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**FRICTION OF SELF-LUBRICATING SURFACES
BY ION BEAM TECHNIQUES**

FINAL TECHNICAL REPORT

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SUMMARY

UES, Inc. conducted a research and development program designed to establish conditions for ion implantation/mixing of suitable additives into the surfaces of bulk ceramics and metals for obtaining self-lubricating low friction and wear characteristics. The substrates considered were ZrO_2 , Al_2O_3 , Si_3N_4 , steel and Ni-base superalloy. The lubricant additives chosen were $\text{BaF}_2/\text{CaF}_2/\text{Ag}$, MoS_2 , WS_2 and B_2O_3 .

The initial tasks of the program were to synthesize these lubricant compounds by co-implantation of constituent elements if sufficient beams of desired elements were obtained. The final tasks were to investigate high energy (MeV) ion mixing of deposited coatings as well as to investigate ion beam assisted deposition using low energy ion beams.

It was shown that MoS_2 can be synthesized by co-implantation of Mo^+ and S^+ in ceramic materials with appropriate choice of energies to obtain nearly overlapping depth profiles. A low temperature, $\sim 500\text{-}700^\circ\text{C}$, annealing was necessary to precipitate stoichiometric MoS_2 phase. MoS_2 synthesized ceramic surfaces have shown reduced friction and wear. It is believed that other dichalcogenides can be synthesized by ion implantation as well.

The sliding life of DC magnetron sputtered MoS_2 films of thicknesses $\sim 7500\text{\AA}$ on ceramic materials such as sapphire, Si_3N_4 and ZrO_2 were improved by ten to thousand fold after 2 MeV Ag^+ ion mixing. The microstructure of these films were amorphous. The improvement in wear life was correlated with a significant improvement in adhesion of the film with the substrates and a small increase in density of the ion irradiated film. Ion mixed sputtered- WS_2 film also performed significantly better under severe traction test conditions as compared to commercial coatings.

Ion beam assisted deposition (IBAD) and ion beam mixing were utilized to fabricate self-lubricating coatings of CaF_2/Ag and $\text{BaF}_2/\text{CaF}_2/\text{Ag}$ composites. In IBAD, a low energy ($\sim 500\text{ eV}$) Ar^+ bombardment was used in combination with electron beam evaporation of coating materials. In ion beam mixing, magnetron sputter deposition was used to deposit a mixed

composite coating of $\text{CaF}_2 + \text{Ag}$ which was subsequently ion beam mixed with 1 MeV Ag^+ at a fluence of $1 \times 10^{16} \text{ cm}^{-2}$. Both IBAD and sputtering of BaF_2 and CaF_2 resulted in a near stoichiometric composition with very fine microstructure. Friction coefficients below 600°C were approximately 0.2-0.3 in the case of coated Rene 41 alloy, but were reduced to about 0.1-0.15 at 800°C for coated Si_3N_4 .

Ion implantation of B^+ into M50 steel and sapphire was not very effective in reducing friction and wear. It was anticipated that the formation of boric acid in the contact region during sliding in laboratory air will cause the reduction of both friction and wear.

Thus, the major accomplishments in this program were:

1. MoS_2 was synthesized by ion implantation of constituent elements into ceramic surfaces. High volume concentration of MoS_2 precipitates near the surface was necessary to reduce the friction coefficient and wear.
2. High energy (MeV) ion beam mixing of sputtered MoS_2 coatings on ceramic materials resulted in a very significant improvement in sliding life. The factor of improvement was in the range 10 to 1000 depending on the material and sliding conditions. Improvements were also demonstrated in WS_2 coated M50 steel after ion beam mixing.
3. Well adherent thin composite coatings of $\text{BaF}_2/\text{CaF}_2/\text{Ag}$ and CaF_2/Ag were fabricated by both ion beam assisted deposition and sputter deposition followed by high energy ion mixing. These coatings demonstrated low friction and wear in the temperature range 22°C to 800°C .

1.0 INTRODUCTION

Engineering components for use in advanced transportation systems, such as in low heat rejection diesel and automotive gas turbine engines and turbomachinery, etc., are required to

operate under harsh environmental and tribological conditions [1]. The demands for hard and tough materials to improve component performance at high temperatures led to the selection of ceramics for various engine components. The operating conditions in advanced transportation systems cannot permit the use of liquid lubricants. Solid lubricants offer a unique way of overcoming some of the problems associated with liquid lubricants by providing friction and wear resistance, corrosion and oxidation resistance and reliable/predictable performance in high temperature applications [2-4].

In order to provide low friction, a solid lubricant must possess either low shear strength at least in one crystallographic direction or can undergo plastic deformation. Lamellar solids such as graphite and MoS_2 possess weak interatomic bonding between planes enabling easy shear, thus providing low friction. Soft metals, such as Pb and Ag, easily undergo plastic deformation providing low friction, but not as low as lamellar solids. Some inorganic solids, such as CaF_2 and BaF_2 , provide lubrication at higher temperature ($0.3-0.6T_m$, T_m =melting temperature) due to the onset of plastic deformation at higher temperature.

Early procedures for application of solid lubricant coatings included burnishing of dry powder and bonded coatings. Bonded coatings were applied by incorporating powder into synthetic resin binder. Plasma spray has been used to coat high temperature solid lubricants, such as BaF_2 , CaF_2 and Ag. More recently, vacuum deposition techniques, such as thermal evaporation and sputtering, have been used for applying solid lubricant coatings. With the increased emphasis being placed on high precision and durable coatings, interest has also increased in the development of ion beam technologies for producing such coatings and surface modifications.

UES, Inc., under DOE Contract No. DE-AC02-88CE90026, has performed a program to investigate ion implantation and ion beam mixing techniques to fabricate self-lubricating, well adherent coatings that will produce minimal surface distortion in finished materials. The coating materials considered were: MoS_2 , WS_2 , $\text{BaF}_2/\text{CaF}_2/\text{Ag}$ and B_2O_3 . The initial approach was to ion implant specific elements to synthesize the above mentioned compounds in the near surface

region. Ion beam assisted deposition and ion mixing of thin films were investigated as alternative approaches.

2.0 BACKGROUND

It is now well established that optimized sputtered MoS_2 films display excellent lubricating properties when used under sliding or rotating conditions in dry air, in inert gas or in vacuum [5-7]. However, the endurance was found to be reduced by 2 or 3 orders of magnitude when the films were exposed to air. A fundamental problem with sputter deposited films is their morphology [7]. Sputtered films generally develop a low density, 2-dimensional columnar void structure: platelets of MoS_2 grow near-normal to the substrate with edge-sites exposed outward [7]. The edge sites react readily with oxygen and water vapor causing increased friction and wear of the film. Spalvins [7] observed that during sliding, platelets fracture and most of the film is worn away; only about $0.2\text{ }\mu\text{m}$ of the underlying layer is left to provide lubrication. Consequently, development of ion beam techniques for producing MoS_2 beneath the surface or a well adherent and densified MoS_2 coatings have tremendous potential for applications in transportation systems.

Boron or boron oxide was chosen because of their lubricating property as boric acid when formed in contact with humid air. Boric acid has a layer lattice structure similar to MoS_2 thus providing low friction [8]. This is a very useful lubricant up to about 150°C . It decomposes to boric oxide at about 185°C , thus losing its lubricating ability. For high temperature air applications, alternative solid lubricant materials need to be investigated.

Over the years, some unconventional solid lubricants based on oxides and fluorides have been identified for high temperature applications [3,4]. These are PbO , TiO_x , CdO , LiF , CaF_2 , BaF_2 . Use of oxides has been limited because of their lubricating ability within a narrow temperature range. Fluorides, particularly $\text{CaF}_2/\text{BaF}_2$ eutectic lubricate from $500\text{--}950^\circ\text{C}$ in oxidizing and reducing atmosphere. The lubricating ability of these materials is claimed to be from the existence of planes of perfect cleavage in their crystal structure suggesting low shear strength. In order to increase the lubricating ability over a wide range of temperature, NASA has

formulated a composite of $\text{BaF}_2/\text{CaF}_2$ with Ag [2]. They used plasma spray to lay down these coatings on various surfaces. The plasma spray process consists of transporting powders of the coating components with a carrier gas through a very high temperature, high energy arc containing ionized gas, usually argon. The particles in their passage through this plasma of argon are melted. They impinge on the material to be coated and adhere by a combination of mechanical and diffusion bonding. An excess coating thickness is applied and then machined back to the desired thickness. Thus, plasma spray process has serious limitations for close tolerance applications, such as in bearings. Also, the coatings developed by this technique are generally porous and do not adhere well to the substrate. Adhesion is a major problem with conventional vacuum deposited coating also. Whenever there is a sharp interface between the coating and the substrate in a tribological mechanical component, the interface becomes the site for the degradation of the coating. It is usually the weakest region in the system and quite often yields under stresses associated with operations. Ion beam techniques, such as ion implantation, ion beam assisted deposition and ion beam mixing, have the potential to generate dense, highly adherent coatings and self-lubricating surfaces.

The synthesis of lubricious compounds near the surface by ion implantation is attractive because the adhesion problem associated with coating is no longer present. Also, the dimensional changes in the ion implanted materials are negligible compared to that in the coated materials. Since the implantation induced solid lubricant material will be somewhat embedded in the substrate material and not be in direct contact with the atmosphere, it is possible that the temperature at which oxidation occurs can be raised. One disadvantage of the ion-implanted technique is that it produces a thin ($\leq 0.2\text{-}0.3\text{ }\mu\text{m}$) modified surface layer that may not last very long in an actual application. Also, because of the limitation imposed by sputtering, the volume concentration of the implanted species will not exceed a certain limit (depending upon the energy of the incident ion, the nature of the incident ion and the substrate), thus limiting the extent of improvement. However, due to the aforementioned advantages of ion implantation, it may be a technique of choice, where a limited improvement in the material's life is sufficient.

Ion beam assisted deposition as a process has been investigated for a number of applications over the last few years [9-12]. Most ion beam assisted deposition studies were done

for optical applications since non-porous coating could be fabricated with bulk-like properties. In particular, bulk-like refractive indices have been obtained. Low energy ion or neutral atom bombardment of surfaces and coatings during deposition has been shown to have a pronounced effect on material properties. Typically, low energy refers to the range 1 eV to 10 keV incident particle energies in which case the collisional processes affect the surface and near surface region, giving a gradation of effects from the surface toward the bulk. Higher ion energies, as used in ion implantation, result in deeper sub-surface effects and associated sputtering phenomena. Ion energies (~ 10 eV) which are too low to displace lattice atoms may enhance chemical reactivity (reactive deposition, reactive etching, reactive plasma cleaning) or enhance the desorption of weakly bonded atoms. At higher energies, collision cascades are generated, resulting in the disruption of lattice structure in the near surface region. Also, the high defect density due to nuclear energy loss and high effective temperature due to electronic energy loss may result in enhanced diffusion in the near surface region.

Ion beam assisted deposition may result in changes in a number of film properties compared to a non-bombarded deposition. In addition to impurity and stoichiometry control, ion bombardment can also modify the coating morphology, film stress, grain size, crystalline orientation and mechanical properties of the coatings. Morphology changes are found to be similar to those obtained by raising the substrate temperature in vacuum condensation.

In ion mixing, vacuum deposited coatings are irradiated with high energy ions, the range of which corresponds to the thickness of the coatings, thus resulting in mixing at the interface. The mixing rate generally depends on three different mechanisms [13]. The first and theoretically best understood mechanism is recoil implantation, the efficiency of which is rather low. Second is the cascade mixing mechanism for which kinematic collisional models have been worked out that show it to be generally more efficient than recoil implantation. The third and most complex mechanism is radiation enhanced diffusion in which case the damage produced by the incident ions increases the probability that thermally activated atomic jump will occur. The mechanism of radiation enhanced diffusion may dominate and accelerate the mixing process if the substrate is held at an elevated temperature. Recently, Cheng et al. [14] have found a correlation between the cohesive energy and the onset of radiation enhanced diffusion in ion

mixing: the higher the average cohesive energy of a binary system, the higher the temperature required for the onset of radiation enhanced diffusion. Thermochemical effects can also play an important role in atomic mixing by ion bombardment as shown by Cheng et al. [15] and Johnson et al. [16]. They have correlated the mixing efficiency of a binary system with the heat of formation of a corresponding binary alloy at the nominal 50-50 compositions. In practical situations, all these mechanisms can be involved so that an experimental determination of the mixing rate is necessary to optimize the parameters involved in fabrication of surface alloys by ion beam mixing.

