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## USES OF ION BOMBARDMENT IN THIN-FILM DEPOSITION

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### ABSTRACT

Use of plasma- and ion-beam-modified surfaces and surface coatings is continually expanding in engineering disciplines. The purpose of these modifications and treatments is to impart favorable properties, such as wear resistance and lubricity, to the surfaces, while at the same time retaining the strength or toughness of the bulk materials. Energetic-ion bombardment can be used to modify the structural and chemical properties of surfaces or applied coatings. Ion-implantation has been used for many years, and recently, other surface-modification techniques, among them ion-beam mixing and ion-beam-assisted deposition, have attracted attention because they permit application of highly adherent lubricious and wear-resistant films. In this paper, ion-beam techniques are described from the viewpoint of ion-surface interactions, and some avenues for the engineering of tribological surfaces are presented.

### INTRODUCTION

In the process of selecting a material, a compromise must often be made between bulk-mechanical properties and surface tribological properties, with neither property being at its optimal value. Metals and alloys are often the materials of choice when properties such as strength, ductility, and toughness are needed. Ceramics and hard compounds are frequently found to be best when excellent tribological properties, such as high-temperature hardness and corrosion resistance, are required. Thus, there is much interest in technologies that allow one to retain the desirable properties of a bulk material while imparting favorable tribological and chemical properties to its surface. Development of heat-resistant metals and engineering ceramics has progressed rapidly, and parallel advances in surface tribology are needed. In particular, the

development of tribological systems for spacecraft (1-2), advanced heat engine (3-4), and aeronautical applications (5) present special obstacles. Plasma processes such as RF and DC magnetron sputtering and plasma-assisted chemical vapor deposition (CVD) have long been used for the application of surface coatings that improve the wear resistance or frictional properties of materials. More recently, ion-beam-based techniques have been studied and used as a means of applying coatings to, or modifying the surfaces of electronic, biomedical, and engineering materials.

The field of ion-assisted processes is broad, and encompasses such techniques as ion plating, activated reactive evaporation, ionized cluster beam deposition, and plasma-enhanced CVD. In this paper we will principally be concerned with techniques that employ beams of ions with well-defined energy and flux. These include ion implantation (II) and ion-beam mixing (IBM) techniques, which use high-energy ions to penetrate tens or hundreds of nanometers into a specimen, and ion-beam-assisted deposition (IBAD), which uses concurrent low-energy ion bombardment to alter the properties of growing films. When a surface is bombarded with energetic ions, the chemical, microstructural, and physical properties of the surface can be significantly changed. The nature of the changes depends on the ion species, mass, energy, dose, and the temperature of the substrate. Ions with high kinetic energies will penetrate into the near-surface region and produce chemical changes. Collisions of the ions with specimen atoms will disorder and displace large numbers of atoms from their equilibrium lattice sites. Low-energy ion bombardment can be used to densify growing films by eliminating the columnar microstructure that commonly occurs during deposition at low temperature.

Many combinations of ion and film deposition parameters are possible, and noteworthy advances have been made in decreasing friction and wear. Some approaches are extensions of conventional methods of tribology. For example, when a steel rolling element is implanted with N atoms, the nitrides that form increase wear resistance (6). Other approaches make use of ion bombardment to provide novel and perhaps unexpected means of reducing friction or wear. Steels

implanted with Ti, C, and N became amorphous and experienced considerably less dry-sliding friction (7).

II, which uses high-energy ions that penetrate directly into the substrate to cause microstructural and chemical changes, has proven successful for a wide variety of applications (8). The technique of II deposits no film so the problem of film delamination is eliminated. However, it is limited in terms of the quantities of atoms that can be injected into the treated parts. Lubrication for corrosional use may require the introduction of alloying elements in much larger quantities. IBM and IBAD are relatively new techniques, but are attracting increasing attention because they allow deposition of thicker films of varied composition and structure. IBM and IBAD are processes that use energetic ions to modify a film. In IBM, one or more thin films are applied to the substrate and then the atoms in the film are collisionally "mixed" by high-energy ions. In IBAD, a film is bombarded with ions during deposition. Sometimes the energetic particles are neutralized, so we will call any energetic particle an ion, even if it is uncharged.

