross-sectional BFTEM image taken at the center of the wear track is shown in Figure 4.7. There are clearly identifiable tribochemical and structural changes that occurred in this film during sliding at 750 °C. There are discernable Ag clusters surrounded by Ta$_2$O$_5$ near the surface while AgTaO$_3$ remains intact below the sliding interface. The segregation at the surface makes sense as the Ta-O bond is much stronger than the Ag-O bond [47, 81]. At high temperatures, the Ag-O would easily break leaving behind an intact Ta$_2$O$_5$ layer below [47]. This and other images also show a reduction in thickness after sliding to ~440nm from an original coating thickness of ~2 µm.

![Figure 4.7: Cross-sectional BFTEM image of various chemical phases taken inside the center of wear surface after 750 °C.](image-url)
An SEM planar image in the center of the wear track after 10,000 cycles of sliding is displayed in Figure 4.8(a). The corresponding FIB X-SEM image after the initial polish highlighting the area that was analyzed in the TEM can be seen in Figure 4.8(b). A HAADF-STEM image and EDS chemical maps inside the 750 °C wear track are shown in Figure 4.8(c). A section of the HAADF-STEM image shows the corresponding elemental composition along the selected cross-section. Figs. 4.8(d) and (e) show additional HAADF-STEM images along the wear track. These images and maps are critical in determining the solid lubrication chemical and structural phases responsible for the observed low friction (CoF ~ 0.06). Several observations are notable: 1) the worn coating was found to be relatively conformal and uniform in thickness (~400 nm) across the ~25 µm sectioned wear track distance, 2) AgTaO₃, Ta₂O₅, and Ag nanoparticles were present in varying amounts along the wear surface, 3) oxidation and diffusion inside the wear track are very apparent, and 4) Inconel substrate major alloying species (Ni, Fe, and Cr) are oxidizing and diffusing ~100 nm into the AgTaO₃ base coating. The stoichiometry of the AgTaO₃ and Ta₂O₅ phases inside the wear tracks were inferred based on the previously discussed Raman spectroscopy and XRD analyses which corroborate these TEM and EDS results.

Additional supporting BFXTEM images from low to high magnification of the various phases taken inside the center of the wear track are displayed in Figure 4.9. In addition to the AgTaO₃, Ta₂O₅, and Ag nanoparticles shown in Figure 4.9(a-c), there is evidence of a sliding-induced mechanically mixed layer (MML) in Figure 4.9(d) that is indexed to monoclinic AgTaO₃ (101) [PDF # 22-473] and orthorhombic Ta₂O₅ (001) [PDF # 25-922] phases based on the FFT pattern shown in the inset. The slight
streaking in the circled AgTaO$_3$ spots in the FFT pattern indicates there is increased structural disorder of this phase in the MML, which is a result of the friction process. The observed clusters of Ag with a crust of Ta$_2$O$_5$ on the surface in Figures 4.8 and 4.9 suggest the decomposition of AgTaO$_3$ into Ag and Ta$_2$O$_5$. In addition to the MML, the reduced friction coefficient maybe due to the existence of this layer on the surface with the potential for re-construction of AgTaO$_3$ through the wear process.
Figure 4.8: (a) SEM image inside the center of the wear track for S4 after tribotesting at 750°C for 10,000 cycles (S.D.=sliding direction). The rectangular bar is e-beam and then i-beam deposited Pt to protect the surface during cross-sectional FIB-milling. (b) Corresponding FIB-XSEM image inside the wear track after the initial polish. (c) Z-contrast/HAADF X-STEM image taken from the box location in (b) and corresponding elemental EDS maps of the worn coating and Inconel substrate taken from the red box. (d) and (e) Additional HAADF X-STEM images along the wear track.
A snapshot of a simulation of AgTaO$_3$ at 12 ns and 750 °C is shown in Figure 4.10. The illustration reveals that the silver atoms form clusters (circled in yellow) and are surrounded primarily by tantalum and oxygen atoms. This model coincides with the aforementioned experimental observations. The AgTaO$_3$ structure is predominant further from the surface which is also in agreement with Figures 4.8 and 4.9. Both

*Figure 4.9: Bright field XTEM sequence of low to high magnification (a→d) images of various phases taken inside the center of the wear track for S4 after tribotesting at 750 °C for 10,000 cycles. Inset in (d) is FFT image that is indexed to AgTaO$_3$ (101) and Ta$_2$O$_5$ (001) phases that have been mixed during sliding to create a mechanically mixed layer (MML).*
experimental and simulated findings suggest silver segregation at the surface plays a significant role in reducing friction at high temperatures.

Local density distribution in the simulation was also calculated by the Martini group to quantify the presence and evolution of silver clusters during sliding. To provided further evidence of the connection between the observed composition at the tribofilm surface and low friction coefficients. They divided the model film into 0.5 nm cubes (3262 cubes in total) and calculated the number and type of atoms in each cube.
This approach allows us to determine both the quantity of high-density silver cubes (identified as cubes with at least 70% silver) at each simulation timestep as well as the average size of silver cluster (regions with multiple adjacent high silver density cubes). The results are shown in Figure 4.11. No high-density cubes exist at the onset of the simulation as the entire film is crystalline AgTaO₃ (in which the silver density is 20%). When a normal load is applied laterally, the number of high silver density cubes gradually increases. While this trend is observed at both 27 and 750 °C, it is more significant at the higher temperature. This is consistent with the identifiable Ag clusters after sliding tests at 750 °C observed in figures 4.8 and 4.9. The average volume of each silver cluster is also telling as silver cluster volume are approximately twice as large at 750 °C than those in the simulation at 27 °C.