3.0 TECHNICAL OBJECTIVES

Based on the background information presented above, the following major technical objectives were set:

1. To synthesize MoS_2 , B_2O_3 , $\text{BaF}_2/\text{CaF}_2/\text{Ag}$ by ion implantation of constituent ion species.
2. Ion mixing of electron beam evaporated or sputter deposited MoS_2 , WS_2 , $\text{BaF}_2/\text{CaF}_2/\text{Ag}$ layers.
3. Ion beam assisted deposition of $\text{BaF}_2/\text{CaF}_2/\text{Ag}$ layers.

Substrates of Al_2O_3 , ZrO_2 , Si_3N_4 , Ni-base superalloy and steel were used for these investigations.

The research approach described in this report was designed to meet the objectives stated above and represent a direct technical response to the programmatic scope and work statement. It is the opinion of the author that this research has contributed to the development of ion beam techniques to produce solid lubricant coatings of much superior quality in terms of performance that the similar coatings produced currently in the industry.

4.0 RESEARCH WORK CARRIED OUT

4.1 ION IMPLANTATION INDUCED SYNTHESIS OF MoS₂

4.1.1 Experimental Description

Ions of Mo⁺ followed by S⁺ were implanted into polished polycrystalline α -Al₂O₃ and yttria-stabilized ZrO₂. Similar implants were also performed in amorphous SiO₂ layer grown on a Si substrate. The implants were made with 175 keV Mo⁺ at 1×10^{17} cm⁻² and 74 keV S⁺ at 2×10^{17} cm⁻² for Al₂O₃ and ZrO₂ substrates. The implant conditions for SiO₂ substrate were 175 keV Mo⁺ at 4.97×10^{16} cm⁻² and 74 keV S⁺ at 1.02×10^{17} cm⁻². The energies of the Mo⁺ and S⁺ were chosen to provide a nearly overlapping depth profile in all substrates. The dose levels were chosen to obtain a composition of 1:2 for Mo:S. The projected ranges of implanted ions in Al₂O₃ and ZrO₂ substrates were between 500 and 600 Å. The projected range of implanted ions in SiO₂ was ~900 Å.

Although all the substrates were kept at room temperature during ion implantation, a crude measurement indicated that the substrate temperature during implantation might have risen to about 200°C. Post-annealing of the as-implanted materials was done at 700°C for 3 hours in an oxygen-free atmosphere.

Rutherford backscattering (RBS) and Auger electron spectroscopy (AES) techniques were employed to determine the composition and profiles of the implanted species before and after annealing. RBS spectra were taken by using both 3.05 MeV He⁺⁺ and 2 MeV He⁺⁺ beams at normal incidence and at a scattering angle of 168°. The choice of 3.05 MeV He⁺⁺ was made in order to increase the detection sensitivity for surface oxygen owing to the elastic resonance with a cross section about 13 times higher than the RBS cross section. Plan view TEM samples (2×2 mm²) were prepared by mechanical grinding followed by ion milling from the unimplanted side only. A cross-(x)sectional TEM (XTEM) sample of Mo⁺ + S⁺ implanted Al₂O₃ was also prepared employing a technique described elsewhere [17]. In some cases a thin layer of carbon was deposited on the TEM sample in order to avoid charging effects in the electron microscope.

Selected area (SAD) patterns were obtained to determine the structure of the implanted layers. To determine the grain size of the MoS_2 phase, dark field micrographs were obtained by taking part of the 002 diffraction ring in the objective aperture. TEM studies were performed employing a Hitachi H600 scanning transmission electron microscope operated at 100 kV.

4.1.2 Results

4.1.2.1 RBS and AES Analysis

The RBS spectra of $\text{Mo}^+ + \text{S}^+$ as-implanted and annealed ($700^\circ\text{C}/3$ hours) Al_2O_3 using 3.05 MeV He^{++} are shown in Figure 1. Although the doses were adjusted in the ratio of 1:2 for Mo:S for MoS_2 formation, the analysis of RBS spectra of as-implanted Al_2O_3 indicated 1:2.7 for Mo:S. A rough calculation revealed that a surface layer of thickness about $200\text{\AA}$ was sputtered away during Mo implantation. This must have resulted in a loss of implanted Mo. This was also evident from the rather sharp high energy edge of Mo signal. The annealing resulted in a loss of S to bring the ratio Mo:S back to desired 1:2.

Figure 1. RBS Spectra of $\text{Mo}^+ + \text{S}^+$ Implanted and Annealed ($700^\circ\text{C}/3$ Hours) Al_2O_3 .

Because of the overlap of Mo and Zr signals in RBS spectra, AES was performed to determine the profiles of Mo and S in the as implanted and annealed ZrO_2 . Figure 2(a) shows the AES profile of Mo^+ and S^+ implanted ZrO_2 . The ratio of Mo:S is found to be approximately 1:3 as opposed to a desired 1:2, which is due to surface sputtering loss of Mo. Figure 2(b) shows the AES profile of Mo^+ and S^+ implanted and annealed ($700^\circ\text{C}/3$ hours) ZrO_2 . After annealing, the Auger profiles of Mo and S show the concentration ratio of Mo:S to be 1:2 around the peak of the depth distribution.

Figure 2. Auger Profiles of $\text{Mo}^+ + \text{S}^+$ Implanted ZrO_2 (a) As-implanted and (b) Annealed ($700^\circ\text{C}/3$ Hours).

The RBS spectra of as implanted and annealed ($700^\circ\text{C}/3$ hours) SiO_2 substrate using 2 MeV He^{++} are shown in Figure 3. The almost overlapping RBS spectra of implanted and annealed samples showed that the implanted species (Mo and S) did not move upon annealing. The analysis of the RBS spectra of as implanted and annealed SiO_2 samples indicated 1:2.2 for Mo:S. Also the thickness of the SiO_2 layer was estimated to be $\sim 3100\text{\AA}$.

Figure 3. RBS Spectra of $\text{Mo}^+ + \text{S}^+$ Implanted and Annealed ($700^\circ\text{C}/3$ Hours) SiO_2 .

4.1.2.2 TEM Analysis

Transmission electron microscope (TEM) analyses were performed to determine the phases formed in the implanted regions of various substrates.

Figure 4 shows TEM results of as-implanted ($\text{Mo}^+ + \text{S}^+$) Al_2O_3 substrate. From the XTEM micrograph (Figure 4(a)) the thickness of the implanted region was found to vary from $980\text{\AA}$ to $1300\text{\AA}$. Careful observation of the SAD pattern (Figure 4(b)) revealed the presence of two spotty diffraction rings superimposed upon diffuse rings. Two Bragg diffraction spots were also observed. The presence of diffuse rings in the SAD pattern indicates the amorphization of the implanted region. From the standard analysis, the d values of the two spotty diffraction rings were estimated to be $6.12\text{\AA}$ and $3.05\text{\AA}$, which in turn match well with that of the known d values of 002 and 004 reflections of MoS_2 (JCPDS 6-0097). The Bragg diffraction spots observed in Figure 4(b) are attributed to 104 reflection of $\alpha\text{-Al}_2\text{O}_3$. The above observations clearly indicate the amorphization and the formation of MoS_2 phase in $\text{Mo}^+ + \text{S}^+$ implanted Al_2O_3 . The TEM results of $\text{Mo}^+ + \text{S}^+$ implanted and annealed Al_2O_3 are shown in Figure 5. The SAD pattern (Figure 5(a)) from the plan view samples consisted of sharp diffraction rings and Bragg diffraction spots. However, no diffuse rings were found in the SAD pattern. The absence of

a

b

Figure 4 (a) XTEM bright-field micrograph and (b) SAD pattern of as-implanted ($\text{Mo}^+ + \text{S}^+$) Al_2O_3 .

Figure 5 (a) SAD pattern and (b) dark-field micrograph of implanted (Mo⁺ + S⁺) and annealed (700°C/3 h) Al₂O₃.

diffuse rings indicates a complete recrystallization of the amorphous layer after annealing. The d values of the observed diffraction rings were estimated and listed in Table I, together with the known d values of MoS₂ phase. The close match between the observed d values with the known d values of MoS₂ showed the formation of MoS₂ phase. The Bragg diffraction spots were found to be due to α -Al₂O₃. These observations indicate the presence of randomly oriented crystallites of MoS₂ in the perfectly crystalline α -Al₂O₃. From the plan view dark field micrograph (Figure 5(b)), the grain sizes of MoS₂ phase were estimated to be 200-650Å.

Table I. Analysis of the SAD Pattern (Figure 5a) of Mo⁺ + S⁺ Implanted and Annealed Al₂O₃

Observed d Values	Known d Values of MoS ₂ (JCPDS 6-0097)	hkl
6.13	6.15	002
3.07	3.075	004
	2.737	100
2.63	2.674	101
	2.501	102
2.22	2.227	103
2.050	2.049	006
1.815	1.830	105
	1.641	106
	1.581	110
1.54	1.538	008
1.49	1.478	107

White et al. [18] have shown that single crystal α -Al₂O₃ can be amorphized by a stoichiometric implant Al + O at liquid nitrogen temperature. Similar results were also observed by Zhou et al. [19]. McHargue and Yust [20], and McHargue et al. [21] reported room temperature implantation of Cr⁺ and Fe⁺, respectively, up to a dose of 1×10^{17} cm⁻² into single

crystal α - Al_2O_3 . In both cases, the implanted surface remained crystalline, however, in the present work Al_2O_3 surface was amorphized after $\text{Mo}^+ + \text{S}^+$ implantation. A careful comparison with the present work reveals that the mass of implanted ions and total doses employed in the work of McHargue et al. were lower. It should be mentioned that the present work was performed on polycrystalline α - Al_2O_3 whereas the earlier studies [19-22] were done on single crystal α - Al_2O_3 .

White et al. [18] have also studied the recrystallization of amorphous α - Al_2O_3 formed by a stoichiometric implant at liquid nitrogen temperature. At 800°C they found that amorphous α - Al_2O_3 first transformed to γ - Al_2O_3 phase, and after annealing for very long time (~ 100 hours) it eventually transforms to α - Al_2O_3 . Sood [22] studied the recrystallization of α - Al_2O_3 which was amorphized by implanting In and Zn at liquid nitrogen temperature. In this work [22] the γ - Al_2O_3 phase was not observed. These recrystallization studies showed that the intermediate phase formation during the transformation of amorphous to crystalline α - Al_2O_3 may depend on the presence of certain impurities in the amorphous film [23]. Recently, substrate orientation has also been shown to play a dominant role in deciding the mode of recrystallization of amorphous α - Al_2O_3 [19]. The SAD pattern (Figure 5(a)) of Mo^+ and S^+ implanted and annealed Al_2O_3 showed only the presence of diffraction rings of MoS_2 phase and the Bragg diffraction spots of α - Al_2O_3 . No indication of an amorphous phase or any other Al_2O_3 phase other than α - Al_2O_3 was observed, thus indicating that the presence of Mo and S in the implanted region inhibited the formation of intermediate Al_2O_3 phase during amorphous to crystalline transformation.