Although generally more expensive than CVD or plasma surface treatments, ion-beam-assisted processes have several advantages: 1. the energy and flux of the ions can easily be controlled and the ions are essentially monoenergetic; 2. low background pressures can be maintained, minimizing the introduction of unwanted gases into films; 3. low substrate temperatures can be used because the driving force for atomic rearrangement is supplied by the kinetic energy of the ions instead of by thermal activation; 4. reactive ions may be used to produce compound films of controlled composition and/or structure; 5. the dimensional accuracy of the treated part is preserved because coatings are thin; and 6. the adhesion of thin films to substrates can be markedly improved by bombarding the substrate prior to and during deposition.

Sometimes, no other treatment has been found effective. For example, II is used to increase the durability of critical space shuttle engine bearings that operate under severe tribological conditions (8). For parts that cannot tolerate the high temperatures required for CVD (800-950°C), low-temperature techniques must be used.

ION-SOLID INTERACTIONS

When energetic ions strike a specimen, momentum is transferred to atoms of the specimen. High-energy ions ( $\approx 10$  keV to several MeV) possess enough energy to penetrate deeply into a specimen ( $\approx 1$   $\mu\text{m}$  at 1 MeV, depending on the ion species) to produce collision cascades. A cascade occurs when the impact of an ion produces large numbers of atomic displacements in a small region. Numerous interstitials and vacancies are produced, and many atomic replacements occur. For a short time after an initial collision, the atoms in the region possess considerable vibrational energy, sometimes called a "thermal spike." A crystalline material may be rendered amorphous, or an ordered metallic alloy may become disordered in the region of the cascade. The collision of ions with substrate atoms is a non-equilibrium ballistic process, but investigators think that equilibrium thermodynamic considerations play a much larger role than previously assumed in determining which phases and microstructures will form during irradiation (9).

Low-energy ions ( $\approx 50$  eV to 10 keV) produce small cascades that, through collisions, rearrange atoms in the first several monolayers of the specimen, but do not penetrate to great depths. When a growing film is bombarded, low-energy ions collide with surface atoms and may drive these atoms into pores and vacancies and eliminate a columnar microstructure that is commonly seen in low-temperature deposition. Open clusters of atoms may be compacted to form a film with a dense, equiaxed microstructure (10-11). When chemically reactive ions are used, compounds can be formed as a result of the increased chemical activity of the ionized species and the implantation of the ions just below the surface (e.g., N bombardment of elemental B to produce BN (12)).

When a cascade occurs close to the external surface, sufficient energy may be transferred to one or more atoms so they are dislodged or sputtered from the surface (13). Sputter-etching may be used to remove surface contaminants prior to deposition of a film. In IBM and II, however, sputtering may cause the surface to recede, and may limit the concentration of implanted atoms.

Ion-beam techniques are line-of-sight. This restriction makes rotation of the specimen necessary when parts with all but the simplest geometry are treated, and seriously inhibits the treatment of concavities. To uniformly cover large parts, ion beams must often be rastered.

Medium- and high-energy ion implanters can be costly, but low-energy gridded ion sources tend to be less expensive. As will be described, a novel type of ion implantation has been developed that can be used to circumvent the line-of-sight restrictions. It is called plasma-source ion implantation (PSII).

In the following section, the ion-beam techniques mentioned above will be described in more depth. In the subsequent section, some avenues for lubrication engineering will be discussed. Detailed descriptions of ion-beam technology (14), general ion-beam techniques (15-16), ion-surface interactions (4, 17-18), simulations of thin-film growth of compound (19) and metal (20) films, technical aspects of II (21), and collision cascade effects (22) can be found in the literature.

## DESCRIPTION OF TECHNIQUES

### Ion Implantation

II is the direct implantation or injection of high-energy ions into a workpiece (8, 21), as depicted schematically in Figure 1. Because no coating is applied, the possibility of delamination at an interface is eliminated. Displacement damage occurs when incoming ions collide with and displace atoms in the material from their equilibrium lattice sites, and near-surface regions may be extensively modified (23). As a result of atomic rearrangements and accumulation of implanted atoms, second-phase compounds may form (24), dislocations and point defects may be produced, or the intrinsic stress and hardness of films may be changed (6). Improvements arise from oxidation reduction, the introduction of compressive stresses, or surface hardening. II can be used to amorphize a crystalline material, markedly improving mechanical (7, 25) and corrosional properties (26).

