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Advanced Solid Lubricant Films by Ion-Beam Assisted Desposition

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13. ABSTRACT (*Maximum 200 words*)

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IBAD MoS_2 films exhibit reduced susceptibility to moisture degradation during storage. Alloyed MoS_2 films show increased durability in sliding and rolling contact without sacrificing the ultra-low friction behavior of MoS_2. For high temperatures, a class of binary metal oxide films are being investigated. Candidate lubricants have been chosen based on tribological behavior of oxide and predictions from thermodynamic phase diagrams. A recent study of the Cu-Mo-O system will be presented.

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ABSTRACT

NRL is developing advanced solid lubricating films for bearings assemblies. The films are deposited by ion-beam assisted deposition (IBAD) to thickness that can be controlled from 0.02 μm (1 μinch) to $\geq$ 1 μm (40 μinch). Unlike evaporated or sputter-deposited films, IBAD films are dense and adhere well to virtually all solid surfaces. Durable films have been deposited on bearing steels, Ti alloys and many ceramic substrates, including Si_3N_4, alumina, SiC, TiN and CVD diamond. IBAD's multibeam capabilities have also been exploited to produce binary and ternary alloys over a wide range of stoichiometries. Studies of two solid lubricating films, MoS_2 and ternary metal oxides, will be highlighted.

IBAD MoS_2 films exhibit reduced susceptibility to moisture degradation during storage. Alloyed MoS_2 films show increased durability in sliding and rolling contact without sacrificing the ultra-low friction behavior of MoS_2. For high temperatures, a class of binary metal oxide films are being investigated. Candidate lubricants have been chosen based on tribological behavior of oxide powders and predictions from phase diagrams. A recent study of the Cu-Mo-O system will be presented.

1. Introduction

For bearings and other moving mechanical assemblies that must operate in extreme environments, solid lubricating films offer some advantages over liquids, such as less contamination of sensitive parts in vacuum and greater stability at elevated temperatures and high speeds. To realize these benefits, a solid lubricant must adhere to the bearing material (whether metal or ceramic), exhibit both storability and durability, and give low friction (torque) and friction noise (torque noise). In many cases, the method by which the solid lubricant is applied to the assembly will control these performance criteria.

Traditionally, solid lubricants have been applied by burnishing, bonding, and, more recently, sputter deposition. Sputtered coatings have found widespread use as solid lubricants for space applications due to better endurance [1], as well as control of composition and thickness which can be attained. However, sputtered lubricating films need further development; for example sputtered coatings are often of low density and crystal orientation unfavorable for low friction, i.e. MoS_2 basal plane perpendicular to the surface [2,3,4,5], and are degraded by moisture [6,7].

Some of these deficiencies can be addressed by ion-bombarding the sputtered film. For example, post ion bombardment of sputter-deposited lubricants has been shown to give increased endurance [8,9] and, in one case [10], to decrease friction. Also,

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alternating sputter deposition and low-energy ion bombardment produced dense and oriented films [11]. Finally, simultaneous atom bombardment during deposition gave excellent endurance and low friction in room air [12]. A physical vapor deposition technology that combines sputter deposition with concurrent ion bombardment of the growing film is ion-beam-assisted deposition (IBAD).

IBAD has several well known advantages over traditional sputter deposition [13]. Films are usually very adherent, due to the sputter cleaning and interfacial mixing afforded by direct ion bombardment. IBAD films can thereby be grown on substrates that show poor adhesion with other deposition processes. Films attain bulk density due to the energy imparted by the ions during deposition. Films can therefore be deposited at lower temperature, often at room temperature. The microstructure (and orientation), composition and mechanical properties can be tailored by controlling the deposition parameters.

This paper reports on the tribological behavior of coatings produced by the IBAD method. Composition and structure data and friction and wear behavior were evaluated for a variety of processing parameters and substrates [14,15,16,17,18,19,20]. Most of the investigations have focused on lubrication at room temperature using MoS_2 and MoS_2-like (alloyed, composition modulated, ...) coatings. Towards the end, we present some recent work on lubrication at elevated temperature (up to 923K) using "double oxide" coatings.