Figure 6 shows the plan view TEM results of $\text{Mo}^+ + \text{S}^+$ implanted ZrO_2 substrate. The presence of sharp diffraction rings and the absence of any diffuse rings in the SAD pattern (Figure 6(a)) indicated that the surface region of ZrO_2 remained crystalline after ion implantation. The estimated d values of all the diffraction rings except the innermost one were found to match well with the known d values of cubic ZrO_2 (JCPDS 7-337). The estimated d value, $6.12\text{\AA}$, of the innermost diffraction ring was found to match well with that of the 002 reflection of MoS_2 indicating the formation of MoS_2 phase. It should be mentioned that 002 reflection of MoS_2 has

Figure 6 (a) SAD pattern and (b) dark-field micrograph of as-implanted ($\text{Mo}^+ + \text{S}^+$) ZrO_2 .

the highest intensity (JCPDS 6-0097). The AES analysis (Figure 2(a)) of the implanted region of ZrO_2 indicated the Mo to S ratio to be 1:3 while the TEM analysis showed the formation of MoS_2 having Mo to S ratio 1:2. Thus, there is excess sulfur in the implanted region, the material state of which is not clear from the SAD pattern. An EDAX analysis was also not very conclusive because of the overlap of the Mo peak with Zr and S. The grain size of MoS_2 phase was estimated to be 90-390Å from the dark field micrograph (Figure 6(b)). Shown in Figure 7 are the plan view TEM results of $\text{Mo}^+ + \text{S}^+$ implanted and annealed ZrO_2 . The diffraction rings observed in the SAD pattern (Figure 7(a)) are indicative of small crystallites oriented randomly. The estimated d values of the diffraction rings are listed in Table II together with the known d values of ZrO_2 and MoS_2 . The close match between the observed d values with those of ZrO_2 and MoS_2 indicates the formation of MoS_2 phase in the ZrO_2 matrix. The grain size of MoS_2 phase was estimated from the dark field micrograph (Figure 7(b)) to be in the range of 130-700Å.

Cohen et al. [24] have studied 210 keV Yb^+ implanted single crystal ZrO_2 using RBS-channeling techniques. At the Yb^+ dose level of $1.2 \times 10^{17} \text{ cm}^{-2}$ the lattice disorder in the implantation region was found to be very high ($\chi = \text{aligned yield/random yield} = 0.90$), but not amorphous as that would have resulted in a $\chi = 1$. A TRIM calculation indicated that the amount of disorder (No. of vacancies/ion) present in Yb^+ (210 keV, $1.2 \times 10^{17} \text{ cm}^{-2}$) implanted ZrO_2 is about the same as in Mo^+ (175 keV, $1 \times 10^{17} \text{ cm}^{-2}$) plus S^+ (74 keV, $2 \times 10^{17} \text{ cm}^{-2}$) implanted ZrO_2 . The present observation that Mo^+ and S^+ implanted ZrO_2 remained crystalline is in agreement with the work of Cohen et al.

Figure 8 represents the plan view TEM results of Mo^+ and S^+ implanted amorphous SiO_2 substrate. Sharp diffraction rings superimposed on a background of diffuse rings were observed in the SAD pattern (Figure 8(a)). The d values of the sharp diffraction rings were estimated and found to match well with that of the known d values of MoS_2 listed in Table I. The diffuse rings were assigned to that of the amorphous SiO_2 substrate. These observations showed the formation and random orientation of MoS_2 phase in an amorphous SiO_2 substrate. The grain size of MoS_2 phase was estimated from the dark field micrograph (Figure 8(b)) to be in the range of 100-400Å. Shown in Figure 9 is the plan view TEM results of implanted and annealed SiO_2 substrate. The sharp diffraction rings plus the diffuse rings present in the SAD pattern (Figure 9(a)) are

$^+$ JCPDS 7-337 $^{++}$ JCPDS 6-0097

Figure 7. (a) SAD pattern and (b) dark-field micrograph of implanted ($\text{Mo}^+ + \text{S}^+$) and annealed ($700^\circ\text{C}/3 \text{ h}$) ZrO_2 .

Table II. Analysis of the SAD Pattern (Figure 7(a)) of $\text{Mo}^+ + \text{S}^+$ Implanted and Annealed ZrO_2

Observed d Values	Known d Values of MoS_2 (JCPDS 6-0097)	hkl	Known d Values of Cubic ZrO_2 (JCPDS 7-337)	hkl
6.11	6.15	002		
	3.075	004		
2.91			2.92	111
	2.737	100		
2.66	2.674	101		
2.51	2.501	102	2.53	200
2.25	2.277	103		
2.08	2.049	006		
	1.830	105		
1.77			1.80	220
	1.641	106		
	1.581	110		
1.51	1.538	008	1.53	311
1.44	1.478	107	1.464	222
	1.368	200		
	1.340	108		
	1.298	203		
1.25	1.251	116	1.267	400

indicative of small crystallites oriented randomly in an amorphous matrix. The estimated d values of the diffraction rings are found to match well with the known d values of MoS_2 phase listed in Table I. This observation showed that MoS_2 phase persists in the amorphous SiO_2 even after annealing at 700°C . The grain size of MoS_2 phase was estimated from the dark field micrograph (Figure 9(b)) to be in the range of 100-450Å.

The mixing rate generally depends on the
theoretically best understood mechanism is
low. Second is the cascade mixing mechanism
worked out that show it to be generally more
most complex mechanism is radiation enhanced
the incident ions increases the probability that
mechanism of radiation enhanced diffusion
the substrate is held at an elevated temperature
correlation between the cohesive energy and

PARAMETERS

50 keV

1.00 uA

.003 s

20.0 V

1000 V

10 Vp-p

250 eV

100

Figure 9 (a) SAD pattern and (b) dark-field micrograph of implanted (Mo⁺ + S⁺) and annealed (700°C/3 h) SiO₂.

4.1.2.3 Thermodynamic Calculations

As discussed in the previous section, TEM analyses clearly revealed the formation of MoS_2 phase in the Mo^+ and S^+ implanted regions of Al_2O_3 , ZrO_2 and SiO_2 substrates. In order to check whether the MoS_2 phase formation in the oxides investigated is consistent with the thermochemical considerations, we performed calculations to predict the phase equilibrium in the near surface region of implanted substrates before and after annealing at 700°C . The thermodynamic calculation was carried out using a computer program, SOLGASMIX, derived from Eriksson et al. [25-27]. The SOLGASMIX program requires the input of standard Gibbs energies of formation for all compounds which may form in the system and the initial concentrations of the elements. The standard Gibbs energies of formation for the thermodynamic calculations were obtained from the thermochemical tables [28,29]. This program is capable of treating several phases simultaneously, e.g., a gas mixture and several condensed phases, by redistributing elements involved in a system to the pre-defined species of known thermodynamic stabilities, so that a state of minimal Gibbs energy is reached.

It should be noted that the present thermodynamic calculations are intended to theoretically predict the final products of an equilibrated system at given temperatures. Therefore, the driving force toward the equilibrium is indicated by the calculated results. However, the calculations do not reveal the reaction kinetics and the path of phase transformation. Thus, the required time for reaching the equilibrium is not considered in the calculations. Many possible condensed binary phases are considered in the thermodynamic calculations. For example, Mo-Al, Mo-S, Al-S, Mo-O, in Al_2O_3 ; Mo-Zr, Mo-S, Zr-S, Mo-O, in ZrO_2 ; and Mo-Si, Mo-S, Si-S, in SiO_2 were considered.

As mentioned earlier, compositional analyses (RBS and AES) indicated that S to Mo atomic ratio was about 2.2 to 3 in the as-implanted materials while it was close to 2 after annealing. With these results in mind, thermodynamic calculations were performed while varying S to Mo atomic ratio from 1.5 to 3.3. In all cases the calculation predicted MoS_2 as the major phase to be present in the surface regions of Mo^+ and S^+ implanted substrate materials.

Thermodynamic calculations were also performed at two different temperatures, namely, 400K and 1000K. At both temperatures the major calculated phase was found to be MoS₂.

The results of the thermodynamic calculations presented in this section clearly predict the formation of MoS₂ phase in Mo⁺ and S⁺ implanted Al₂O₃, ZrO₂ and SiO₂ substrates. This prediction is in agreement with the TEM results. Although ion implantation is a non-equilibrium process, the thermodynamic calculations presented here will have an important implications in future ion implantation works. This calculation will be extremely helpful in knowing *a priori* the chances of obtaining a desired binary phase by ion implantation of the constituent elements in a given material.

4.1.2.4 Friction and Wear Testing

Friction and wear tests were performed on the reciprocal motion test apparatus described elsewhere [30]. Torroidal sample, Figure 10(a-c), was cut from torroid with 7 mm large radius and 10 mm small radius as shown in Figure 10(a). The sample was fixed on the stationary holder and pressed against a counterbody. The counterbody, Figure 10(b), was attached to the reciprocating beam that was driven by means of a connecting rod, and eccentric powered by a dc electric motor. The contact configuration of the sample and the counterbody is shown in Figure 10(c). The counterbody was oscillating from the left to the right while the sample was held stationary. The oscillation stroke was kept constant at 20 mm. Only like material pairs were tested. Ion implantation was done only to the torrodial samples. Before and after each experiment, all samples were cleaned with acetone in the ultrasonic cleaner and their macroscopic dimensions were measured with tool microscope. During all wear experiments, the load (1.96N) and the maximum sliding velocity (0.08 n/sec) were kept constant. All wear experiments in these experimental series were conducted at room temperature in air.

After each wear experiment, the dimensions of the elliptical wear scar were measured with light microscope and the volume of the worn out torroidal segment was calculated. Four experimental series were conducted. The first two experimental series were devoted to the establishment of a statistical base for friction and wear measurements for alumina and zirconia

Figure 10. Sample and Counterbody. (a) Torroidal Sample; (b) Counterbody; (c) Frictional Contact Configuration. Counterbody is Reciprocating from the Left to the Right and Back.

unimplanted samples. Seven pairs of each material were tested. The duration of each experiment was two hours. The friction force was continuously monitored. The wear volume was measured after completion of the experiment.

The last two experimental series were devoted to the measurement of friction forces and wear rates of the ion implanted samples that were annealed at 700°C for three hours. Three pairs

of each material were tested. The conditions of the experiment were maintained the same as for the first two experimental series.

4.1.2.5 Friction and Wear Results

The friction coefficient of ZrO_2 and Al_2O_3 as a function of time are shown in Figures 11 and 12, respectively. The dotted lines on Figures 11 and 12 correspond to the 95 percent confidence intervals of experimental data points scatter for the unimplanted samples. The friction coefficients for both the Al_2O_3 and ZrO_2 samples are relatively low (about 0.15) in the beginning of the experiment and then gradually increase to a level of about 0.4.

The friction coefficient of the implanted ZrO_2 samples (Figure 11) was considerably lower than unimplanted and stayed below the confidence limit interval for about 80 minutes. As a

Figure 11. Friction Coefficient of ZrO_2 vs. time. Δ -Average Values of Unimplanted Samples. + 's Connected with the Dotted Lines Indicate Borders of the 95 Percent Confidence Limit Intervals for the Scatter of the Experimental Point of the Unimplanted Samples. $\bullet$ -Average Values of Implanted Samples.

Figure 12. Friction Coefficient of Al_2O_3 vs. time. ▲-Average Values of Unimplanted Samples. +'s Connected with the Dotted Lines Indicate Borders of the 95 Percent Confidence Limit Intervals for the Scatter of the Experimental Point of the Unimplanted Samples. ●-Average Values of Implanted Samples.

result, the wear volume of the implanted ZrO_2 samples (Figure 13) was lower than unimplanted by a factor of 4.6 and was also lower than unimplanted and implanted Al_2O_3 samples by factors of 2.9 and 2 correspondingly.

The friction coefficient of the implanted Al_2O_3 samples, being always slightly lower than average values of unimplanted Al_2O_3 samples (Figure 12), was always inside the confidence limit interval. As a result, the wear volume of these samples is only slightly lower than the unimplanted samples (Figure 13).

Figure 13. Wear Volumes of Implanted and Unimplanted Alumina and Zirconia Samples. Filled up Bars are Data for the Unimplanted Samples. Dotted Bars are Data for the Implanted Samples. The Numbers are the Actual Average Wear Volumes.

4.1.3 Discussion and Conclusions

The results presented above demonstrate that MoS_2 can be synthesized in SiO_2 , Al_2O_3 and ZrO_2 surfaces by co-implanting Mo^+ and S^+ ions and subsequent annealing. Although the conditions for implantation and annealing were the same for both ZrO_2 and Al_2O_3 , the friction and wear of ion implanted ZrO_2 were reduced while no appreciable effect was observed for Al_2O_3 . The experimental results presented here do not provide a ready explanation of the difference in behavior between ZrO_2 and Al_2O_3 . However, it should be noted that there are two major differences between Al_2O_3 and ZrO_2 ; first, the thermal conductivity of Al_2O_3 (25.1 W/m.K) is much higher than that of ZrO_2 (3.8 W/m.K); and second, the microstructure of the annealed implanted Al_2O_3 showed large grain crystals ($\geq 2\mu\text{m}$) as revealed from spot pattern

while the ZrO_2 showed ring pattern indicating randomly oriented small crystallites of sizes about the same as that of MoS_2 precipitates ($<0.1 \mu\text{m}$). The implication of the first point is that the friction induced heat at the contact point in ZrO_2 will be more than that in Al_2O_3 .