In principle, any desired atomic species that can be ionized and accelerated may be implanted. Because no coating is applied, dimensional tolerances are strictly maintained. Equipment for II tends to be costly because relatively large accelerating voltages (tens to hundreds of keV) are necessary to implant atoms to useful specimen depths. During implantation, essentially

all the kinetic energy of the incoming ion is dissipated into heat, and a means of removing heat from the surface may be needed.

Of particular note is the development of PSII (27) which is a technique in which a plasma is first established around an electrically conducting workpiece and then the workpiece is pulse-biased momentarily to a high negative voltage (10-100 kV). Ions accelerate toward and implant into the workpiece from all sides. PSII circumvents some of the line-of-sight drawbacks of conventional ion implantation, and has been used to implant hardened steel punches with N (28).

#### Ion-Beam-Assisted Deposition

In IBAD, a growing film is bombarded with a beam of (usually low-energy) ions (29) obtained from an ion source (e.g., a Kaufman source) that is operated independently of the source of vapor atoms. Because directed ion beams can be easily neutralized, problems arising from substrate charging are avoided. IBAD of a thin film is depicted in Figure 2.

The depositing material can originate from an evaporation source, or a second ion gun can be used to sputter material onto the substrate. The purpose of the low-energy bombardment is twofold. First, during deposition, the incoming ions drive individual atoms or aggregates of atoms into voids in the growing surface, thereby forming a denser film (10-11). The columnar film morphology commonly produced during physical-vapor deposition (PVD) can often be eliminated. A low beam energy also minimizes substrate damage in electronics applications. Second, energetic, reactive ions, such as N, react strongly with substrate atoms to form compounds that would otherwise require high substrate temperatures. The impact of the energetic ions/atoms leads to virtually 100% incorporation into the film. Thus, IBAD with reactive ions is a low-temperature process, sometimes referred to as reactive IBAD or RIBAD. A comprehensive review of IBAD can be found in ref. 30; ion-beam technology is described in ref. 31.

In both IBAD and plasma techniques, the ions or atoms arrive at the specimen surface with kinetic energies much greater than can be produced by heating. We have found that IBAD has several potential advantages. First, the energy of the arriving ions can be well controlled. Second, because a plasma need not be sustained, coating can be done in a good vacuum ( $<10^{-2}$  Pa) where

the mean free path of ions and atoms is greater than the size of the chamber. Third, insulating substrates can be bombarded. As in plasma processing, the thickness of the IBAD film is not restricted to the penetration depth of high-energy ions.

The ion energy need not be large to improve film properties: large changes in Nb film stress were obtained by means of 100-eV Ar-ion bombardment (32). Another advantage of using low kinetic energies is low incorporation of inert-gas ions into the film (33-34). Increases in film adhesion result from initial sputter cleaning and increased chemical reactivity but excessive sputtering of the deposited film material can adversely affect the film microstructure (35). With suitable vapor sources, multicomponent films can be applied.

Compound films can be produced when reactive gases, such as O<sub>2</sub> or N<sub>2</sub>, are used. Cubic BN (12, 36) and TiN (37), for example, have been produced when evaporated Ti or B metal is bombarded with N ions. IBAD has been used to produce optical coatings with superior film packing at low temperatures (38).

The energy of bombarding ions must be selected with care. The use of low energy ( $\approx 50$ -200 eV) ions during IBAD seems to be more beneficial than ions of higher energy ( $>1000$  eV). Nickel films produced by 1500-eV IBAD had lower density (lower than films receiving no ion bombardment), higher resistivity, and appreciably more Ar incorporation than did films bombarded with 100-eV Ar ions (33). For Ag films, 1000-eV Ar-ion bombardment produced striking porosity (35). The best quality CeO<sub>2</sub> optical films were obtained with 200-300-eV bombardment (39); this result was in agreement with the molecular dynamics calculations of Müller (19). This densification is thought to arise from ion-atom collisions in the growing film: arriving ions compact surface atoms and aggregates of atoms into the growing film, thereby densifying the film (10). Arriving vapor atoms fill vacancies that are left at the surface. At much higher energies, ions penetrate larger distances, creating damage much deeper in the film, where refilling is not possible. In the case of Ni films, it was thought that such incorporation of Ar, and the formation of very fine grains, was responsible for the lowered density. For Ag films it was thought that sputter texturing played a role in the observed porosity.