Figure 4.11: Number of high density Ag cubes (black circles) and the average volume of multi-cube clusters (red triangles) at different temperatures (solid - 750 °C and hollow - 27 °C) obtained from MD simulations.
The results presented thus far show that friction decreases with increasing temperature (simulation and sliding experiments), silver clustering with surrounding Ta$_2$O$_5$ is present near the sliding surface (simulations and cross-sectional characterization of the coatings), and the number and volume of silver clusters increase with sliding distance at higher temperature (simulations). Collectively, these results suggest that there is a connection between the presence of the tribofilm and low friction at high temperatures observed for AgTaO$_3$.

4.2.3 Load test of AgTaO$_3$

While the previous investigations focused on the performance and characterization of the coating as a function of temperature, it is also important to investigate the coating as a function of load. Below the coating was wear tested at 1N, 2N, 5N, and 10N. Then numerous characterizations were performed to compare to the previous results.

![Figure 4.12: Steady-state CoF for silver tantalate as a function of load tested at 750°C.](image)
Wear tests as a function of load were performed at 750 °C. Figure 4.11(a) shows that the steady state friction force increased with normal load from 1 to 10 N. Therefore, the coefficient of friction, shown in Figure 4.12(b), was found to increase from a minimum value of 0.04 to 0.16. Additionally, these coatings visually displayed an increase in wear with increasing normal load. At 10 N, coating failure occurred after ~600 cycles. Hence a second wear test was conducted for 300 cycles in order to allow the analysis of the chemical and structural properties of the wear track prior to failure. Tribotests under smaller loads were carried out to completion without coating failure.

Figure 4.13: Scanning Auger nanoprobe maps acquired after wear testing at 750 °C under a load of (a) 2N and (b) 10N. Atomic percentages in selected areas are also listed for each map.
Auger electron spectroscopy (AES) maps were acquired inside and outside the wear track for coatings tested at 1, 2, 5, and 10 N loads. Shown in Figure 4.13 are elemental composition scans for samples tested under (a) 2 N and (b) 10 N, respectively. For smaller loads, the surface of the wear track was covered primarily with Ag with the exception of a few Ta- and O-rich patches located primarily in the center of the tracks. The depleted areas were caused by higher contact pressures at the center of the wear track because the silicon nitride counterface was spherical in shape. The semi-elliptical Hertzian contact pressure distribution caused the lower shear strength Ag to be extruded to the edges of the wear track. As the load was increased to higher values (5 and 10 N), the presence of Ag on the surface of the wear track was found to decrease dramatically, since silver was more easily extruded from the center of the wear track. The increase in the steady state friction with load may be attributed to the depletion in the soft Ag phase, which results in the counterface pushing the relatively soft silver to the edges of the wear track.

Raman spectra were analyzed both inside of the wear track for varying normal loads. These spectra revealed that the surface of the wear track consists primarily of AgTaO$_3$ and Ta$_2$O$_5$. Figure 4.14 shows that the intensity of the peaks associated with Ta$_2$O$_5$ located in the 800-900 cm$^{-1}$ range, was found to decrease monotonically with an increase in load. This decrease in intensity may be due to the more substantial amorphization of the Ta$_2$O$_5$ with load and the presence of silver nanoparticles, which are not Raman-active, but may enhance the Raman signal of oxides if their size and distribution are on the nanometer scale [106]. As a result, the decrease in the Raman signal with an increase in load may be associated with the lower content of finely
dispersed silver particles in the wear track. In addition, it is well known that Raman peak intensity scales with coating and transfer film (tribofilm) thickness [107, 108]. In our case, a decreasing tribofilm thickness with increasing normal load could also account for decreasing Raman Ta$_2$O$_5$ peak intensities shown in Figure 4.14. This Ta$_2$O$_5$ phase has been previously determined to be a component of such a tribofilm at 750 °C [109, 110].

Figure 4.14: Raman analysis inside of the wear track for coatings tested at 750 °C case, a decreasing tribofilm thickness with increasing normal load could also account for decreasing Raman Ta$_2$O$_5$ peak intensities shown in Figure 4.14. This Ta$_2$O$_5$ phase has been previously determined to be a component of such a tribofilm at 750 °C [109, 110].

To investigate the mechanisms that are responsible for the trends observed in the tribological properties of AgTaO$_3$ at high temperatures under different loads, a systematic cross-sectional investigation was carried out using BFTEM and HAADF-
STEM with EDS mapping. These techniques were utilized to study any structural or chemical changes that occurred inside the wear track as a consequence of tribotesting.

*Figure 4.15:* SEM images of (a) unworn AgTaO$_3$ coating at 750 °C and (b) worn AgTaO$_3$ coating at 750 °C under a 1N normal load and 10,000 cycles. The dashed lines denote the wear track edges, S.D. = sliding direction, and the box shows the location of the cross-section FIB-cut to acquire the images in Figure 4.14.