A higher temperature at contact point in ZrO_2 may cause interdiffusion of MoS_2 precipitates through grain boundaries creating a continuous MoS_2 film between the contacting surfaces resulting in low friction and wear. In Al_2O_3 , the diffusion of MoS_2 precipitates may be hindered by lower contact temperature and lower bulk diffusivity of MoS_2 precipitates in Al_2O_3 grains, thus prohibiting the formation of continuous film.

In conclusion, 1) Ion implantations of $\text{Mo}^+ + \text{S}^+$ into $\alpha\text{-Al}_2\text{O}_3$ and partially stabilized ZrO_2 , and subsequent annealing at 700°C produced MoS_2 precipitates of sizes $.015\text{-}0.7 \mu\text{m}$ in the near surface region; 2) Friction and wear at room temperature in air were considerably reduced in ion implanted ZrO_2 . No appreciable effect was found for the ion implanted Al_2O_3 .

4.2 HIGH ENERGY (MeV) ION MIXING OF MoS_2 COATINGS

Sputtering has been successfully used to apply coatings of MoS_2 on a variety of materials including ceramics [5-7]. A sharp interface between the coating and the substrate is usually obtained in the conventional sputter deposition process. Whenever there is a sharp interface between the substrate and a coating in a tribocomponent, the interface becomes the site for the degradation of the coating. It is usually the weakest region in the system and quite often yields under stresses associated with operations. Ion beams have been used in the past to improve the adhesion of a variety of coatings on a variety of substrates [31-33]. For example, dramatic improvements in bonding of gold films on teflon, ferrite, sapphire and SiO_2 by bombarding them with energetic ions were observed [31]. Both heavy and light ions were used in increasing the bonding of various films/substrate combinations. The mechanism of bonding improvement with heavy ions is thought to be the well-known ion beam induced atomic mixing at the interface. However, the bonding improvement with light ions such as H^+ or He^+ is thought to be due to electronic excitation since the atomic mixing due to nuclear collisions (recoils/cascade) is

negligible or absent in such instances. Thus, there is tremendous opportunity in applying these techniques of ion beam enhanced adhesion for improving the wear life of tribological coatings.

So far, only a few studies have been performed on the ion beam modification of solid lubricant coatings. Chevallier et al. [34] have shown that by bombarding with 400 keV Ar^+ , Kr^+ and Xe^+ ions, the sliding life of MoS_2 on stainless steel could be increased by a factor of 2. Because of the limited range of such ions at 400 keV, irradiations were performed on 50 nm thick films and then redeposited to obtain a total film thickness $\sim 2 \mu\text{m}$. Kobs et al. [35] have performed similar experiments on bearing steel. They used 200-400 KeV Ar^+ and N^+ ions at a dose of $1 \times 10^{16} \text{ cm}^{-2}$ and found an enhancement in sliding life up to about 6 times at a low load (5 N). The film thickness was below $0.5 \mu\text{m}$ because of the limitations of ion energy available to the researchers.

In this section, we present the results of our investigations of high energy (MeV) ion irradiation on the compositional, microstructural and tribological properties of magnetron sputtered MoS_2 films on sapphire, silicon nitride and zirconium oxide. MeV ion beam processing has an advantage over keV ion beam processing because of the penetrability of MeV ions to depths on the order of microns.

4.2.1 Experimental Details

MoS_2 films of thicknesses in the range 50 nm-750 nm were deposited on NaCl, Si, Sapphire (Al_2O_3), Si_3N_4 and ZrO_2 substrates by DC magnetron sputtering in a vacuum chamber with a base pressure of $1.3 \times 10^{-4} \text{ Pa}$. The NaCl and Si wafers were used as substrates for compositional and structural characterizations. Films were deposited by using a power of 200 W on a 5.08 cm diameter target at an Ar pressure of about 4 Pa, and at a deposition rate of 0.8 nm/sec. Ion irradiation of these coatings was made by using 2 MeV Ag^+ ions at a dose of $5 \times 10^{15} \text{ cm}^{-2}$. The energy of the beam was such that the mean range approximately corresponded to the thickness of the film. Rutherford backscattering spectroscopy (RBS) and Auger electron spectroscopy (AES) were used to analyze the stoichiometry of the film. RBS analysis was carried out by using 3.05 MeV He^+ to enhance the sensitivity for detection of oxygen through

the elastic resonance. AES was carried out in a vacuum chamber with a background pressure in the low 10^{-8} Pa range. An electron beam of 5 keV, 1 μ A was used with 10 eV peak-to-peak modulation. Sputtering was performed with 2 keV Ar^+ at an angle of about 30° to the surface normal. Transmission electron microscopic (TEM) analysis was used to determine the microstructure of the films. Thinner films (~ 50 nm) deposited on NaCl were used for that purpose. TEM specimens were prepared by dissolving the NaCl in water and lifting the film on a Cu grid. Also, x-ray diffraction analysis was performed on films of thickness ~ 750 nm deposited on Si wafer. A commercial pin-on-disc tribometer (CSEM-Tribometer) was used to measure friction. The sapphire ball was 6.35 mm in diameter and had a surface finish of approximately 0.002 μm CLA. The Si_3N_4 and ZrO_2 balls were 9.5 mm in diameter. The discs had a surface finish comparable to that of the ball counterface. The balls were firmly secured to the stationary holder of the CSEM-tribometer to assume a ball-on-disc configuration. The discs were attached to the horizontal chuck driven by a variable speed electric motor. Frictional force was monitored by a linear voltage displacement transducer attached to the ball holder and was recorded throughout the friction tests. All tests were performed at room temperature (about 23°C). An air tight Plexiglass enclosure allowed test to be run in both argon and dry air environments. Dead weights of 2 N to 10 N were used during friction tests that were conducted at a constant velocity of approximately 0.06 m/sec. The lifetime of films was represented by the number of revolutions to failure. Depending on wear track diameter, rotational velocity ranged from 30 to 150 rpm. Tribometer was calibrated by applying incremental forces to the pin holder in tangential direction with the increments ranging from one tenth of 1 N to 2 N.

For tribological measurements, the 38 mm discs were first coated with MoS_2 by sputtering and then irradiated only in the central region covering an area of $1.5\text{ cm} \times 1.5\text{ cm}$. The wear tracks were run both inside and outside the ion bombarded area for direct comparison.

4.2.2 Results

4.2.2.1 RBS and AES Analysis of Film Composition and Mixing

RBS spectra of MoS₂ film on sapphire before and after ion irradiation with 2 MeV Ag⁺ at $5 \times 10^{15} \text{ cm}^{-2}$ are shown in Figure 14. The ion irradiated film was somewhat thicker than the unirradiated film, thus showing broader Mo and S signals. However, the slopes of the trailing edges of both Mo signals are the same, indicating no mixing with the sapphire beyond the depth resolution which is about 30 nm under the present experimental conditions. The oxygen is present in the surface layer of both as-deposited and ion-mixed MoS₂. Also, the initial deposit was considerably deficient in S, probably because of preferential sputtering effect. However, after a period of time, a steady state concentration level of S was reached that corresponds to a stoichiometry MoS_{1.77}. The stoichiometry of rf-magnetron sputtered MoS_x films from MoS₂ target has been reported by other authors [34,35] to be in the range $x=1.6-1.9$, consistent with our result.

Figures 15(a) and 15(b) show the AES sputter profiles of MoS₂ coating on sapphire before and after ion bombardment. The presence of oxygen and carbon is clearly evident in these profiles. About 4-5% C and 1% O are usually measured from a clean surface by AES in this vacuum system. Therefore, about 5% C and 3-5% O can be assumed to be present in the film. The interface has a little more of C present as expected because of hydrocarbon adsorption. The slopes of Mo, S, Al and O profiles remained the same after irradiation, indicating no mixing at the interface within the depth resolution ~20 nm.

In order to determine if any chemical interaction between MoS₂ and sapphire has taken place after ion mixing, AES line shapes of S(LMM) and Mo(MNN) were recorded after sputtering at various depths as shown in Figure 16. The curves indicated by 80 and 84 minutes sputter represent the interface region while the one with 60 minutes sputter represents bulk of the film. Again, no difference in line shape is observed except a shift in energy position for the one at 84 minutes. This shift was caused by charging of the sapphire substrate by the electron beam.

Figure 14. Rutherford Backscattering Spectra of MoS₂ Films on Sapphire Before and After Ion Irradiation with 2 MeV Ag⁺, 5×10¹⁵ cm⁻².

Figure 15. Auger Sputter Profiles of MoS₂ Coatings on Sapphire:
(a) Before and (b) After 2 MeV Ag⁺, $5 \times 10^{15} \text{ cm}^{-2}$ Irradiation.

UES MoS₂/A1203 Implanted Region
S LMM & Mo MNN 80 min Sputter

110: 122890.004

Figure 16. Auger Line Shapes of S(LMM) and Mo(MNN) Peaks Corresponding to Figure 15b after Sputtering at Various Depths.

4.2.2.2 Microstructure

Figure 17 represents the selected area diffraction (SAD) pattern and the dark field micrograph of the as-deposited MoS_2 film on NaCl substrate. The presence of diffuse ring in the SAD pattern is indicative of the amorphous nature of the film. Dark field micrograph was taken by placing the objective aperture on part of a diffuse ring. The featureless morphology observed in the dark field micrograph also confirms the amorphous nature of the MoS_2 film. The structure of the 750 nm thick MoS_2 film deposited on Si substrate was determined by x-ray diffraction (XRD). No diffraction peaks were observed indicating the amorphous nature of the film in agreement with the TEM results. The SAD pattern and dark field micrograph of ion irradiated film appeared about the same as Figure 17. SEM examination of the film before and after irradiations also revealed featureless morphology.

Figure 17. SAD Pattern and Dark-Field Micrograph of the As-deposited MoS_2 Film on NaCl Substrate.

Sputtered MoS₂ films by rf diode and rf magnetron techniques usually exhibit crystalline structure at ambient substrate temperature, 20-30°C [5-7]. Amorphous microstructure was reported only at cryogenic substrate temperature [6]. Also, the surface morphology of sputtered MoS₂ as observed by SEM usually shows well known needle structure [5-7]. In contrast, the present results show featureless morphology consistent with amorphous microstructure.

4.2.2.3 Friction and Wear

The friction coefficients as a function of sliding distance (number of revolutions) under various load and ambient conditions are compared for as-sputtered and ion irradiated MoS₂ films. Figure 18(a-d) show the friction coefficient as a function of number of revolutions under various loads and humidity conditions for as-deposited and 2 MeV Ag⁺, 5×10¹⁵ cm⁻² irradiated MoS₂ films on sapphire substrates. The following observations can be made from Figure 18.

1. The endurance of the ion beam mixed MoS₂ film is about an order of magnitude higher than the as-sputtered film under all conditions.
2. The friction coefficient for ion beam mixed MoS₂ film is always higher than the as-sputtered film in the beginning; though at 2 N load and 0-1% relative humidity, the as-sputtered film also showed rather high starting friction coefficient.
3. The ion beam mixed MoS₂ films are significantly more resistant to humidity than as-sputtered films.

Figure 19 shows the friction coefficient as a function of number of revolutions for Si₃N₄ sample under a load of 5 N. As-deposited film broke immediately as opposed to the ion bombarded film that provided lubrication with a friction coefficient of 0.05 up to about 100,000 cycles. Figures 20(a) and 20(b) show the friction coefficient as a function of number of revolutions for ZrO₂ at 5 N and 10 N loads, respectively. Here again, about an order of magnitude increase in wear life with a friction coefficient of about 0.025 was obtained for ion irradiated films.

(a)

(b)

Figure 18. (a-d) Friction Coefficient as a Function of Number of Revolutions Under Various Load and Ambient Conditions for As-sputtered and Ion-mixed MoS₂ Film on Sapphire.