Because the energy and flux of the ions can be controlled and independently measured, the relative arrival rate of ions to depositing atoms can also be measured and controlled. The ion/atom arrival-rate ratio (R) can be adjusted to optimize film properties. The film microstructure, residual stresses, and packing density can often be controlled by suitable choice of ion parameters. In illuminating examples, investigators were able to change the residual stress of IBAD chromium (40) and tungsten (41) films from tensile to compressive by increasing R. Because the deposition parameters (ion energy, ion flux, ion species, film composition, and deposition rate) can be independently varied, the effects of IBAD are only beginning to be explored.

### Ion-Beam Mixing

IBM, depicted in Figure 3, is a process in which one or more thin films are applied and then subsequently "mixed" with high-energy ions (42-43). When an incoming ion collides with an atom in the substrate, a collision cascade occurs. Mixing results from the atomic motion associated with the production of large numbers of interstitials and vacancies near the cascade and from the large amount of disorder in the region of the displacement cascade. The amount of mixing depends strongly on temperature, and is generally larger than would be expected from simple ballistic mixing of atoms. When the collisional damage occurs at the interface between the film and the substrate, the film adhesion can be markedly improved. In one example, a six fold increase in wear life of MoS<sub>x</sub> films was obtained (44).

At low temperatures, where diffusion is slow, elements can be mixed to produce phases that otherwise are energetically unfavorable. IBM is increasingly being used by the materials science community to study interface behavior and to produce compound films, e.g., oxide superconductors (45). As with II, IBM can change the residual stress as a result of volume expansion in the film (46). Because the displacement cascades are on the order of nanometers in size, alternating thin layers of elements may be necessary if a thick film is to be mixed.

## EXAMPLES OF APPLICATIONS IN TRIBOLOGY

### Surface Modifications for Lubricity

A tribosystem comprises the components in relative motion (macroscopic), any applied lubricants (liquid, solid, or vapor), the texture and chemistry of the sliding surfaces, any reaction products that form, and the environment to which the tribosystem is exposed. During operation, mechanical and chemical interactions may occur between each of the sliding surfaces, the lubricants, the reaction products, and the environment.

The "lubricant" that is applied to (or incorporated into) the sliding or rolling surfaces may be an oil, a vapor, a solid compound (inorganic or organic), a chemical, a soft metal, or a combination of these. Various elements or compounds incorporated into the sliding surfaces can promote or inhibit chemical reactions that affect lubrication. Depending on the lubrication mechanism, the goal may be to inhibit or to hasten particular reactions. For example, friction may be reduced by the application of a thin coating that reacts with the environment to form a lubricious film during operation. If corrosion is a problem, wear may be inhibited by producing an amorphous surface layer. For severe loading, surface hardening by ion implantation may be the most effective route. Ion-beam processing will be beneficial if the surface can be engineered to improve lubricity or wear resistance.

A solid lubricant is a material that can shear or slide easily between rubbing parts and prevent the parts from coming into direct contact (47). If a thin layer of a low-shear-strength material is deposited on a harder substrate, this soft film will deform first during sliding, protecting the underlying substrate. As originally proposed by Bowden and Tabor (48), the hardness of the sliding substrates determines the real area of contact, but the resistance to shear is that of the soft film that separates the two surfaces. The coefficient of friction of solid lubricants varies with the load. For light loads, the soft film does not shear, and the coefficient of friction is determined by the sliding friction between the soft film and the counterface. At large pressures, the solid film is forced to shear (48), and for increasing pressures, the coefficient of friction may become quite small. For soft metals, such as Sn and Pb, coefficients of friction of less than 0.02 have been reported (49). Films from tens of nm to several  $\mu\text{m}$  in thickness seem to reduce friction best (50-

51). Films of this thickness may easily be applied by IBM or IBAD. Solid lubricants become attractive in cryogenic or high-temperature applications where liquid lubricants fail (52).

Because refractory ceramics possess good high-temperature strength and heat-insulating properties, they are the optimum materials for use at high temperature (53). Ceramics generally possess a higher sensitivity to thermal stress than do metals. It has been suggested that very high surface temperatures are generated as microscopic asperities slide past one another (54) and that this flash heating may cause softening, adhesion, and cracking of the asperity tips and thus, frictional losses and wear. In a study of ceramic wear for advanced heat engines, it was reported that partially-stabilized zirconia, lubricated with mineral oil, experienced rapid wear that resulted from local spalling caused by thermal hot spots (55). It is likely that the flash temperatures may be considerably reduced by depositing a thin metal film with good heat conductivity onto one or both sliding surfaces.