STEM with EDS mapping. These techniques were utilized to study any structural or chemical changes that occurred inside the wear track as a consequence of tribotesting.
at 750 °C under different loads with comparisons to the unworn coating. Figure 4.15 shows a surface SEM image of unworn AgTaO₃ coating at 750 °C. It is apparent that the surface has roughened with ‘node-like’ features on top as a result of heating. Cross-sectional HAADF-STEM (not shown) of this coating at 750 °C, Extensive investigations presented above illustrate that there is decomposition of AgTaO₃ into Ta₂O₅ and Ag in the wear track under 1N load., with the latter mainly present as large surface nodules. Oxidation and diffusion in these nodular regions are very apparent since the Inconel substrate’s major alloy species (Ni, Fe, and Cr) are oxidizing and diffusing ~100 nm into the AgTaO₃ coating. Below these nodules, a continuous, ~500 nm thick AgTaO₃ coating is present as well as in regions where there are no nodules. While the nodules are predominately composed of Ag, some fine scale Ta₂O₅ is also apparent which XRD did not detect. Figure 4.15(b) is an image of the wear track tested at 750 °C under a 1 N normal load. It is apparent that the Ag-containing nodules have been compacted, sheared off, and likely recirculated during sliding, since they act as stress concentrators. The shearing/extrusion of the Ag-containing nodules is especially evident at high normal loads of 5 and 10 N and compares well to the Figure 4.14 images. The underlying, ~500 nm thick AgTaO₃ layer, is exposed and can further undergo decomposition during sliding into Ta₂O₅ and Ag, as we show below with both TEM and MD analyses. Therefore, both thermal and tribo-mechanical stress can cause decomposition of AgTaO₃.

Figure 4.16(a) shows a HAADF-STEM image of the wear track cross-section taken in the center of the wear track after testing at 750 °C under a 1 N load. The location of the cross-sectional FIB-cut is denoted by the box in Figure 4.16(b). Below
the e-beam the tribofilm and coating, whose thickness as mentioned above is ~500 nm protective Pt (ePt) layer are two of the aforementioned Ag-containing nodules on top of compared to the ~1500 nm thick unworn coating. It is likely these Ag-containing nodules were sheared in the sliding contact and make up a large portion of the wear track area, much like the AES map in Figure 4.12(a) showing Ag in the wear track under 2 N load.
Figure 4.16: (a) Cross-sectional Z-contrast/HAADF X-STEM image of a selected region in the wear track at 750 °C under a 1N normal load and 10,000 cycles. (b) Higher magnification HAADF X-STEM image of the selected region in (a). (c) Corresponding EDS maps of the selected region in (b). (d) EDS line profile map of the region highlighted in (a). (e) and (f) are BF-TEM images of the two selected regions in (a).
This Ag is also responsible for the decrease in friction during interfacial sliding at low normal loads. Figure 4.16(b) depicts a higher magnification of a selected region shown in Figure 4.16(a). This figure reveals that there are four distinct zones in the underlying tribofilm and worn coating. At the bottom (zone I) is a homogeneous and dense structure that corresponds to the original AgTaO₃ coating and below it is the aforementioned oxide layer of Inconel, the thin dark layer in Figures 4.16(a) and (b). Segregation of Ag and formation of nanoscopic Ag clusters occurred in zone II and into zone III. Therefore, zone II consists of Ag clusters (light spots in STEM Figure 4.16(b) image and dark spots in BF-TEM Figure 4.16(f) image) surrounded by a AgTaO₃ matrix. The small dark spots in zone II of Figure 4.16(b) corresponds to some porosity that formed likely due to the migration/diffusion of Ag. The average Ag cluster size in zone II increased from ~ 30 nm close to the substrate to ~ 100 nm near the surface suggesting a diffusion-driven size gradient. Zone III consists of larger Ag clusters embedded in a porous Ta₂O₅ phase. The boundary between zones II (AgTaO₃/Ag) and III (Ta₂O₅/Ag) could be caused by both diffusion and the location of the subsurface shear stress during sliding. The top layer (zone IV) suffers the highest interfacial shear stress that results in the formation of a thin mechanically mixed layer (MML) created during the sliding process [15]. This zone is characterized by a porous columnar Ta₂O₅ structure and Ag particles. Above this MML, are the aforementioned Ag-containing nodules that diffuse to the surface seen in some areas on the wear track surface, such as those shown in Figure 4.16(a). The transformation of the Ta₂O₅ into a columnar structure is inferred to be the result of capillary movement of the silver as it rises toward the surface to form the silver nodules.
Figure 4.16(c) shows an elemental EDS map of the region, denoted in Figure 4.16(b) that confirms the lighter regions in the TEM images correspond to Ag-rich particles. Figure 4.16(d) shows elemental composition line profile along the yellow arrow depicted in Figure 4.16(a). This figure confirms the formation of Ag-containing nodules on the surface of the wear track as well as spikes of Ag that correspond to the agglomeration of Ag within the Ta$_2$O$_5$ (zone III) and AgTaO$_3$ (zone II) matrices. Ta decreased towards the surface confirming that zones III and IV are less dense than zones I and II. Figures 4.16(e) and (f) are corresponding BF-TEM images of the four zones in the tribofilm and coating that confirm the size of Ag particles (dark areas) increases toward the surface. In these higher magnification images, there are clearer differences in tribofilm morphology and structure amongst the zones. Going from zone I toward the surface, the porosity increases. The degree of porosity in the zones is significant because it shows the relationship between silver clustering/diffusion and sliding shear stress. Zone IV MML under the highest interfacial shear stress exhibits the highest porosity and largest sized Ag clusters. These figures also show the relatively higher porosity of the MML and tribofilm compared to the films tested under a 2 N load (Figure 4.19). In addition, the number of Ag clusters is higher and the thickness of the MML (zone IV) is reduced for the sample tested under a 1 N load. When comparing the 1 and 2 N load tribofilms that are generated, the density of the tribofilm increases at higher loads. Not shown are the 5 and 10 N load cross-sectional structures. It is apparent that under these higher loads the tribofilms become less stable in supporting the load. In addition, the low friction Ag phase is no longer present in the wear track (Figure 4.16(b)) and the underlying film eventually wears away, e.g. 10 N load test.
Lastly, Figure 4.17 shows corresponding SAED patterns acquired from BF-TEM images of zones II and III. Figure 4.17(a) BF-TEM image of zone II and the accompanying SAED pattern in Figure 4.17(c) confirm the presence of AgTaO₃ and decomposition of Ag and Ta₂O₅ with strong diffraction spots for pure Ag that agrees with increasing Ag content in this zone. Figures 4.17(b) and (d) were acquired from zone III and show that similar phases are present. This phase identification corroborates the aforementioned TEM analysis.