(c)

(d)

Figure 18. (a-d) Friction Coefficient as a Function of Number of Revolutions Under Various Load and Ambient Conditions for As-sputtered and Ion-mixed MoS₂ Film on Sapphire.

Figure 19. Friction Coefficient as a Function of Number of Revolutions for As-sputtered and 2 MeV, $5 \times 10^{15} \text{ cm}^{-2}$ Ion-mixed MoS_2 Film on Si_3N_4 .

(a)

(b)

Figure 20. Friction Coefficient as a Function of Number of Revolutions for As-sputtered and 2 MeV, $5 \times 10^{15} \text{ cm}^{-2}$ Ion-mixed MoS₂ Film on ZrO₂: (a) 5 N, (b) 10 N.

4.2.3 Discussion

The increased sliding life of ion beam mixed MoS_x films has been shown previously by several authors. Mikkelsen et al. [36,37] have shown a factor of 5 enhancement of sliding life of $\text{MoS}_{1.7}$ film on AISI 52100 bearing steel after ion mixing with 400 keV Ar^+ , $3 \times 10^{15} \text{ cm}^{-2}$. This bombardment has resulted in the amorphization of as-deposited crystalline films. Chevallier et al. [34] have bombarded a 50 nm thick MoS_2 film on stainless steel by 400 keV Ar^+ , Kr^+ and Xe^+ ions at varying doses and then continued the sputter deposition to obtain about 2 μm thick film. Depending on the ion dose, an adhesion improvement and a sliding life enhancement of approximately a factor of 2 were obtained. Significantly higher enhancement (a factor of 6 at 5.1 N load) in sliding life was obtained by Kobs et al. [35] when they bombarded a MoS_2 film on AISI M2 tool steel by 200 keV N^+ or 400 keV Ar^+ .

The increased endurance life has been generally attributed to the improvement in film-substrate adherence as well as structural and density change.

The question may be raised, "how important is the adhesion improvement as compared to structural and density change in improving the sliding life?" The structure and density appear to play a major role since only a factor of 2 improvement was obtained by Chevallier et al. [34] when they improved the film-substrate interface adhesion by ion mixing of an initially thin layer (50 nm) prior to the deposition of 2 μm thick layer without ion bombardment.

In the present work, both as-deposited and ion bombarded films were amorphous and, therefore, the improvement can only be due to increase in adhesion and density of the ion beam mixed film. We performed experiments to determine the influence of beam parameters on the wear life, adhesion and density of ion irradiated films which will be described below.

4.2.3.1 Adhesion Measurements

Initial tests of adhesion were performed by using commonly used Scotch tape test that compares the adhesion of film to substrate with the adhesion between tape and the film surface.

The test is "passed" if the tape comes off the film rather than dislodging the films. In the case of MoS₂ film on sapphire, even the as-deposited films passed the Scotch tape test showing their good adhesion strength. Thus, Scotch tape test could not be employed to compare the adhesion strengths of ion irradiated films and unirradiated films.

Rubbing with Q-tip also failed to dislodge any material from both as-deposited and irradiated films.

The adhesion strengths were then measured by using a commercial pull testing machine (Sebastian I). Aluminum pins (2.69 mm diameter) were bonded to the film with an epoxy that was cured for 2 hours at 125°C. Usually, three tests were made on each specimen, and average values are reported. Pull tests were carried out for three doses of 2 MeV Ag⁺ ions and two doses of 1 MeV H⁺ ions. The results are summarized in Table III.

Table III. Measured Adhesion Strength of MoS₂ Films on Sapphire

Ion	Ion Dose (cm ⁻²)	Adhesion Strength (MPa)
Ag ⁺	0	14.4
	1×10 ¹⁵	>68.9
	5×10 ¹⁵	>68.9
	1×10 ¹⁶	>68.9
H ⁺	0	7.16
	5×10 ¹⁵	9.98
	1×10 ¹⁶	7.3

The above table clearly shows a dramatic increase in adhesion strength due to ion bombardment. No dose dependence could be measured because the epoxy failed for all three doses indicating that the bond strengths of irradiated films are higher than the yield strength of epoxy being used.

We made preliminary investigations of the change in density of the film due to ion irradiations. A part of the film on a sapphire sample was irradiated with 2 MeV Ag^+ ions at a dose of $5 \times 10^{15} \text{ cm}^{-2}$. A thickness profilometer was used to measure the step height between the bombarded and the unbombarded areas. The bombarded area was found to be depressed by about 50 nm for the 500 nm thick film. The depression could be the result of both densification of the film as well as loss due to sputtering. Knowing that the sputtering theories are quite well established, we can calculate the loss due to sputtering using a computer code [38]. The loss due to sputtering is calculated to be 9 nm. Thus, a reduction in thickness of 41 nm could be assigned to the densification of the film. Similar experiments with H^+ irradiated sample did not reveal any changes in thickness.

4.2.4 Dose Dependence of Wear Life

Irradiations were performed with 2 MeV Ag^+ ions at $1 \times 10^{15} \text{ cm}^{-2}$, $5 \times 10^{15} \text{ cm}^{-2}$ and $1 \times 10^{16} \text{ cm}^{-2}$, and 2 MeV H^+ ions at $1 \times 10^{16} \text{ cm}^{-2}$. About 7500 Å thick MoS_2 coatings on sapphire substrates were used for these tests. Because of limited time and budget, it was not possible to run these tests up to the extent of failure represented by the steady rise in friction coefficient by a factor of 2. A new criterion of failure was developed by following the spike in the friction coefficient value in the chart recorder that showed that the film starts to break initially at certain small portion of the microscope. Experiments were performed under argon atmosphere using the pin-on-disc test set-up at the Oak Ridge National Laboratory in collaboration with C. Yust. The results of these tests are plotted in Figure 21. It shows that the cycles to penetration is about the same for $1 \times 10^{15} \text{ cm}^{-2}$ and $5 \times 10^{15} \text{ cm}^{-2}$, but increases for $1 \times 10^{16} \text{ cm}^{-2}$. Since no more than two measurements were performed at each dose, the error in the measurement can be large, and the variation between $1 \times 10^{15} \text{ cm}^{-2}$ and $5 \times 10^{15} \text{ cm}^{-2}$ could be within the measurement error. Even the wear life of $1 \times 10^{16} \text{ cm}^{-2}$ irradiated coating is within 20% of the wear life of lower dose implants. Although this variation can be real, the major improvement seems to take place at a rather low dose indicating that a small amount of mixing at the interface is adequate to increase the adhesion of the film to the substrate. Increasing the depth of mixing with increasing dose has only a minor effect on the wear life of the coating.

Figure 21. Dose Dependence of Wearlife for 2 MeV Ag^+ Irradiated MoS_2 Film.

The strength of adhesion for even the lowest dose irradiation exceeded the limit of Sebastian pull testing machine as shown in Table III. Therefore, we were not able to determine whether the adhesion strength increased with dose or not. Also, the decrease in thickness of the film due to irradiation induced densification was not distinguishable for the doses employed here using a surface profilometer with $50\text{\AA}$ resolution. Thus, other more sensitive techniques have to be employed to determine the differences in adhesion strength and density of coatings irradiated at various doses.

The friction coefficient and wear life of 1 MeV H^+ , $1 \times 10^{16} \text{ cm}^{-2}$ irradiated MoS_2 film on sapphire has remained about the same as that of unirradiated film. Adhesion strength of the H^+ irradiated film has not improved, as expected (see Table III). This clearly indicates that the generation of collision cascade through the displacements of lattice atoms are necessary for both mixing and densification of the film leading to the improved adhesion and wear life. The energy loss of high energy H^+ ions due to nuclear collisions is negligible, thus explaining the results.

We performed measurements to explore the dependence of the wear life on the speed of rotation of the coated discs. Table IV lists the results at two different speeds, .063 m/sec and 0.2 m/sec. It is clear that the wear life at higher speed is longer than the wear life at lower speed at all doses, including unirradiated coatings.

Table IV. Dependence of Wear Life on the Speed Doses

Test Condition	Dose, Ag ⁺ (cm ⁻²)	Speed (m/s)	Avg. Cycles to Penetrate
1	0	.063	16,500
2	1×10 ¹⁵	.063	47,100
3	0	.063	24,800
4	5×10 ¹⁵	.063	58,150
5	0	.063	17,200
6	1×10 ¹⁶	.063	65,000
7	0	.20	75,000
8	1×10 ⁵	.20	130,000
9	1×10 ¹⁶	.20	143,000

4.2.5 Traction Tests of Ion Mixed MoS₂ and WS₂ Coatings on M50 Steel

It was shown that ion mixing of DC magnetron sputtered MoS₂ coating on ceramic substrates with 2 MeV Ag⁺, 5×10¹⁵ cm⁻² improved the wear life by 10 to 100 times depending on the substrates. In order to test whether ion mixing can improve the performance of a commercial MoS₂ coating on M50 steel under more severe test conditions than our previously performed pin-on-disc tests, we have undertaken a joint test program in collaboration with Williams International and MRC Bearing Co. Williams International has supplied a M50 disc with MoS₂ coating deposited by Ovonic, Inc. We have coated another similar disc with sputtered WS₂ coating. Both discs were subjected to similar ion beam treatments and then tested by MRC Bearing Co. in their traction test rig.

The utilization of traction testing to evaluate ceramic materials provides frictional information which is used to predict bearing heat generation rates. It is also an excellent way

to evaluate the material response to normal and tangential contact stress. The development of a tangential stress as the contacting bodies depart from pure rolling to incipient sliding and gross slip is an essential feature of the testing process.

4.2.5.1 Traction Tests

The traction tests of coated surfaces were performed by MRC Bearing Co. using the test device developed for evaluating materials and lubricants in complex environments. The test apparatus allows the study of the traction force generated between a single ball and a flat disc as a function of speed, contact stress, degree of slip, temperature, lubricant and material. A schematic of the test apparatus is shown in Figure 22. During testing, the ball drive axis is positioned at an angle to the disc to provide a uniform slip velocity across the circular area of contact. For high temperature testing, the specimens are enclosed in a chamber and heated to the desired temperature up to a maximum of 816°C. The test ball is attached to a drive quill made from a high tungsten, low thermal expansion material. The quill is mounted by way of a tapered seat fit into a rigid high speed spindle assembly. The spindle is mounted on a pair of dovetail slides and a sine plate so that any desired contact geometry can be established at any disc track radius. This also permits several test runs to be made on each ball and disk specimen. A specially designed and constructed electronic control and data acquisition system is utilized for the high temperature traction tester.

Test specimens consisted of 2.064 cm diameter silicon nitride balls and 10.16 cm diameter coated M50 steel disc. The ball speed is held constant at 6.35 ms^{-1} and the disc speed is varied to attain the specified percentage of slip. All test disk surfaces had a measured surface roughness of $0.063 \text{ }\mu\text{m}$ to $0.076 \text{ }\mu\text{m}$. The ball specimens had bearing quality surface finish. A traction test procedure based on prior experience gained in other test programs was adopted. The procedure consisted of +1% slip running (30 seconds to reach +1% slip) and contact loads of 5.44 kg (1.2 GPa) and 11.3 kg (1.86 GPa) at a temperature of 315°C were used.

Figure 22. A Schematic Diagram of the Traction Testing Apparatus.

Two discs were coated: one with 1 μm thick MoS_2 by Ovonic, Inc. using their proprietary process, the other with WS_2 at UES by using DC magnetron sputtering from a 5.08 cm gun at a power of 300 W. The coated discs were irradiated with 2 MeV Ag^+ at a dose of $5 \times 10^{15} \text{ cm}^{-2}$.

Figures 23(a) and 23(b) show the plots of traction coefficients as a function of time for contact loads of 5.44 kg and 11.3 kg, respectively, for as deposited Ovonic MoS_2 coating. Ignoring the very start of the run, it can be seen that the traction coefficient stays at a level ~ 0.1 for about 6 minutes and 2 minutes for 5.44 kg and 11.3 kg, respectively, before it starts to rise and saturates to a level of 0.4.

Figures 24(a) and 24(b) show the same as above for ion-irradiated coating. The traction coefficient at 5.44 kg remained at a level of 0.05 for about 12 minutes and then rises to about 0.124 and stays there another 6 minutes before gradually increasing to a level of 0.35. The life of the coating has increased to about 5 minutes at 11.3 kg load as compared to 2 minutes for the as deposited film. Thus, a significant improvement is attained by MeV ion irradiation of the commercial MoS_2 coatings.