We have found a substantial increase in wear resistance for  $\text{Al}_2\text{O}_3$  (56), and  $\text{Si}_3\text{N}_4$  (57) coated with Ag. Figure 4 shows the wear rates of ceramic balls sliding on uncoated and Ag coated ceramic flats. Other workers have reported improvements in friction and wear after application of ion-beam-mixed Nb films to SiC (58).

One of us (AE) has examined in detail the triboproperties of boric acid (59). Boric acid is a layered-lattice compound that has found to be remarkably lubricious. For room-temperature M-50 steel pin-on-disk tests, coefficients of friction were found to be 0.05-0.07 (60).

$\text{WS}_2$  is a well-known solid lubricant that has a layered-lattice structure. It has been reported that the frictional properties of sputter deposited  $\text{WS}_2$  were further improved by post-deposition bombardment with 50 keV He and Ar ions (61). The bombardment was found to favorably alter the crystallinity of the  $\text{WS}_2$  films.

Compound films (oxides, fluorides, chlorides) are solids that show promise for reducing friction and wear at operating temperatures where organic lubricants decompose, or where the film is prone to oxidation. Several low-melting-point oxides, such as PbO or  $\text{B}_2\text{O}_3$  may be good lubricants at high temperatures if a practical way to incorporate the compounds into the tribosystem

could be developed. We have found that  $B_2O_3$  coatings reduce friction and wear (62). Other examples of oxide lubrication have been reported. It was shown that, when layers of Co and Ti-Ni were applied to and ion-beam mixed into steel substrates, the elevated-temperature ( $800^\circ C$ ) sliding wear was greatly reduced (63). Evidence obtained with Auger spectroscopy showed that deformed layers became oxidized during testing, and that the presence of the oxides was responsible for enhanced lubrication (64). The beneficial oxide layer was observed in a simulated diesel-engine environment (65). When delamination of applied film occurred, it was accompanied by serious wear, but low coefficients of friction (0.06-0.09) were obtained. This beneficial effect was also observed with ion-beam-mixed Fe-Ti on steel (66) and Co-implanted partially-stabilized zirconia, where a coefficient of friction of 0.09 was measured (67).

Solid lubrication requires good adhesion of the applied films to the surface; if a film is rapidly removed it is useless as a long-term lubricant. Chemical bonding is often poor at a ceramic/metal interface for applied metals that do not form compounds or easily wet ceramics. However, dramatic increases in film adhesion can be attained by using ion bombardment. Increases are thought to result from several processes (46): 1. sputter cleaning of contaminants from the substrate prior to deposition; 2. mechanical interlocking of film and substrate; 3. formation of a compositionally graded zone between the film and substrate; and 4. formation of interfacial bonding compounds with reactive ions. Martin (68) has proposed that ion bombardment can enhance the wetting of metal islands to ceramic surfaces, thereby increasing the real area of interfacial contact.

Prior to deposition, the ion bombardment available with IBAD both sputter cleans the substrate and changes the chemical bonding at the interface. The adhesion of evaporated Ag to  $Al_2O_3$  and  $ZrO_2$  can be greatly improved with O-ion presputtering (69-70). Clark et al. (71) found increased adhesion after Xe-ion irradiation of metal films on  $SiO_2$  substrates resulting from the formation of metal silicides. Very good adhesion of IBAD Au to glass was attained when the growing film was bombarded with O ions (72). Negligible improvements were seen for Ar ions, even at 1000 eV, which shows that interface chemistry, not collisional mixing, is important here.

We have found, however, that Ar-ion bombardment increases the adhesion of Ag films to both  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$ , and O-ion bombardment is even more effective (69-70). In contrast, for Au on  $\text{Al}_2\text{O}_3$ , Salem et al. (73) found no appreciable difference between the pull-test adhesion values produced by 550-eV Ar-ion bombardment and 650-eV oxygen-ion bombardment ( $\approx 19$  MPa), but both were far superior to those of unassisted coatings. For Au on  $\text{SiO}_2$ , however, bombardment with Ar or O did not seem to produce an effect and adhesion remained below 0.07 MPa. Kikuchi et al. (74) measured the adhesion of Ag films deposited onto glass substrates by glow discharge and found strength increases of up to 50 MPa. Again, Ar and O were equally beneficial, suggesting that adhesion increases can be attributed to surface cleaning or surface roughening.