2. Experimental

A schematic of NRL's IBAD system is shown in Fig. 1. Films were deposited in a vacuum chamber equipped with three 3-cm argon ion sources of the Kaufman type. Two focussed ion beams, usually operated at 1 keV and at currents up to 70 mA, impinged on selectable sputtering targets. The third, with a broad beam, was directed at the substrates for sputter cleaning and to provide an assist ion beam during deposition. This beam was usually operated at 1 keV and at 40 mA for cleaning and 1 to 6 mA in the assist mode. The substrate stage rotated during deposition to improve the film uniformity; the temperature could be control from ambient to 620 K. The stage was also used for vacuum annealing films after deposition. The cryopumped chamber's base pressure was about 10^{-5} Pa, and the operating pressure

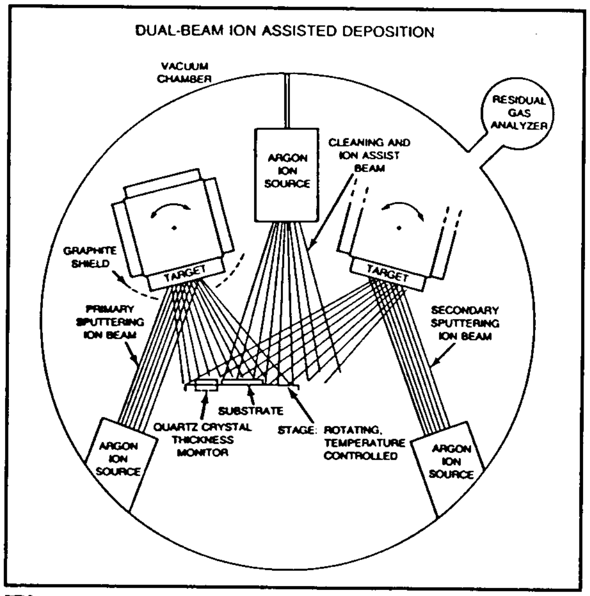

Figure 1 NRL chamber for ion beam assisted deposition of solid lubricating coatings.

about 0.05 Pa. A residual gas analyzer monitored the residual gas composition and the purity of the argon ion source gas. A quartz crystal thickness monitor provided thickness and rate data during deposition.

For IBAD MoS_2, the deposition process typically consisted of several minutes of assist beam sputtering to clean the substrate surfaces, IBAD of a base layer from a TiN target to a thickness of 10 to 90 nm, and IBAD of the MoS_x top layer to a thickness of 100 to 600 nm. Three techniques were used to form this top layer: sputtering from an MoS_2 target, cosputtering MoS_2 and sulfur, and cosputtering Mo and S. Deposition rates for the third method were 20 to 40 nm/minute, several times those of the first two. The base TiN layer serves as a diffusion barrier [15], not as a "thin hard coatings" as often speculated.

3. Results and Discussion

Films prepared under various conditions have been analyzed for composition and structure. We typically produce films having S/Mo ratios between 1.7 and 2.1 with no changes in tribological behavior. The films consist mainly of nanocrystalline ($\approx$ 10 nm) (002) or (100) platelets, although some amorphous material can be present. A majority of the platelets are aligned with their basal (002) planes parallel to the substrate, the desired orientation for low friction behavior. (Note: with sputtered films, this orientation is achieved by "run-in" during which time substantial amounts of the film are worn away.) Due to continuous ion bombardment, IBAD films, unlike sputtered films, are fully dense. The films have a silvery appearance, unlike the non-dense sputtered films which look black.

Friction and wear properties have been evaluated in dry and humid environments. In dry sliding, the friction coefficients are in the range called ultra-low friction (ULF), often from 0.005 to 0.02. The actual value depends on the interfacial shear strength, S, and the Hertzian pressure, P_H, according to the formula [21]

$$\mu = S/P_H.$$

The shear strength of IBAD films is 15 to 20 MPa, a value comparable to the bulk shear strength of MoS_2. Sliding in moist environments results in an order of magnitude increase in the friction coefficient and orders of magnitude lower endurance.