Figures 25(a) and 25(b) show the plots of traction coefficients as a function of time for WS_2 coated disc at loads of 5.44 kg and 11.3 kg, respectively. The traction coefficient at 5.44 kg remained at a level between 0.05 and 0.1 for about 18 minutes before increasing to a level of 0.2. At 5.44 kg, the traction coefficient was about 0.1 for about 12 minutes and then increased to about 0.35. These results are significantly better than Ovonic MoS_2 coating, both before and after ion irradiations.

In conclusion, the wear life of ion mixed commercial MoS_2 coating was ~ 2 -3 times longer than the as-deposited coating under the traction test conditions employed here. The WS_2 coating deposited and ion mixed at UES showed a longer wear life than the ion mixed Ovonic MoS_2 coating.

(a)

(b)

Figure 23. Traction Coefficient as a Function of Time for As-Deposited Ovonic MoS₂ Coating for Contact Loads of (a) 5.44 kg and (b) 11.3 kg.

Figure 24. Traction Coefficient as a Function of Time for 2 MeV Ag^+ , $5 \times 10^{19} \text{ m}^{-2}$ Ion Irradiated Ovonic MoS_2 Coating: (a) 5.44 kg and (b) 11.3 kg.

Figure 25. Traction Coefficient as a Function of Time for 2 MeV Ag^+ , $5 \times 10^{19} \text{ m}^{-2}$ Ion Irradiated WS_2 Coating: (a) 5.44 kg and (b) 11.3 kg.

4.3 ION BEAM PROCESSING OF BaF₂/CaF₂/Ag COATINGS

IBAD and ion beam mixing techniques were utilized to fabricate self-lubricating coatings of CaF₂/Ag and BaF₂/CaF₂/Ag composites. In IBAD, a low energy (~500 eV) Ar⁺ bombardment was used in combination with electron beam evaporation of coating materials. In ion beam mixing, magnetron sputter deposition was used to deposit a mixed composite coating of CaF₂ + Ag, which was subsequently ion beam mixed with 1 MeV Ag⁺ at a fluence of $1 \times 10^{16} \text{ cm}^{-2}$.

It should be noted that the synthesis of BaF₂/CaF₂/Ag through ion implantation was ruled out early in the program because of unacceptably low current of Ba⁺ and Ca⁺ ions.

4.3.1 Experimental Description

4.3.1.1 Substrates

Circular flat discs of 40 mm diameter and 4 mm thickness of both Si₃N₄ and rene 41 Ni-base superalloy were machined to be used as substrates. The discs used for friction and wear tests in the pin-on-disc machine were polished to 0.05-0.06 μm CLA. In addition, NaCl, graphite and Si(100) wafers were used as substrates for coatings to facilitate characterizations of composition and microstructure.

4.3.1.2 Ion Beam Assisted Deposition (IBAD)

A schematic representation of the IBAD system is shown in Figure 26. An electron beam evaporation source provided a vapor of the desired materials which subsequently condensed on the substrate. A quartz thickness monitor, shielded from the ion beam, measured the deposition rate. A Kaufman-type ion gun delivered ions to the depositing coating on the substrate. Two small Faraday cups were placed on both sides of the substrate to continuously monitor the current during deposition. A 500 eV Ar⁺ ion beam was used while depositing the CaF₂/Ag bilayer or BaF₂/CaF₂/Ag multilayered structures on Si₃N₄. The layer thickness for the bilayer deposition

Figure 26. Schematic of Ion Beam Assisted Deposition System at UES.

was: $\text{CaF}_2=170$ nm and $\text{Ag}=80$ nm. The multiple layers were made up of 22 nm BaF_2 and 25 nm CaF_2 alternating with 3 layers each, covered by a 105 nm Ag layer.

4.3.1.3 Sputter Deposition

A magnetron sputter gun (US GUN II) mounted in a diffusion pumped chamber utilizing a 5.08 cm diameter target was used to deposit co-sputtered $\text{CaF}_2 + \text{Ag}$ coatings. The target was made by mixing 60 gms Ag and 20 gms of CaF_2 fine powder and cold pressing at 6.6 MPa. The cold pressed target was sintered at 700°C for 14 hours. This target was electrically conductive and could be used for DC magnetron sputtering. Films were deposited by using a power of 100 W at an Ar pressure of 40 mTorr.

4.3.1.4 Characterization

Composition

Rutherford backscattering (RBS) analysis was used for composition analysis of the deposited coatings. RBS analysis was performed by using either a 2 MeV or a 3 MeV He^{++} beam incident normally on the substrate. The energy analysis of the backscattered ions were performed with a detector at a scattering angle of 178° .

Microstructure

Microstructure of the films were determined from transmission electron microscopic (TEM) analysis using the Hitachi H-600 STEM microscope. For quick evaluation of microstructure, some thin (<100 nm) films were deposited on NaCl crystals. The films were then lifted onto carbon coated Cu grids upon dissolving the NaCl substrate in water. Some TEM samples were also prepared from Si substrates by chemical thinning from the back side.

4.3.1.5 Friction and Wear Tests

The friction and wear tests were performed in a high temperature controlled atmosphere test system at Oak Ridge National Laboratory. The system utilized the pin-on-disc wear test geometry and is fitted with a resistance heater furnace capable of providing test temperatures up to 1000°C, Figure 27. The Si_3N_4 spheres of about 9.5 mm diameter were held in the end of a rod supported by a fixture fitted with force transducers. The discs were clamped against a rotation system driven by a variable speed motor. The sphere and disc elements were translated along a vertical axis to meet within the furnace, forming the test configuration. The force transducers provide continuous measurement of both normal and tangential forces, although typically the values were recorded periodically for short durations. Load was applied to the pin by dead-weight loading. The friction and wear of the coated specimens were evaluated at room temperature, 400°C and 600°C for Rene 41 substrates. The Si_3N_4 specimens were tested at 800°C. An oscillating sliding motion was used; the arc length of the sliding path was 10 mm, and the average sliding velocity was 0.04 m/sec. The test atmosphere was laboratory air for the room temperature tests; at elevated temperatures a nitrogen atmosphere was used. In the case of Rene 41 substrates, the normal load applied during testing was 1 N, and the resultant average contact pressure was 0.2 GPa. However, in the case of Si_3N_4 substrates, it was found necessary to minimize the initial contact stress. This was accomplished by preparing a flat on the Si_3N_4 balls by sliding against a Si_3N_4 disc. A fixed load of 1 N was used for 10 minutes at an average sliding velocity of 0.04 m/sec to prepare the flat. The circular wear scars formed on the Si_3N_4 spheres were subsequently used on the ion beam modified disc surfaces. The average diameter of the flat scar was about 460 μm . The wear flats served as contact surfaces for friction and wear measurements on coated and uncoated discs. A normal load of 3 N was applied to the contact area which resulted in an average contact pressure of 18.1 MPa. The angular width of the reciprocating motion was 45° on wear track diameters of 20-28 mm. This resulted in a maximum sliding velocity of 0.063 m/sec and an average velocity of 0.04 m/sec. The tests were run for 3 minutes in the case of Si_3N_4 and for 10 minutes in the case of Rene 41. Both tangential and normal force values were recorded periodically for intervals of 24 seconds during the run. The extent of surface damage was determined by surface profilometry and optical microscopy.

Figure 27. Schematic Diagram of the Controlled Atmosphere High Temperature Test System. (A) Sphere Used as Pin Member Held in Rod (D). (B) Disc Clamped to Top of Rotating Stage (C). (E) Terminus of Pin Rod and Location of Normal and Tangential Force Transducers. (F) Heating Elements Enclosed Within Quartz Cylinders, the Outer Cylinder (G) Coated with Gold. (H) Insulation at Top and Bottom of Furnace. (I) Water-Cooled Plate. (J) Variable Speed Drive Motor. (K) Baseline for System on Which Enclosure (L) is Seated.

4.3.2 Results

4.3.2.1 Composition

Figure 28 shows the RBS spectrum of an IBAD CaF_2/Ag bi-layer on a Si substrate with thicknesses 170 nm and 80 nm, respectively. From the area under the peaks of Ca and F, one can calculate the composition of the film. The composition of CaF_2 was found to be stoichiometric. Figure 29 shows the RBS spectrum of the magnetron sputtered $\text{CaF}_2 + \text{Ag}$ film on Si. All three components, Ca, F, and Ag, are found to be present from the surface inward. The presence of a small amount of Ar is indicated in the spectrum. The composition of the film can be calculated from the area under the peaks: $\text{CaF}_{2.35}:3.5 \text{ Ag}$. The target composition was $\text{CaF}_2:6.5 \text{ Ag}$. Thus, the film is enriched in CaF_2 as compared to the target. This must be due to the higher sputtering yield of CaF_2 as compared to Ag. Thus, with proper adjustments of target stoichiometry, a desired film stoichiometry can be achieved.

4.3.2.2 Microstructures

Figures 30(a) and 30(b) represent a selected area diffraction (SAD) pattern and a dark field micrograph, respectively, of the CaF_2 film deposited on a NaCl substrate by electron beam evaporation. The d values of the diffraction rings observed in the SAD pattern were estimated. Most of the estimated d values matched well with the known d values of CaF_2 . However, two of the observed d values, viz., 0.24 nm and 0.169 nm do not match with any of the known d values of CaF_2 . The diffraction rings corresponding to these two d values are possibly due to CaO. The intensity distribution along the diffraction rings is indicative of the textured nature of the film. The grain size of the CaF_2 was estimated from the dark field micrograph to be 4-28 nm.

Figures 31(a) and 31(b) represent, respectively, the SAD pattern and the dark field micrograph of a $\text{CaF}_2 + \text{Ag}$ film deposited on NaCl by magnetron sputtering. The sharp diffraction rings observed in the SAD pattern are indicative of the small crystallites oriented randomly in the film. Analysis of the SAD pattern showed the presence of CaF_2 (cubic) and Ag

Figure 28. Rutherford Backscattering Spectrum of CaF_2/Ag Bilayer Coating on Silicon.

Figure 29. Rutherford Backscattering Spectrum of Magnetron Sputtered CaF_2+Ag Mixed Layer on Silicon

Figure 30 (a) Selected area diffraction pattern and (b) dark field micrograph of CaF_2 film deposited by electron beam evaporation.

Figure 31 (a) Selected area diffraction pattern and (b) dark field micrograph of CaF_2+Ag film deposited by sputtering.

in the film. The dark field micrograph shown in Figure 31(b) was obtained by taking part of the first two diffraction rings corresponding to the CaF_2 structure. The grain sizes of CaF_2 was estimated from Figure 31(b) and found to vary from 20-50 nm. The sizes of the Ag grain could not be estimated because of the close proximity of Ag and CaF_2 diffraction rings.

4.3.2.3 Friction and Wear

Three different coating configurations were tested for friction and wear:

- Type 1. A magnetron sputtered CaF_2 + Ag coating of composition $\text{CaF}_{2.35}$:3.4 Ag that was ion mixed with 1 MeV Ag^+ at a fluence of $1 \times 10^{16} \text{ cm}^{-2}$;
- Type 2. An IBAD bi-layer consisting of CaF_2 of 170 nm thickness covered by an 80 nm thick Ag layer;
- Type 3. An IBAD multilayer coating consisting of 3 alternating pairs of 22 nm thick BaF_2 and 25 nm thick CaF_2 layers covered by a 105 nm Ag layer.

1. Rene 41 Substrate

The friction coefficient as a function of time for an uncoated sample at room temperature (RT) and 400°C are shown in Figure 32. The friction coefficient at both temperatures is initially in the range of 0.6-0.8, and remains at that level throughout the tests. The friction coefficient at 400°C is slightly higher than the RT values at the beginning of the tests, ~0.8, than the steady RT value of ~0.65.

Friction coefficients as a function of time for each coating configuration are shown in Figures 33, 34 and 35. Although the normal load was nominally 1 N for all tests, the recorded normal force was different in some cases, as indicated in the figures. A comparison of the friction coefficient values for each of the

Figure 32. Friction Coefficient Versus Time for Uncoated Rene 41.