As an alternative to depositing solid lubricants on sliding surfaces, lubricious materials could be directly implanted into sliding surfaces to a concentration that would enable thin layers to regenerate as wear occurred, as seems to have occurred after B was implanted into steel (75).

Oil-based lubricants often use organic additives that are able to form films that separate the sliding surfaces during surface-to-surface contact. Materials that do not react readily to form reaction films, e.g., most ceramics and metals such as Ti, Cr, and Ni, may be subject to rapid wear during boundary regime conditions. For improved lubrication, incorporation of a catalytic compound directly into the sliding surfaces by II, or application of a strongly bonded catalytic film to the surfaces by IBAD or IBM may be a way of promoting the formation of protective films.

#### Surface Modification for Wear Reduction

Surface wear depends critically on the hardness of the rubbing surfaces. II has been used extensively to improve the wear resistance in various Fe-, Ti- and Cr-base alloys and ceramics, such as  $\text{Si}_3\text{N}_4$ , by surface hardening and/or production of compressive surface stresses (76). Implantation of N into steels has long been used to impart wear resistance. The mechanism is believed to be the formation of hard nitrides,  $\gamma\text{-Fe}_4\text{N}$ ,  $\epsilon\text{-Fe}_3\text{N}$ , and  $\zeta\text{-Fe}_2\text{N}$ , with the  $\gamma$  phase being the most effective (77). The beneficial effects of N implantation are found to persist even after the modified layer has been worn away. For a long time, the reason for this was not well understood. It was found that N implantation caused the formation of hard martensite and nitrides,

and the hard N-implanted layer spread the stresses to the underlayer, promoting hardening and wear resistance of the underlayer (6).

Because sputtering effects limit the amount of retained N it has often been assumed that improvements will be limited for implantation doses above  $\approx 2 \times 10^{21}$  ions  $m^{-2}$ . Unexpectedly deep penetration, however, of N has recently been observed for 60-keV N of steel at 500°C (78-79). The depth of penetration extended much deeper ( $>10 \mu m$ ) than would be expected by thermal diffusion, and excellent wear resistance was found. The interstitials and vacancies (which are mobile at 500°C) that are produced in the near-surface region are thought to greatly accelerate diffusion of N atoms into the bulk. As has been pointed out, vacancies and interstitials can migrate rapidly (several  $\mu m s^{-1}$ ) at elevated temperatures (80).

Hard compound films for wear resistance, such as TiN, can be produced by CVD and plasma processes, but also by IBAD (29, 81). Evaporation of Ti with concurrent bombardment with energetic N ions produced TiN films that exhibited greater adhesion than those produced by PVD techniques, and work has been done to understand the causes of property variations in TiN films (82) and ways to control stoichiometry (37). Other hard nitride coatings (BN,  $Si_xN_y$ , and  $Ti_xN_y$ ) showed low friction ( $\mu \approx 0.1$ ) against steel (83). Alternately, MeV N of N directly into Ti produces significant surface hardening (24).

Another possibility is the production of wear-resistant hard iron borides by IBM (84). Iron borides can be formed at moderate temperatures by N (85) or IBM. The effect of mixing is the formation of hard, polycrystalline  $Fe_2B$  and  $Fe_3B$  phases at 450°C (86).

Diamond may be the ultimate hard coating. Diamond films have been produced by several high-temperature techniques, such as microwave-enhanced CVD (87) or combustion synthesis (88), but a low-temperature process would be of immense practical use. Good growth rates have been achieved, but the goal of making smooth diamond films has remained elusive; rough diamond films are very good abrasives. Diamond is also of interest because of its large heat conductivity (at room temperature and above) and its probable low friction. Attempts to produce diamond coatings with ion beams have been partially successful. Carbon films containing diamond (detected by

Raman spectroscopy) and diamond-like coatings have been grown (89-90). A report of room-temperature diamond synthesis from a C-ion beam (91) was later found to be in error (92). For tribological applications, however, it may not be necessary to achieve 100% diamond for a film to be useful. Amorphous or diamond like C films are extremely hard and may serve the purpose almost as well.

Surface wear also depends critically on the residual surface stress of applied coatings. Ion-beam processes can be used to control the residual stresses in materials, either by the use of IBAD to modify growing films (40), or by II to induce compressive stresses. Very modest bombardment during film growth may be sufficient to effect a stress reversal (32). This is especially important for ceramics, which are generally weak under tensile stress.