Figure 4.17: BF-TEM images of tribologically-induced zones II (a) and III (c) and accompanying SAED patterns (b) and (d), respectively.
Figure 4.18 shows a 3D APT reconstruction of Ag-, Ta-, and O-ions acquired from a specimen collected from an AgTaO₃ film after sliding at 750 °C under a 1 N load.

At the particular location selected for APT sample preparation, the grey silver spheres indicate the preferential migration of Ag and its agglomeration at the surface of the wear track. Below the Ag layer is the Ta₂O₅-rich layer which supports the decomposition of the AgTaO₃. These observations are in agreement with the data collected from TEM and EDS in Figure 4.17.

Consistent with the experimental measurements (Figure 4.12), the simulations predicted that friction force increases with normal load at 750 °C as shown in Figure 4.19. However, the simulations do not capture the increase of CoF. This can be explained by the fact that the simulations only capture part of the wear process at the higher loads. Specifically, the model atoms redistribute but cannot leave the periodic simulation cell such that removal of Ag from the wear track observed experimentally (and the likely source of the increasing CoF with load) does not occur in the model. The simulations also provided information at 27 °C which can be used for comparison and so facilitates understanding of the high temperature measurements. We observe in Figure
4.19 that both the friction force and the average friction coefficient (slope of a linear fit) at 750 °C are much smaller than those at 27 °C for all loads. In the case of nanoscale interactions, the relationship between friction force and normal load cannot be simply described by Amontons' Law due to the significant effect of adhesion. By extrapolating the data, we find that the friction force at zero load (and therefore the adhesion) is smaller at the higher temperature.

Previously suggested that the temperature-dependence of AgTaO₃ is due to sliding and temperature induced structural change that provides the tribofilm with low shear resistance [16]. Specifically, experiments and simulations showed that groups of silver atoms formed at the sliding interface. Note that the number of Ag atoms in the simulation does not change, i.e. the clusters are formed from the Ag atoms initially present in the AgTaO₃ film. To quantify this effect in the simulation, we divided the film

![Figure 4.19: Model-predicted friction force as a function of normal load at 27 and 750 °C. The straight lines represent linear fits to the data at each temperature.](image)
into identical cubes with side length of 0.5 nm and identified high-density Ag cubes, N, as cubes consisting of more than 70% Ag atoms. We apply this same analysis here. Figure 4.21 shows that N increases with time and temperature at all loads. In addition, the results indicate that, in general, N decreases with normal load; this trend is particularly evident at the end of the simulation (8ns) and more pronounced at the higher temperature. To correlate the silver clustering with friction force, we measured the shear stress for each cube. The distribution of high-density silver cubes at 1000 nN load and 750°C is shown in Figure 4.22 as a function of normalized stress, where stress is normalized by the maximum value. This shows that highest density silver regions correspond to the lowest shear stress in the simulation cell which supports the suggestion that silver segregation and clustering plays a role in enabling low friction.

Figure 4.20: Number of high-density Ag cubes as a function of normal load (black squares - 1000 nN, red circles - 2000 nN, and blue triangles - 3000nN) and temperature (Solid 750 °C and hollow 27 °C).
The results shown in Figure 4.22 are representative of our observations for other loads and temperatures.

The results we have shown here, strongly support the hypothesis that increasing temperature results in decreased friction due to the increased segregation of silver.
atoms and the low shear resistance those atoms provide. However, looking more closely at Figure 4.22; this does not appear to be the only mechanism for load dependence. At the lower temperature, the number of silver clusters is not significantly lower at the higher load where we observe higher friction. To explain the load dependence, we instead consider the porosity of the film. Recall that the TEM results suggested increasing load resulted in less silver and lower porosity. Although the relationship is not direct, we can correlate a decrease of the model-predicted average density to an increase in porosity. As shown in Figure 4.16, the density of the film increases with increasing load, but the effect of temperature is negligible. Therefore, although silver clusters may dominate the effect of temperature on friction, load affects

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure4.22.png}
\caption{Percent of high-density Ag cubes as a function of normal stress in the case of 8 ns after initial sliding at 750 °C with 1000 nN normal load.}
\end{figure}
friction through the combined effects of decreasing silver and resulting decreased porosity.