IBAD films in dry environments have very high endurance. Wear rates at very high Hertzian pressures (1.4 GPa) are exceedingly small; we measure them at 1 nm per one to ten thousand passes. Several examples of durable films will be given later. One of the advantages of the IBAD process is that films store well in humid air. IBAD films stored over 2 years in ambient air (20 to 60%RH) exhibited no chemical or structural degradation, as measured by Auger and X-ray photoelectron spectroscopies and by X-ray diffraction. Also, IBAD coating performance after storage in humid air appear to be

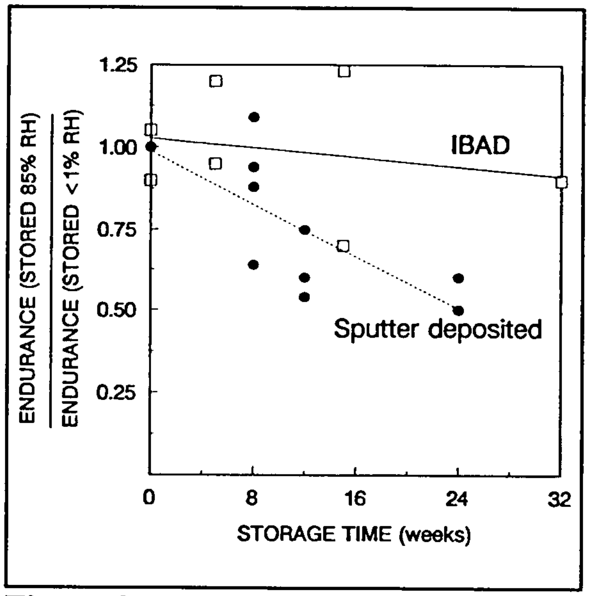

Figure 2 Effects of humid air storage on coating endurance for IBAD and sputter-deposited MoS_2.

Table I

SUBSTRATES LUBRICATED WITH IBAD COATINGS	
METALS	CERAMICS
Fe	SiC
Ti	Si_3N_4
Mo	TiB_2
Ni	Al_2O_3
Al	CVD Diamond
Si	glass
Ta	
Pt	
52100 Steel	
440C Steel	
M50 Steel	
AMS 5749 Steel	
Rene 41	
Inconel 625	
Ti-6Al-4V	

better than for sputtered films; this is seen in Fig. 2 which compares the change in endurance of films stored in humid vs dry air over 8 months [22]. The IBAD films suffered far less degradation than sputter deposited films. We attribute the improved storage behavior to the dense, basal orientation of the films; by contrast, sputter-deposited films have an open (porous) structure with edge-oriented platelets growing perpendicular to the substrate. Recently, IBAD MoS_2 films were evaluated for resistance to atomic oxygen and were found to outperform sputter-deposited solid lubricating films in both static oxidation and post-oxidation wear tests [23]. The atomic oxygen resistance is also attributed to the dense, basal oriented structure that IBAD provides. We comment that while friction is not dependent on processing parameters, the endurance of the film can be optimized by choosing the proper ion assist beam currents [16].

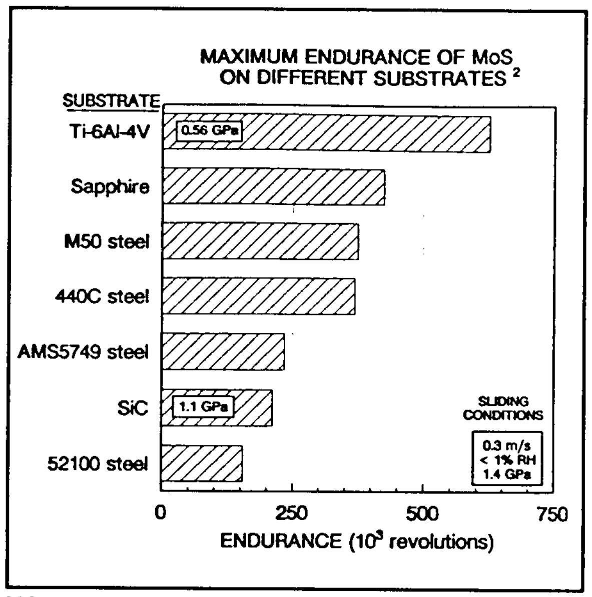

Figure 3 Endurance of IBAD MoS_2 on different substrates.