Laser processing is a proven method for the production of wear resistant materials. Recently, some work has been conducted on the use of both II and laser technologies (93). In this study, laser melting was used first, for local hardening; Ne II was then used to produce a compressive stress in the surface region. The observed significantly reduced wear was attributed to a compressive stress. Bubbles of Ne gas formed in the implanted region, but this did not seem to be deleterious.

Much of the work done on wear reduction in tribological systems is directed toward improving the mechanical properties of sliding surfaces. However, corrosion or oxidative wear can be a serious problem. The tribology and chemical behavior of specialty alloys are receiving increasing study owing to the need to extend the operating life of medical prostheses in the body. Nitrogen (94) and Ir (95) II have been found to dramatically extend the wear life of Ti alloys, apparently due to inherently less electrochemical corrosion and hardening of the Ti surface (thus protecting it from wear debris). Surface coatings have long been used to protect substrates from attack by forming a protective scale, or by reducing the corrosion rate. A good coating should resist penetration of agents that could cause corrosion at an interface. We have found that low-energy (150-eV) ion bombardment during deposition reduces the porosity of vapor-deposited Cr

coatings (96). In another study, environmental attack of reflective Ag coatings was markedly reduced by 300-eV Ar bombardment (97).

### Combined Effects

Promising results have been reported on the effects of combining hard compounds, for wear resistance, with lubricious metals, for friction reduction. A good example is a plasma-sprayed application of a chromium carbide coating with additions of Ag and Ca/BaF<sub>2</sub> (98-99). The coating was tested at temperatures to 900°C and very little wear and moderate coefficients of friction ( $\mu \approx 0.2$ ) were reported. The hard carbide component has excellent durability but poor lubricity. The soft Ag and fluorides were added to reduce friction at low and high temperatures, respectively. The addition of a thin Ag overlayer provided added run-in protection (100). The plasma-spray process that was used to deposit the coatings has the drawback that diamond grinding was needed to produce a finished part. Thus, the use of ion-beam techniques for depositing hard/soft films may be a viable way of producing components with preserved dimensional tolerances.

### CONCLUDING REMARKS

New technology goes through several stages of development. Initial "grand predictions," as Sioshansi has put it, are often followed by disappointment as problems of commercialization are experienced (8). If early problems can be overcome, significant advances can be realized. Some approaches such as ion implantation have already found acceptance in a wide range of applications. Much work will be needed to evaluate new approaches to lubrication.

Ion implantation, ion-beam mixing, and ion-beam-assisted deposition (IBAD) can be used to modify the structural or chemical properties of surfaces or to control the microstructure of coatings during deposition. Research trends seem to be shifting toward IBAD because thicker layers can be produced and compound films are possible at low temperatures. In the past few years, considerable progress has been made in IBAD optical films and TiN hard coatings, and interest in IBAD seems to be expanding to include tribological applications. Because the



deposition parameters (ion energy, ion flux, ion species, film composition, and deposition rate) can be varied at will, much work is needed for a full understanding of ion-coating interactions.

Some concepts for the engineering of novel lubrication systems with ion beams have been mentioned, such as the incorporation of lubricious elements directly into surfaces, the solid-state mixing of elements to produce novel compounds, and the production of reaction films that form lubricious layers. Two or more approaches may be combined to exploit synergistic effects. Many of the approaches are not fundamentally new, but new processing techniques afford an opportunity for progress in improving lubrication for severe tribological conditions.

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#### FIGURE CAPTIONS

Figure 1. Schematic representation of ion-implantation.

Figure 2. Schematic representation of ion-beam-assisted deposition.

Figure 3. Schematic representation of ion-beam mixing.

Figure 4. Comparison of sliding wear of a)  $\text{Al}_2\text{O}_3$  balls sliding on uncoated and Ag-coated  $\text{Al}_2\text{O}_3$  flats, and b)  $\text{Si}_3\text{N}_4$  balls sliding on uncoated and Ag-coated  $\text{Si}_3\text{N}_4$  flats. Test conditions: Load 10 N, sliding speed  $0.05 \text{ m s}^{-1}$ , relative humidity 45%, ball radius 6.35 mm, sliding distance 205 m.