Figure 4.23: (a) XRD of coating before (i) and after (ii) wear testing at 750 °C and (b) coefficient of friction of wear test coating at 750 °C over 10,000 cycles.

4.3 Silver-Tantalum Oxide Coatings

Figure 4.23(a) shows XRD patterns for the films (i) before and (ii) after wear testing at 750 °C. XRD analysis of the as-deposited coating revealed the creation of an off-stoichiometric tantalum oxide phase. No silver-based phase was observed in the XRD pattern. Silver, present in low concentration, is likely to be evenly distributed throughout the film, similar to the study performed by Lee et al. [111] on Ag:Ta$_2$O$_5$, where the silver concentration was higher than in the current study and they had to anneal the sample at 700 °C for an hour to induce the formation of Ag nanoparticles which were on the order of 5 nm in size. Since the lower silver concentration and the samples are not heat treated in this study, it is reasonable to expect that the silver is not on the order of dimensions observable by XRD. The coating was then subjected to high temperature wear testing at 750 °C. Figure 4.23(b) shows the frictional behavior of the
Ta_{x}O_{5-x}/Ag coating. During the first 1350 cycles of the test, the coefficient of friction was in the 0.33 ± 0.19 range. As the test proceeded, the coefficient of friction steadily dropped to reach a value of 0.14 ± 0.09 which was maintained until the end of the test. Post-test XRD data (Figure 4.23(a)) revealed the formation of two new phases, namely AgTaO_3 and silver deficient Ag_2Ta_4O_{11}. We believe that the deposited coating was metastable and that thermo-mechanical and thermo-tribological testing resulted in Ag diffusing to the surface, which reacted with the Ta_{x}O_{5-x} phase to produce AgTaO_3. The time-dependent enhanced lubricity of the coating is hypothesized to be the result of the increased silver content and the formation of the silver tantalate phases. In the

Figure 4.24: (a) Scanning Auger electron spectroscopy mapping of the coating surface and wear track after wear testing at 750 °C and (b) cross-sectional transmission electron microscope (TEM) of cross-section of wear track showing.
steady state, we observed that friction was slightly higher for the TaₓO₅₋ₓ/Ag system (0.14) than that reported for AgTaO₃ (0.06), but was much lower than that of Ta₂O₅ (0.5). Interestingly, the wear rate was lower for TaₓO₅₋ₓ/Ag (1 × 10⁻⁷ mm³/N.m) than for the lubricious AgTaO₃ (4 × 10⁻⁷ mm³/N.m), probably due to the combination of the low CoF and the relatively high hardness (due to the low Ag content) of the tantalum oxide phase. The wear rate for Ta₂O₅ was found to be 8 × 10⁻⁶ mm³/N.m.

Figure 4.24(a) shows scanning Auger sanoprobe (SAN) maps acquired after wear testing at 750°C. These maps demonstrate that silver had diffused to the surface of the coating as a result of the external thermal and mechanical stimuli. Silver was found to be primarily present in the middle and the outside of the wear track. This behavior is different from that observed for AgTaO₃ under the same testing conditions where Ag was primarily pushed to the edges of the wear track [112]. The incomplete coverage of silver in the wear track is likely the cause in the increase CoF on TaₓO₅₋ₓ/Ag compared to AgTaO₃. This is supported by the observation that Ta₂O₅, which is a much harder phase that does not shear easily, displayed a CoF of ~0.5 under the same testing conditions. Figure 4.24(b) shows HAADF-STEM image of the wear track after wear testing of the TaₓO₅₋ₓ/Ag coating at 750 °C. This figure reveals that the tribolayer consisted of two distinct regions, a highly porous top layer and a much denser underlayer. Throughout the dense and porous regions we observed veins and particles of silver that agglomerated as a result of the sliding process. The highly porous regions are likely due to silver diffusion to the surface.

Figure 4.25(a) shows the friction force for each model film. In general, the friction initially increased (consistent with a run-in process) and then approached a steady state.
around the fifth cycle. In the steady state, the Ta$_2$O$_5$ exhibited the highest friction, and then friction decreased with increasing Ag content. This is consistent with trends reported in previous experimental work where adding/increasing Ag decreased friction in Mo$_2$N/MoS$_2$/Ag [113] and YSZ-Ag-Mo nanocomposites [114], as well as other coating materials (such as TiN, CrN, ZrN, DLC and TaN) [115-119]. This correlation between friction and Ag content can be attributed to the fact that Ag facilitates sliding over a range of temperatures due to its low shear strength [120]. We also observed that AgTaO$_3$ exhibited the lowest friction, slightly lower even that the Ta$_2$O$_5$/Ag film with similar Ag content (i.e. 20%), which is consistent with our experimental results.

The various model films were also characterized in terms of their wear resistance, as shown in Figure 4.25(b). We observe that the wear rate (slope of the depth vs cycle plot) reached approximately a constant value in steady state. Also, for each cycle, the wear depth increased with increasing Ag content, with Ta$_2$O$_5$ exhibiting
the best wear performance. We also observed less wear on the AgTaO$_3$ film than the Ta$_2$O$_5$/Ag films. This is inconsistent with the experimental result that Ta$_{x}$O$_{5-x}$/Ag exhibited less wear than AgTaO$_3$. However, it has been reported that the effect of incorporating of Ag into a coating is non-monotonic. Specifically, the wear performance of a coating material improves with a small amount of Ag, but may deteriorate as more Ag is added [115-118]. The experimental results are consistent with the former trend while the simulation results reflect the latter. The discrepancy is likely related to relative sizes of the model and experiment. Specifically, in the 14 at.% Ag model film, all the Ag atoms are localized at the sliding interface, whereas, in the experiment, the Ag is likely not distributed evenly within the film and the actual amount of silver in the material at the sliding interface may be less than 14 at.%. The simulation results in Figure 4.25(c) suggest that the actual percent silver in the interface during experiment is likely less than 6 at.%.