Figure 33. Friction Coefficient Versus Time for Sputtered and Ion Mixed CaF₂+Ag Layer on Rene 41.

Figure 34. Friction Coefficient Versus Time for Ion Beam Assisted Bilayer CaF_2/Ag on Rene 41.

Figure 35. Friction Coefficient Versus Time for Ion Beam Assisted Multilayer $\text{BaF}_2/\text{CaF}_2/+ \text{Ag}$ on Rene 41.

temperatures investigated indicated that for each of the coated specimens, the friction coefficient remains in the range 0.2 to 0.3 only at 600°C. At both RT and 400°C, the friction coefficient is initially 0.2 to 0.3, but increases steadily during the test. In the RT tests, the value attained at the end of the ten minute test is about 0.5.

In the case of the type 2 coating, the integrity of the coating was maintained during the entire test at 400°C, even though the load was higher than 1.2 N (Figure 34). The friction coefficient remained about 0.3 during the test and the specimen surface was not heavily disturbed. The surface condition corresponding to a test at 400°C, 1.3 N, 612(b), is shown in Figure 36, where it can be seen that the center of the wear track showed a loss of surface to a depth of 100 nm, slightly deeper than the original silver layer (80 nm), but well within the total thickness of the original coating. The removal of the silver layer is often not detected in the profilometer traces, apparently due to the softening of the silver after exposure to the elevated temperatures and the consequent penetration of the silver layer by the profilometer tip. In the case of the type 3 coating, the friction coefficient remained about 0.4 during the test at 400°C except in one instance, where it increased to 1.0 (Figure 35). Inspection of the corresponding wear track and surface profilometry of that track showed that the coating had been completely removed at the track center and a large groove about 3.5 microns deep was formed in the specimen surface. A similar result was obtained in a duplicate test on the type 3 coatings at 400°C, and the wear groove formed was again about 3 microns deep. However, at a lower load, 0.6 N, the coating remained intact and the friction coefficient stayed below 0.5 for the entire test. In the RT tests, the friction coefficient did not become greater than 0.5 even when the substrate was exposed, and the deformation of the substrate was not as severe.

At 600°C the friction coefficient did not become greater than 0.3 for any of the coated specimens, and the coating was retained for the entire test duration.

Figure 36 Optical Micrographs of Wear Track Specimen, Type 2 (612B), Run at 400°C

Surface profilometry confirmed the appearance of moderate surface material removal for each of the coated specimens. For example, Figure 37 shows a trace of the surface for specimen 615(A) indicating removal of approximately 160 nm of the 250 nm thick coating. At the center of the wear path the depth of material removal is greater, indicating the beginning of significant wear of the substrate.

2. Silicon Nitride Substrate

Figure 38 shows the friction coefficient as a function of time for IBAD bi-layers CaF_2/Ag on Si_3N_4 at both RT (22°C) and 800°C. The friction coefficient in the beginning of the test is 0.1 and 0.2 at 800°C and RT, respectively, as compared to 0.5-0.7 for uncoated Si_3N_4 . The friction coefficient at 800°C remained at about 0.1-0.15 for a considerable length of time, finally reaching a value of about 0.3 at the end of the experiment. However, the RT friction coefficient monotonically increased to about 0.6 as compared to about 0.8 for uncoated Si_3N_4 .

Wear was studied by inspecting the wear scars of the balls and the wear tracks in the flat plate under the optical microscope. Figures 39(a-d) show the optical micrographs of wear scars of the Si_3N_4 balls before and after the friction tests on the Si_3N_4 discs without (39(a,b)) and with (39(c,d)) CaF_2/Ag coating. The wear volume has been measured from these wear scars and the results listed in Table I. It can be seen that a significant wear reduction, about a factor of 7, has taken place at both RT and 800°C. The wear of the disc could not be determined because of the absence of well-defined grooves as indicated by surface profilometry, and relatively high initial surface roughness. However, optical microscopy was used to qualitatively evaluate the wear of the flat plates. For example, Figures 40(a) and 40(b) show the comparison of the wear tracks in Si_3N_4 made by sliding the Si_3N_4 ball without and with the CaF_2/Ag coating, respectively. It is clear that the wear track is wider in the uncoated sample as compared to the coated sample, and that the Ag coating in the coated sample is dragged toward the center of the track.

Figure 37. Surface Profilometer Scan of the Wear Track of Specimen Type 2, 600°C (615A).

Figure 38. Friction Coefficient Versus Time of Ion Beam Assisted CaF₂/Ag Coating on Si₃N₄ at 22°C and 800°C.

Microstructure of the films were determined from transmission electron microscopic (TEM) analysis using the Hitachi H-600 STEM microscope. For quick evaluation of microstructure, some thin (<100 nm) films were deposited on NaCl crystals. The films were then lifted onto carbon coated Cu grids upon dissolving the NaCl substrate in water. Some TEM samples were also prepared from Si substrates by chemical thinning from the back side.

104X

Figure 39 Optical Micrographs of Wear Scars of Si_3N_4 Balls (a) Before, and (b) After the Friction Test on Uncoated Si_3N_4 Disc, (c) Before and (d) After the Test on CaF_2/Ag Coated Si_3N_4 Disc.

INDUSTRIAL CONTACT/TECHNOLOGY TRANSFER

1. Mr. Hudson Scheifele of Williams International contacted us for testing the high energy ion beam enhanced MoS_2 and WS_2 coatings for their applications. We provided ion mixed MoS_2 and WS_2 coatings on 4 inches diameter M50 discs and Si_3N_4 balls for traction tests. Results of these tests are included in the present report (see Section 4.2.4.1). Results showed improved life of ion mixed coatings as compared to other commercial coatings under the severe traction test conditions. Based on these results, Fuels and Lubrication Branch of the U.S. Air Force at the Wright-Patterson Air

A

B

Figure 40 Optical micrographs of wear tracks in Si_3N_4 (a) without and (b) with CaF_2/Ag coating.

4.3.3 Discussion

The results presented above demonstrate the effectiveness of layered or mixed composite CaF_2 , BaF_2 , Ag coatings in reducing the friction and wear of ceramic-metal and ceramic-ceramic contacting surfaces at room and elevated temperatures. Various compositions of these materials were synthesized by Sliney and co-workers and deposited as coating by plasma spray [2,39]. The coatings deposited by plasma spray are usually rough and porous, and relatively poorly bonded to the substrate, as compared to most PVD coatings. The present paper demonstrates the capability of advanced ion beam enhanced PVD techniques to synthesize precision coatings of CaF_2 , BaF_2 and Ag. Both electron beam evaporation and sputtering processes were able to produce stoichiometric deposition of fluorides. Ion beams were used either during deposition, (IBAD), or after the deposition (IBM), to increase the bonding of the film with the substrate and to densify the film. Both of the processes are known to improve the tribological performance of thin coatings.

The present results show equivalent performance of coatings deposited by either IBAD of layered structures of CaF_2/Ag and $\text{CaF}_2/\text{BaF}_2/\text{Ag}$ or by ion-irradiated co-sputter deposited $\text{CaF}_2 + \text{Ag}$ mixtures. The presence of BaF_2 in the layered structure had no noticeable influence in the friction and wear behavior at both room and elevated temperatures. This is not surprising, since BaF_2 and CaF_2 have similar crystal structure and both are thermally stable under the condition employed in this investigation. The use of BaF_2 in plasma sprayed film is dictated by the need to lower the melting temperature of CaF_2 by forming an eutectic of $\text{BaF}_2/\text{CaF}_2$.

The friction coefficients of uncoated Rene 41 sliding against a Si_3N_4 ball is high, ~ 0.6 - 0.8 , as expected. The wear depth is large because of penetration and plowing of the relatively soft Rene 41 alloy by the Si_3N_4 ball. The friction coefficient at 400°C is only slightly higher, ~ 0.8 , than the friction coefficient at ambient temperature, ~ 0.6 , which may be due to the presence of an oxide layer on the Rene 41 surface. Although an effort was made to maintain a dry nitrogen environment in the friction chamber, visual inspection of the surface after high temperature friction tests revealed evidence of some surface oxidation.

With all three coatings, the friction coefficient started at about 0.2 and reached a steady state value of 0.4 at RT. A friction coefficient of 0.4 is usually obtained from an Ag coated surface, as shown by Erdemir et al. [40] on an IBAD Ag coated ZrO₂ rubbing against an uncoated ZrO₂ ball. In the present investigation, the surface of the layered coatings was Ag and the sputtered coating mixture contained Ag as the dominant component, thus explaining the agreement with Ref. 40. At 400°C, the friction coefficient for the sputtered coating is about the same as that at RT. However, for the IBAD, CaF₂/Ag bi-layer, it is lower, ~0.2-0.3. The friction coefficient for the IBAD multilayer scatters within the range 0.2-0.4. At 600°C, the layered coatings produce friction coefficient values around 0.2, and the sputtered coating showed the largest amount of scatter. Sample-to-sample variations cannot be resolved with the limited test results presently available.

The friction coefficient at 800°C for an IBAD CaF₂/Ag coated Si₃N₄ disc sliding against Si₃N₄ is about 0.1 for the first two minutes, finally reaching ~0.3 at the end of the test. The wear resulting from this test is significantly reduced as compared to uncoated Si₃N₄. It should be noted that, without the addition of Ag, the BaF₂-CaF₂ composite was shown to provide a low friction coefficient, ~0.1, at high temperature, ~800°C [41].

5.0 B⁺ ION IMPLANTATION

B⁺ ion implantation into steel and sapphire samples were performed in order to study the synthesis of boric acid in the contact region through the following reactions as suggested by Erdemir et al. [8].

Discs of sapphire, M50 steel, AlN and Si₃N₄ were implanted with 60 keV B⁺ ions at 5×10¹⁷ cm⁻². The mean ranges in these materials as calculated by TRIM computer simulation are 1580Å, 1030Å, 1800Å and 1772Å in the same order. The Auger sputter profiles of the B⁺

implanted sapphire is shown in Figure 41. The profile clearly indicates that there is no boron in the surface region up to a depth of approximately 500Å and the peak of the distribution is at about 2500Å which is deeper than the calculated mean range.

Preliminary friction and wear tests on the implanted samples were performed by A. Erdemir at the Argonne National Laboratory. A 440C ball was used to run the friction test on B⁺ implanted M50 steel disc, while a sapphire ball was used for the B⁺ implanted sapphire disc. Figure 42 shows the plot of the friction coefficient data for implanted M50 steel. No effect of B⁺ implantation on the friction coefficient was observed. In the case of sapphire, a very small reduction of friction coefficient was observed in the implanted area upon annealing the sample at 325°C for 2 hours (Figure 42). The friction coefficient of the implanted sample before annealing was the same as that of the unimplanted sample. It appears that the annealing might have caused the out diffusion of B toward the surface. From the width of the wear track on both steel and sapphire samples, it appeared that a small reduction occurred in implanted samples.

Thus, in conclusion, the implantation of B⁺ did not produce a significant beneficial effect in terms of reducing friction and wear in the samples studied in this program. Further studies are underway at the Argonne National Laboratory (A. Erdemir) on other substrate materials.

6.0 CONCLUSIONS AND RECOMMENDATIONS

A three year technical effort was conducted to evaluate the ion beam processing technology for the fabrication of solid lubricant coatings and surface modifications. The project demonstrated the potential for ion beam processing techniques, such as ion implantation, ion beam mixing and IBAD to produce precision coatings or surface modifications for reduction of friction and wear, particularly of ceramics.

UES B+ IMPLANTED SAPPHIRE AES Depth Profile

KEY

X Al
Δ B
□ C
★ O

Figure 41. Sputter Auger Profiles of 60 keV B⁺, 5×10¹⁷ cm⁻² Implanted Sapphire.

Figure 42. Friction Coefficient as a Function of Number of Revolutions for B^+ Implanted Steel and Sapphire Samples.