IBAD MoS_2 films have been deposited successfully on a variety of metal and ceramic substrates (see Table I). A chart of maximum endurance on several substrates is shown in Fig. 3. Note the endurance of the coating on Ti-6Al-4V; IBAD MoS_2 can lubricate Ti alloys as effectively as it does steel alloys, even at loads beyond the elastic limit of the Ti substrate [17]. It is commonly accepted and reported in the literature [24,25,26] that Ti alloys are difficult to lubricate. We suspect that the remarkable ability of IBAD MoS_2 to lubricate Ti is due to the improved adhesion associated with the IBAD process.

The protective ability of IBAD MoS_2 can also be seen in the way it alters the wear mode of a normally high-wear couple: sapphire vs CVD diamond. Although sapphire is a very hard material (hardness $\approx$ 22 GPa), it is worn severely by CVD films (see Fig. 4). The wear is by abrasion, as identified by the wear scar on the sapphire ball in Fig. 5. The abrasion is caused by a combination of hardness and roughness (roughness on the 10 to 100 nm scale) of the CVD diamond films [18,19]. When a thin IBAD MoS_2 film is deposited on the same CVD diamond films, the wear is reduced to zero (see Fig. 4). Inspection of the contact area on the sapphire ball (see Fig. 5) shows that, in place of wear, there is a transfer film of MoS_2. The mechanism behind the change in wear mode is apparent: MoS_2 attached itself to the sapphire surface during the early stages of sliding, separated the two surfaces and accommodated the relative motion between the two surfaces. The only "wear" that took place was the transfer (and retransfer) of MoS_2 between the two surfaces.

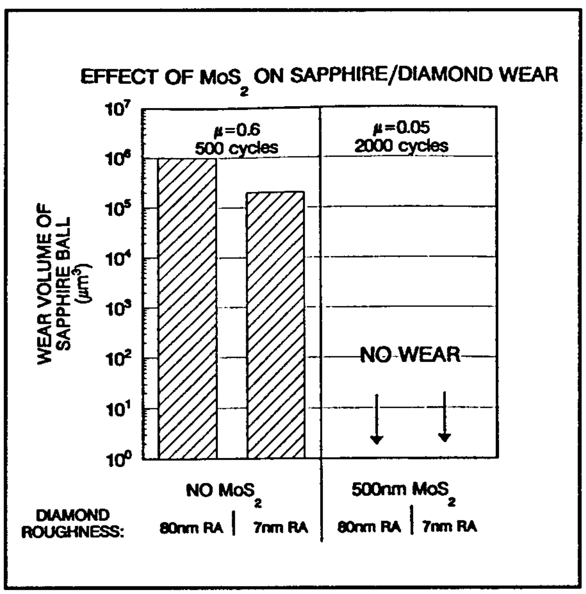

Figure 4 Wear of sapphire ball by bare and IBAD MoS_2-coated CVD diamond.

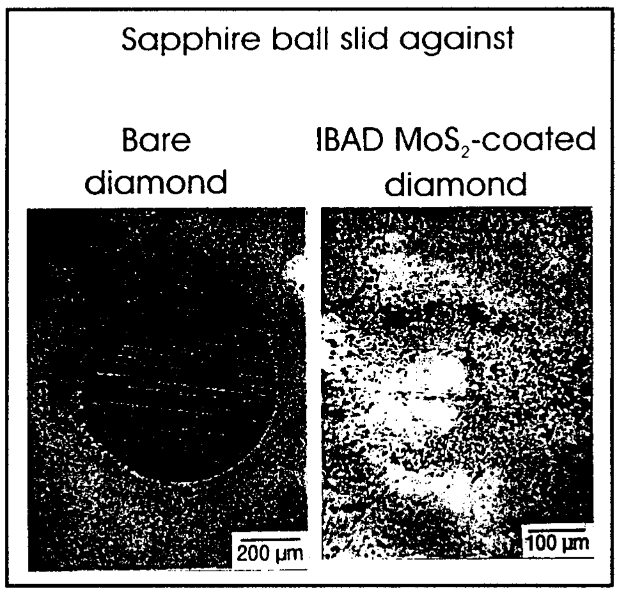

Figure 5 Sapphire ball after sliding against bare and IBAD MoS_2-coated CVD diamond.