To understand the friction and wear trends, we analyzed the evolution of the silver content during sliding. Since both the number and size of silver clusters may affect friction, the overall contribution was quantified as the integral of the probability distribution of cluster sizes. In this study, we focused on the wear track and the silver clusters in that region. Figure 4.25(c) shows that Ag clustering in all Ta$_2$O$_5$/Ag films increased with Ag content. This trend can be directly correlated to the decreasing friction with Ag shown in Figure 4.25(a). However, the fact that the friction for the Ta$_2$O$_5$/20 at.% Ag and Ta$_2$O$_5$/26 at.% Ag was similar indicates that there is a limit to the friction reducing effect of Ag. That is, once the Ag content reaches some critical value (~20% per the results in this simulation) the friction will no longer increase with
increasing Ag. As suggested by previous experimental results on WS₂-Ag [121], this behavior might be attributed to the depth of penetration of the probe, which gradually increases with Ag content due to the softness of silver, leading to increased plowing stress in front of the counterface. This affects the wear behavior and is consistent with the wear results shown in Figure 4.25(b). The trends exhibited by the Ag clustering in the AgTaO₃ suggests that the Ag that is initially evenly distributed in the film gradually forms silver clusters that continue to provide low shear resistance as sliding progresses. The behavior of Ag clusters in AgTaO₃ is further supported by a calculation of the average vertical displacement (towards the surface) of Ag during sliding, which we found to be 0.09 nm and 0.24 nm for the AgTaO₃ and Ta₂O₅/20 at.% Ag films, respectively. This, along with the silver cluster results, indicates that Ag clusters form and migrate to the surface more gradually on the AgTaO₃ films than the Ta₂O₅/Ag films, leading to both lower friction and wear.

4.4 Nitride Coatings

To explore the potential of AgTaO₃ as a lubricious material in a “chameleon” coating design [47], TaN/Ag nanocomposite structures were produced with various Ag contents. Chameleon coatings broaden the temperature range of tribological materials by adjusting their chemistry at interfaces in response to environmental changes. Hence, TaN/Ag was selected with the premise that Ag reduces friction at low to mid-range temperatures (up to 500 °C) and that the lubricious AgTaO₃ (with the existence of the thin Ag/Ta₂O₅ overlayer as suggested by the TEM results discussed above) phase forms on the surface of these materials when operated at high temperatures.
Figure 4.26: XRD patterns of TaN/Ag coatings before and after tribotesting. S=substrate.

Figure 4.27: Steady-state CoF for TaN and TaN/Ag coatings as a function of temperature.
Figure 4.26 shows XRD patterns (a) before and (b) after tribotesting at 750 °C for TaN and of a selected TaN/Ag coating that had a Ag content of 20 at.%. The reference coating displayed characteristic XRD patterns of TaN [104, 122]. The complete oxidation of the coating did not occur – the XRD patterns were consistent with peaks that corresponded to a mixed phase of orthorhombic Ta$_2$O$_5$ (PDF # 54-514) and TaN [123]. An additional peak that corresponds to cubic Ag (PDF # 4-1-2617) was observed for the TaN/Ag coatings. The CoF of the TaN reference coating at 25 °C and 750 °C was 0.91 and 0.49, respectively (Figure 4.27). These values are comparable to those obtained for the Ta$_2$O$_5$ reference coating, as reported in the previous sub-section.

Tribotesting of the TaN/Ag coating showed an improvement in the CoF over the TaN reference coating. The CoF shown in Figure 4.27 consistently decreased from 0.39

Figure 4.28: Post-tribotesting Raman spectroscopy data of TaN/Ag coating inside and outside the wear track, and (b) SEM/EDS micrographs of TaN/Ag coating.
to 0.23 as the temperature increased from 25 to 750 °C. These CoF values are higher than the S3 and S4 coatings shown in Figure 4.15. Once the samples were cooled to RT, XRD data revealed peaks of Ag (4-1-2617), AgTaO₃ (22-473), Ta₂O₅ (54-514), and the substrate (S). Raman spectroscopy data shown in Figure 4.28 revealed a broad peak corresponding to Ta₂O₅ around 820 cm⁻¹ [103]. This change in the Raman active species is consistent with the oxidation temperature for TaN [122]. For the TaN/Ag coatings, prominent peaks that indicate the formation of AgTaO₃ were observed (Figure 4.28) [104]. In addition, a peak at 580 cm⁻¹, which corresponds to Ta₂O₅, was also seen [104, 124]. Despite the same chemical phases (AgTaO₃, Ta₂O₅, and Ag) as detected in the S4 coating, this coating had higher friction likely since the relative amount of these phases was different than the S4 coating studied by TEM analyses. The EDS maps for S4, shown in Figure 4.29, are very similar to those shown for powders, suggesting that the content of elemental Ta was higher in the wear track. Future work will involve FIB/SEM and TEM studies to determine the high temperature solid lubrication mechanisms for this chameleon coating.
CHAPTER 5