6.1 CONCLUSIONS

The following specific conclusions can be drawn from the results of this research:

1. Lubricating dichalcogenides such as MoS_2 can be synthesized in the near surface region of ceramic materials, such as Al_2O_3 and ZrO_2 through ion implantations of constituent elements.
2. Implantation induced synthesis of MoS_2 resulted in the reduction of friction and wear of Al_2O_3 and ZrO_2 .
3. High energy (MeV) ion beam mixing of sputtered MoS_2 coating on sapphire, ZrO_2 and Si_3N_4 resulted in the increase in sliding wear life of the coatings by one to two orders of magnitude.
4. The increased wear life due to MeV ion beam mixing was attributed primarily to the increase in adhesion strength of the coating with the substrate due to ion beam mixing at the interface, and also, to a smaller extent, to an increase in density of the coating.
5. Both sputtering and electron beam evaporation techniques were able to produce smooth, stoichiometric composite coatings of $\text{BaF}_2/\text{CaF}_2/\text{Ag}$.
6. High energy (MeV) ion beam mixing of thin (2500-3000Å) sputtered composite, $\text{CaF}_2 + \text{Ag}$, coatings on Rene 41 Ni-base superalloy reduced the friction coefficient against a Si_3N_4 ball from ~0.7 to 0.4 at RT, and to about 0.2-0.3 at 600°C.
7. Simultaneous ion bombardment with e-beam evaporation resulted in a well-adherent multilayer structure of $\text{BaF}_2/\text{CaF}_2/\text{Ag}$. Thin coatings of CaF_2/Ag

on Si_3N_4 have reduced the friction coefficient against a bare Si_3N_4 ball from ~ 0.8 to 0.4 at room temperature, and to $\sim 0.1-0.15$ at 800°C .

6.2 RECOMMENDATIONS

Based on the results of this program, the following recommendations are made:

1. The processes developed in this program can be further optimized to obtain maximum benefit. For instance, the ion beam parameters, such as dose and energy for synthesizing lubricant compounds, e.g., MoS_2 in the near surface region of a ceramic material should be optimized. Similarly, the ion beam mixing parameters, such as type of ion, energy and dose can be further optimized for improving the wear life of MoS_2 or WS_2 coatings on ceramic and metallic substrates.
2. Application specific testings of the ion beam processed coatings should be performed to evaluate the advantages and limitations of these coatings as compared to the conventionally processed coatings.

REFERENCES

1. H. J. Larson, "26th Automotive Technology Development Contractors' Coordination Meeting, October 24-27, 1988, Dearborn, MI," U.S. DOE, Office of Transportation System, Washington, DC 20585.
2. H.E. Sliney, Symposium on Lubricants for Extreme Environments at the ASME/ASLE Lubrication Conference, Washington, DC, 5-7 October 1982.
3. P. Sutor, MRS Bulletin, May 1991, p. 24.
4. J.K. Lancaster, CRC Handbook of Lubrication, Vol. II, Ed. E.R.
5. E.W. Roberts and W.B. Price, Mater. Res. Soc. Symp. Proc., 140, 251 (1989).
6. T. Spalvins, Thin Solid Films, 73, 291 (1980).
7. T. Spalvins, Thin Solid Films, 96, 17 (1982).

8. A. Erdemir, *Lubr. Eng.*, 47, 168 (1991).
9. J. Franks, *J. Vac. Sci. Technol.*, 16, 181 (1979).
10. E.H. Hirsch and I.K. Varga, *Thin Solid Films*, 52, 445 (1978).
11. J.J. Cuomo, J.M.E. Harper, C.R. Cuarnieri, D.S. Yee, L.J. Attanasio, J. Angielello, C.T. Wu, and R.H. Hammond, *J. Vac. Sci. Technol*, 20, 349 (1982).
12. M.K. Hibbs, B.O. Johansson, J.E. Sundgren, and U. Helmersson, *Thin Solid Films*, 122, 155 (1984).
13. Y.T. Cheng, *Mat. Sci. Rep.*, 5, 45 (1990).
14. Y.T. Cheng, X.A. Zhao, T. Banwell, T.W. Workman, M.A. Nicolet, and W.L. Johnson, *J. Appl. Phys.*, 60, 2615 (1986).
15. Y.T. Cheng, M. Van Rossum, M.A. Nicolet, *Appl. Phys. Lett.*, 45, 185 (1984).
16. W.L. Johnson, Y.T. Cheng, M. Van Rossum and M.A. Nicolet, *Nucl. Instr. Meth.* B7-8, 657 (1985).
17. A.K. Rai, M.H. Rashid, P.P. Pronko, A. Ezis and D.W. Langer, *J. Electron Microsc. Techn.* 5, 45 (1987).
18. C.W. White, L.A. Boatner, P.S. Sklad, C.J. McHargue, J. Rankin, G.C. Farlow, M.J. Aziz, *Nucl. Instrum. Methods Phys. Res.* B32, 11 (1988).
19. W. Zhou, D. X. Cao and D.K. Sood. Presented at the MRS Fall Meeting, (Nov. 27-Dec. 2, 1989). To be published.
20. C.J. McHargue and C.S. Yust, *J. Am. Ceram. Soc.* 67, 117 (1984).
21. C.J. McHargue, G.C. Farlow, P.S. Sklad, C.W. White, A. Perez, N. Komniliotis and G. Marest, *Nucl. Instr. Meth.* B19/20, 813 (1987).
22. D.K. Sood, *Proc. NATO Advanced Study Institute: "Structure - Property Relationships in Ion Beam Surface-Modified Ceramics - Theory and Applications."* Il Ciocco, Castel Vecchio Pascoli, Italy (Aug. 28-Sept. 9, 1988).
23. B.A. Van Hassel and A.J. Burggraaf, *Appl. Phys.* A49, 33 (1989).
24. C. Cohen J. Siegka, M. Berti, A.V. Drigo, M. Croset and M.M. Tosic, *Radiat. Eff.* 64, 221 (1982).
25. G. Eriksson, *Chem. Sci.*, 8, 100 (1975).

26. G. Eriksson, *Acta. Chem. Scand.*, 25(7), 2651, (1971).
27. G. Eriksson and E. Rosen, *Chemica Scripta*, 4, 193, (1973).
28. I. Barin and O. Knacke, *Thermochemical Properties of Inorganic Substances* (Springer-Verlag, NY 1973).
29. M.W. Chase, Jr., C.A. Davis, J.R. Downey, Jr., D.J. Furip, R.A. McDonald, and A.N. Syverud, *JANAF Thermochemical Tables*, third ed. (National Bureau of Standards 1985).
30. V. Aronov, "Wear Mechanisms of Partially Stabilized Zirconia," *SAE Technical Paper Series*, 870420 (1987).
31. B.T. Werner, T. Vreeland, Jr., M.N. Mendenhall, Y. Qui, and T.A. Tombrello, *Thin Solid Films*, 104, 163 (1983).
32. T.A. Tombrello, *Nucl. Instr. Meth.*, 218, 679 (1983).
33. J.F.E. Baglin and G.J. Clark, *Nucl. Instr. Meth.*, B7/8, 881 (1985).
34. J. Chevallier, S. Olesen, G. Sorensen and B. Gupta, *Appl. Phys. Lett.*, 48, 876 (1986).
35. K. Kobs, H. Dimigen, H. Hiibsch, H.J. Tolle, R. Leutenecker, and H. Ryssel, *Appl. Phys. Lett.*, 49, 496 (1986).
36. N.J. Mikkelsen, J. Chevallier, G. Sorensen and C.A. Straede, *Appl. Phys. Lett.*, 52, 1130 (1988).
37. N.J. Mikkelsen and G. Sorensen, *Mat. Res. Soc. Symp. Proc.*, 140, 265 (1989).
38. J.P. Biersack, L. Haggmark, *Nucl. Instr. Meth.*, 174, 257 (1980).
39. H.E. Sliney, *Tribol. Int.*, 15(5), 293 (1982).
40. A. Erdemir, D.E. Busch, R.A. Erck, G.R. Fenske and R. Lee, *Lubr. Eng.*, 47, 863 (1991).
41. H.E. Sliney, *ASLE Trans.*, 8, 307 (1965).

APPENDIX A

PRESENTATIONS/PUBLICATIONS RESULTING FROM THIS CONTRACT

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Synthesis of MoS_2 in the Near Surface Region of Al_2O_3 and ZrO_2 by Ion Implantation, A.K. Rai, R.S. Bhattacharya, S.C. Kung and D. Patrizio, Mat. Res. Soc. Symp. Proc. 157, 549 (1990).

Co-implantation of Mo^+ and S^+ in Al_2O_3 and ZrO_2 and Their Tribological Properties, R.S. Bhattacharya, A.K. Rai, and V. Aronov, Tribology Transactions 34, 472 (1991).

Formation of MoS_2 Phase in Al_2O_3 , ZrO_2 and SiO_2 Through Ion Implantation of Constituent Elements, A.K. Rai, R.S. Bhattacharya and S.C. Kung, J. Appl. Phys. 68, 5169 (1990).

High Energy (MeV) Ion Beam Modifications of Sputtered MoS_2 Coatings on Sapphire, R.S. Bhattacharya, A.K. Rai and A. Erdemir, Nucl. Instr. Meth. in Phys. Res. B59/60, 788 (1991).

Ion Beam Assisted Depositions of TiO_2 and CdO Coating on M50 Steel and Their Tribological Properties, A.K. Rai, R.S. Bhattacharya and C.S. Yust, Nucl. Instr. Meth. in Phys. Res. B59/60, 280 (1991).

Co-implantation of Mo^+ and S^+ in SiO_2 , A.K. Rai and R.S. Bhattacharya, J. Mater. Res. 6, (1991).

Ion Beam Processing of High Temperature Solid Lubricating Coatings, R.S. Bhattacharya, A.K. Rai and C.S. Yust, Submitted to Lubrication Engineering for publication. This is also to be presented at the STLE Annual Meeting at Philadelphia, May 1992.

High Energy (MeV) Ion Beam Modifications of Sputtered MoS_2 Coatings on Ceramics, R.S. Bhattacharya, A.K. Rai, A.W. McCormick and A. Erdemir, To be presented at the 1992 ASME/STLE Tribology Conference, San Diego, October 1992.

APPENDIX B

INDUSTRIAL CONTACT/TECHNOLOGY TRANSFER

INDUSTRIAL CONTACT/TECHNOLOGY TRANSFER

1. Mr. Hudson Scheifele of Williams International contacted us for testing the high energy ion beam enhanced MoS₂ and WS₂ coatings for their applications. We provided ion mixed MoS₂ and WS₂ coatings on 4 inches diameter M50 discs and Si₃N₄ balls for traction tests. Results of these tests are included in the present report (see Section 4.2.4.1). Results showed improved life of ion mixed coatings as compared to other commercial coatings under the severe traction test conditions. Based on these results, Fuels and Lubrication Branch of the U.S. Air Force at the Wright-Patterson Air Force Base is now considering further evaluation of ion mixed coatings.
2. Frank Kustas of Martin Marietta Space Systems, Denver, Colorado was interested in evaluating our ion mixed MoS₂ films on steel substrates. We coated some samples supplied by him which were evaluated and compared with other commercial coatings. Their evaluation was done for a short duration under low stress. It was determined that, although the coatings from all the vendors performed well, ion mixed coatings exhibited the lowest friction value.
3. Mr. Heinrich J. Hess of Rolex SA, Switzerland inquired about the details of MoS₂ synthesis by ion implantation. He is interested in applying this process to small watch parts made of ZrO₂, ruby and various other alloys.
4. The fuels and lubrication group at the Wright Patterson Air Force Base is interested in ion implantation/IBAD of solid lubricants in M50 steel and NBD-100 Si₃N₄ for bearing applications. We received a small grant (\$50K) from them to extend the scope of our research under DOE-Tribology Program to include NBD-100 Si₃N₄.
5. Rabi Bhattacharya and Peter Pronko visited the Cummins Technical Center to discuss applications of ion implantation and mixing of lubricious compounds to their problems in friction and wear. Discussion was held on the possibility of applying high energy ion-mixed MoS₂ coating on plunger assemblies in the new high pressure fuel injectors. A visit by T. Yonushonis and M. Naylor to UES is to take place in the near future for further discussion of joint research in this area.
6. Mr. Mark Baker of Marshall Space Center, Alabama, was interested in evaluating our ion mixed MoS₂ coatings for space applications. We delivered a number of coated rings and blocks for testing under atomic oxygen. Although we did not receive any report of these test results, we were told that the coatings performed well under the conditions employed in the tests. We are pursuing further evaluations for possible applications at NASA.

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