Structural and compositional modifications designed to improve the already good tribological performance of IBAD MoS_2 have also been investigated. Some examples of successful modifications are shown in the next few figures. Two of the most durable coatings tested in sliding contact are the ternary Pb-Mo-S coatings and MoS_2 coatings deposited in partial pressures of H_2 gas. Maximum endurance of these two coatings are shown in Fig. 6, in comparison with the most reliable "optimized" IBAD MoS_2 coatings. We add that WS_2 coatings with about the same endurance as MoS_2 can also be made by the IBAD process, but, in order to take full advantage of the high-temperature stability of WS_2, further work is needed to optimize the deposition process.

IBAD coatings perform well not only under sliding contact, but also under rolling contact. Some results of thrust bearing endurance tests, conducted by Dr. S. Didziulis at the Aerospace Corp., are shown in Fig. 7 [27]. Endurances for the two modified IBAD MoS_2 coatings (sulfur modulated and Pb alloyed) attest to the fact that IBAD films not only outperform traditional MoS_2 coatings like burnished and dc sputtered, but also rank with the best on the newer, long lived films; these films were developed under contract to SDIO in the early 1990s and hold promise for longer-lived and quieter (debris-free) guidance bearings [28].

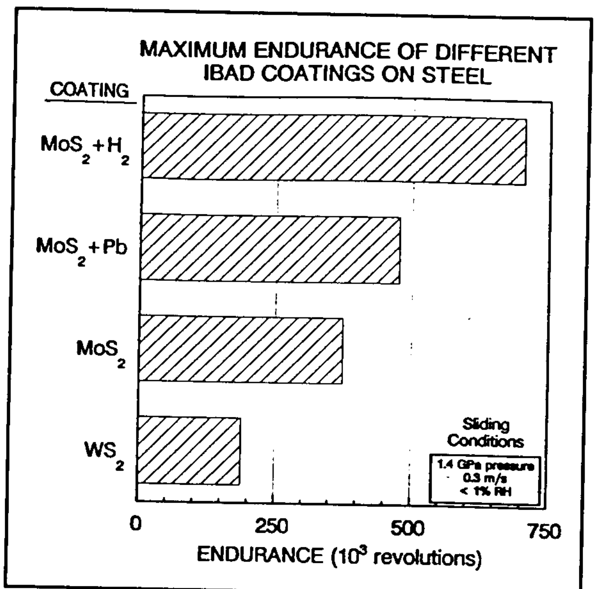

Figure 6 Endurance of different IBAD coatings on steel.

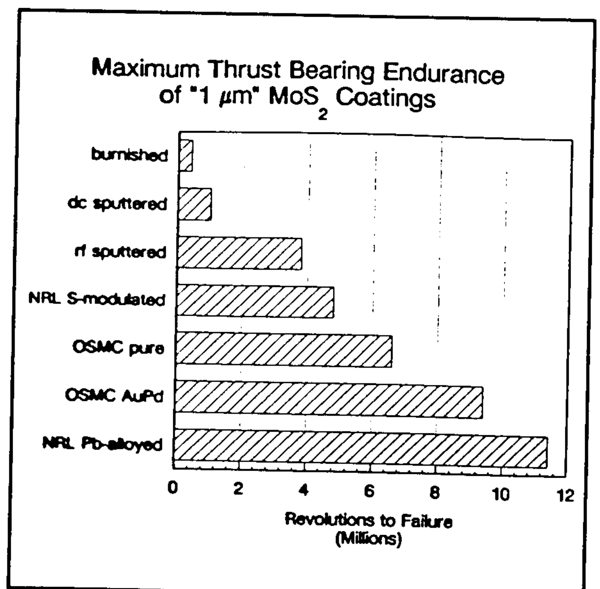

Figure 7 Thrust bearing endurance tests of MoS_2-based coatings (performed by The Aerospace Corp.).