SUMMARY, CONCLUSION, AND SUGGESTED FUTURE WORK

5.1 Summary and Conclusions

Silver tantalate was produced in powder and thin film form to explore high temperature tribological properties. Powders were synthesized using a hydrothermal recipe and were subsequently burnished on Inconel substrates. The powders were useful for identifying low shear strength phases at high temperature. Thin films of Ag-Ta-O with various Ag/Ta ratios and oxygen content and TaN/Ag were fabricated on Inconel substrates by magnetron sputtering from Ag and Ta sources in a reactive oxygen environment. The coatings with a Ag content of an order of 20 at.% had exhibited the lowest friction of all the samples tested due to formation of both silver tantalate and metallic silver phases that provide lubrication at elevated temperatures. Inside the wear track after 750 °C tribotesting, there exists multiple individual (AgTaO₃, Ag, Ta₂O₅) and mixed (AgTaO₃/Ta₂O₅) phases present at the sliding interface responsible for the low friction. The main lubricious contribution, however, comes from the AgTaO₃ layer. This coating displayed a very low CoF of 0.06 when tribotested at 750 °C using a 2 N load. Cross-sectional TEM studies after tribotesting revealed that AgTaO₃ is the main phase that was deposited and that the sliding created a mechanically mixed layer (MML) on the surface of the wear track. A tribofilm of silver clusters and surrounding Ta₂O₅ were observed on the surface suggesting the decomposition of AgTaO₃ into nanocrystalline Ag and Ta₂O₅. These features were reproduced in molecular dynamics simulations [12]. It was deduced that the reduced friction coefficient at high temperatures was due to the existence of this layer on the
surface, with the potential for continued re-construction of the Ag and Ta$_2$O$_5$ tribofilm from silver tantalate through the wear process. The presence of nanoparticles of segregated Ag in the coatings also helped increase the coating toughness.

Additional films of AgTaO$_3$ were produced using reactive unbalanced magnetron sputtering from Ag and Ta targets. These films were found to consist primarily of an AgTaO$_3$ matrix with silver particles inter-dispersed in it. The sliding friction at 750°C was found to monotonically increase when the load was varied from 1 to 10 N. AES, TEM and APT studies revealed the sliding-induced surface and subsurface structural and chemical changes. Cross-sectional chemical and structural analyses revealed four different zones (from bottom to top): (i) worn AgTaO$_3$ coating; (ii) AgTaO$_3$ matrix embedded with Ag nanoparticles; (iii) AgTaO$_3$ matrix embedded with fewer but larger Ag nanoparticles; and, (iv) Ta$_2$O$_5$ matrix embedded with Ag nanoparticles. Transmission electron microscopy (TEM) revealed that the AgTaO$_3$ phase produced clusters of Ag surrounded by Ta$_2$O$_5$ near the surface, where the applied stress was presumed to attain its maximum values. These results were complemented by MD simulations, which predicted an increase of friction force with load consistent with experiment. Taken together, the experiments and simulations indicate that the increase in friction with load is due to the combined effects of decreasing presence of silver clusters in the wear track (silver being sheared/extruded from the wear track) and corresponding increased porosity, both of which result in the material being less able to accommodate interfacial shear. Theoretical and experimental cross-sectional images of the coatings in the wear track revealed that the presence of Ta$_2$O$_5$ and Ag increased dramatically closer to the interface whereas the remainder of the coating consisted primarily of AgTaO$_3$ with a
very small amount of finely dispersed silver. Reconstruction of AgTaO₃ from the Ag and Ta₂O₅ phases from mechanical mixing during wear testing has also been hypothesized [112]. With increased normal force during testing, the diffusion and plowing of the silver from the surface increased, causing the coating to decrease in density and increase in porosity. MD modeling complemented the experimental results and supported the hypothesis that friction increased with load due to changes in the Ag distribution and near-surface density [125].

Additional investigations into the suggestion that low friction in AgTaO₃ is enabled by the reconstruction of the material into Ag and Ta₂O₅ by studying the tribological properties of Ag/Ta₂O₅ nanocomposite coatings using experimental tools in tandem with MD simulations. TaₓO₅₋₅/Ag coatings with a silver content of 14 at.% were produced by unbalanced magnetron sputtering and was found to possess a surface that adapts over time as a result of the combination of elevated temperatures and sliding. Molecular dynamics simulations were performed to study the tribological properties for the films with different compositions. Both the experiments and simulations showed that the surface of the coating was changed over time as a result of the migration of silver to the surface. These changes affected friction and wear of the sliding interface. Results from experiment and simulation revealed that friction decreased and wear increased with increasing Ag content in TaₓO₅₋₅/Ag films. However, both methods also showed that the lowest friction was always observed for AgTaO₃ coatings. A correlation between the tribological and the chemical/physical data suggested that this possibly due to the even distribution of the Ag in the AgTaO₃ and the gradual formation and migration of Ag clusters to the interface. The wear performance was less straightforward since the
experimentally-measured wear was smaller on the $\text{Ta}_x\text{O}_{5-x}/\text{Ag}$ films than the $\text{AgTaO}_3$, while simulations predicted the opposite trend. This difference was attributed to the localization of Ag in the interface in a simulation that is unlikely to occur in the experiment. Overall, the results suggest that it is possible to tune the friction and wear performance of Ag-Ta-O films by tuning the amount of embedded Ag for a given set of operating conditions.