FIGURES

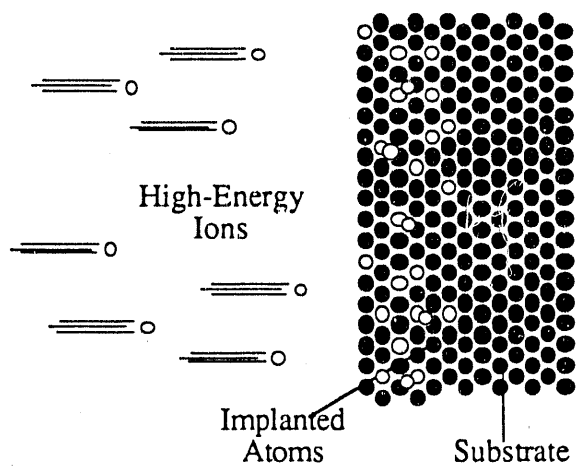


Fig. 1

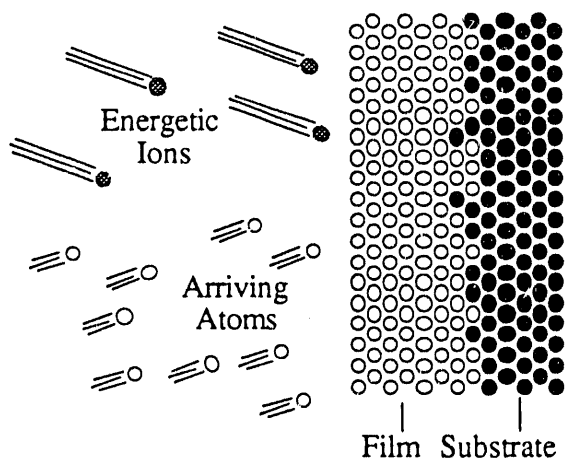
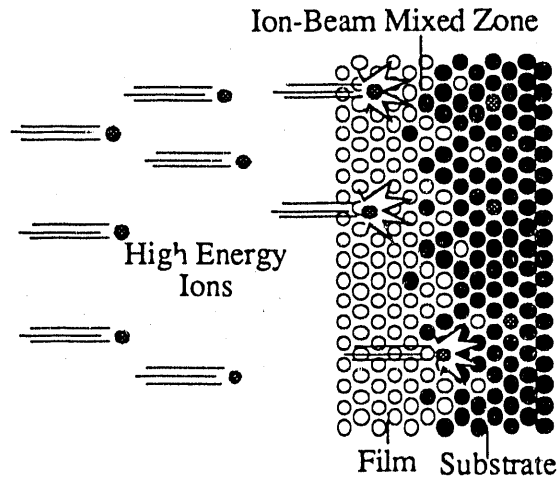
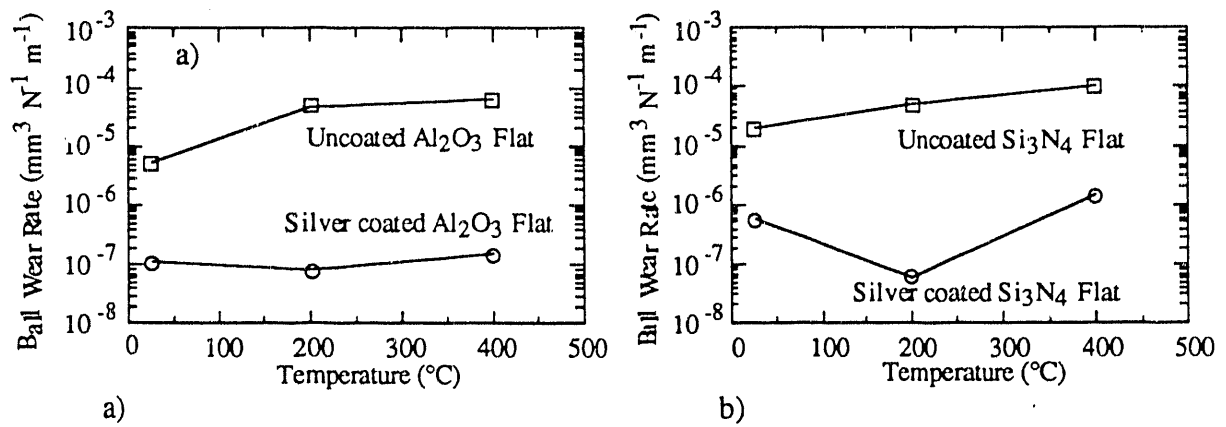


Fig. 2



(fig. 3)



(Fig.4)

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