Our most recent application of the IBAD system has been to develop high temperature solid lubricating films. We chose to pursue the class of lubricants known as "double oxides"; some of which are listed in Table 2. These materials, mainly in powder form, have been shown to provide low friction over a wide range of high temperatures [29]. With the IBAD system, we have been able to deposit binary metal and ternary oxide films. Taking advantage of the dual targets, we can deposit films with a wide

Table II

MIXED METAL OXIDES WITH SOLID-LUBRICATING PROPERTIES.	
Molybdates	$PbMoO_4$, $NiMoO_4$, $CuMoO_4$
Rhenates	$Cu(ReO_4)_2$, $Ni(ReO_4)_2$, $Co(ReO_4)_2$

range of compositions and thereby explore the lubricity of a wide range of compositions and structures available in these ternary systems. Fig. 8 shows the range of compositions accessible for two candidate Co alloys, as verified by Rutherford backscattering spectrometry (RBS). The friction behavior of an IBAD Cu-Mo coatings at 873K is shown in Fig. 9. It displays the same friction coefficient (0.2) as the $CuMoO_4$ powder at this temperature [29]. XRD analysis indicated that the phase was indeed $CuMoO_4$.

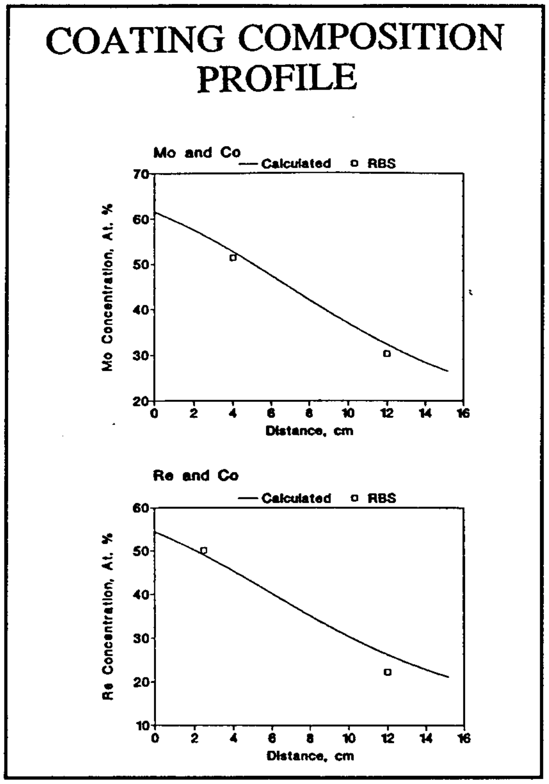

Figure 8 Measured and calculated compositions of Co-based high-temperature candidate lubricants deposited by IBAD.

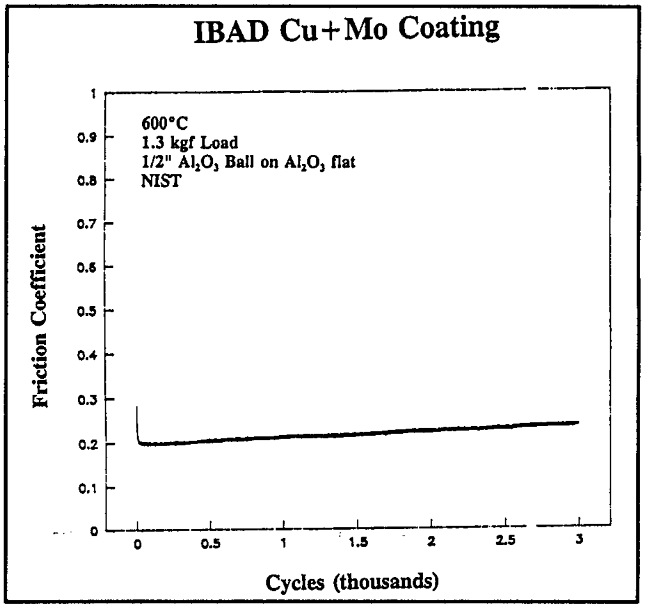

Figure 9 Friction trace of IBAD Cu-Mo coating slid at 873K.

4. Summary

In summary, IBAD coatings have the potential to provide solid lubricating film for a variety of substrates and operating environments. The IBAD MoS_2 coatings are adherent, durable and give low friction in dry atmospheres and are not degraded by moisture storage or by atomic oxygen. Alloyed IBAD MoS_2 coatings promise improved performance in rolling and sliding contact. For high temperatures, IBAD coatings of double oxides hold promise. We recommend IBAD coatings, in particular, for:

- o hard-to-lubricate surfaces like Ti alloys or CVD diamond,
- o assemblies requiring long-term storage, and
- o precision bearings, where thin films are needed to reduce debris noise.

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