5.2 Suggested Future Studies

Although this body of work suggests that the friction reducing quality of the silver tantalate ($\text{AgTaO}_3$) is in large part due to the formation of a tribofilm at elevated temperatures. The tribofilm consisted of silver clusters and surrounding $\text{Ta}_2\text{O}_5$ were observed on the surface suggesting the decomposition of $\text{AgTaO}_3$ into nanocrystalline Ag and $\text{Ta}_2\text{O}_5$. While the silver at the surface decreases friction and the embedded silver increases toughness, as load is increased there is an increase in friction due to the plowing of the silver from the interface. When increased levels of silver are added to a $\text{Ta}_x\text{O}_{5-x}$ matrix, the wear decreases while the friction decreases, however the formation of $\text{AgTaO}_3$ in these coatings, support the hypothesis that reconstruction mechanisms are possible after deconstruction in the other $\text{AgTaO}_3$ coating. There are questions that still remain.

1. Thermal cycling of the coatings was not addressed and as such, after heating the low temperature behavior of the coating is not known. Does the migration of elemental silver to the surface embedded in the Tantalum oxide shear leaving fresh $\text{AgTaO}_3$ coating? Does higher silver content corresponding to higher migration leave the coating too porous for applicability of cycling?
2. The thermodynamics driving the system were not addressed. There is no known phase diagram of the Ag-Ta-O system in the literature. This would help in answering the reconstruction question from silver and tantalum oxide back into AgTaO₃.

3. Does the substitution of copper in for the silver in the crystal lattice behave the same way? It has been seen that the silver is highly influential to the reduced friction at the interface. Does copper migrate out of the lattice?
APPENDIX

MOLECULAR DYNAMIC SIMULATIONS
To complement the experimental measurements, Molecular Dynamics (MD) simulations were carried out using the open source code LAMMPS. The simulation process and can be simply described as a rigid plate sliding over an AgTaO$_3$ tribofilm. The top plate consisted of AgTaO$_3$ atoms that acted as a rigid body. This rigidity assumption means the plate does not represent a real material and we found that model-predicted trends were unaffected its atomic composition. The dimensions of the film were $9.7 \times 1.94 \times 15.52$ nm$^3$ and it contained 25375 atoms. The top rigid plate moved laterally at a constant speed of 5 m/s for 8 ns with a timestep of 1 fs. A schematic of the simulation setup is shown in Figure A.1. Normal loads ranging from 500 to 3000 nN (with an interval of 500 nN) were uniformly distributed on the top plate.

*Figure A.1:* Snapshot of AgTaO$_3$ tribofilm setup.

The sliding tests were performed at two different temperatures, 27 and 750 °C. The bottommost layer of the film was fixed throughout the simulation. The motion of the atoms in the lowermost 2 nm of the film was damped to ensure a smooth transition from
the large shear at the top to the stationary bottom of the simulation cell. The damping coefficients decreased from 0.0064 to 0.0016 nN·s·m⁻¹ with increasing distance from the bottom layer. Periodic boundary conditions were applied in the sliding plane, and the boundary in the z-direction was formed by the rigid atoms at the top and bottom of the tribofilm. Results were obtained by averaging the data from the last 20 nm of sliding, excluding data during the initial, unstable stages of sliding. The Modified Embedded-Atom Method was used to describe atomic interactions in our model using potential parameters recently developed specifically to describe AgTaO₃[126].

Further MD simulations of a rigid hemispherical probe sliding over a tribofilm consisting of Ta₂O₅, Ta₂O₅/M at.% Ag (M=6.3, 14.3, 20.0 and 26.0) or AgTaO₃ was performed. The Ta₂O₅/Ag films were created by embedding ~8 nm³ regions of Ag atoms into the Ta₂O₅ film, where the percent Ag was adjusted by increasing the number of these Ag regions. All films had dimensions of 16.30 (in sliding direction) × 11.44 × 3.88 nm³. To mimic the near-surface reconstruction observed in the experiment, a mechanically-mixed tribofilm was created by first sliding a rigid plate (same cross sectional area as the film) over the material surface. Then a probe was introduced into the model and slid on the resultant tribofilm. During the simulation, the bottom layer of the tribofilm was held fixed, and the probe with 2.72 nm radius moved laterally at a constant speed of 100 m/s for 1 ns with a timestep of 1 fs. The high sliding speed is necessitated by the timescale limitation in MD simulations, particularly for the relatively large number of atoms in this model. A normal load of 300 nN was uniformly distributed on the probe. The temperature of the system was maintained at 750 °C throughout the simulation using a Langevin thermostat. Periodic boundary conditions were applied in
the sliding plane (otherwise, atoms were confined by the rigid boundaries). The friction force was measured as the average lateral force on the rigid probe during each cycle, where a cycle is defined by the probe crossing the periodic boundary of the simulation cell. Wear depth was defined as a vertical distance between the equilibrated film surface and the bottom of the wear track. To quantify the evolution of the films in response to sliding, we identified Ag clusters and characterized their size. A silver cluster was identified as a group of Ag atoms consisting of at least four atoms with each neighboring distance less than 0.25 nm. In our simulations, the Modified Embedded-Atom Method was used to describe the atomic interactions using potential parameters developed specifically for AgTaO$_3$ [126] and all simulations were carried out using the open source code LAMMPS [127].
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