Tribology of Inorganic Nanoparticles

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INTRODUCTION

One of the main tribological properties of rubbed pairs is self-lubrication. The key to self-lubricating materials is the rapid and easy shear and transfer of thin films from one surface to another. The solid lubricants assure a ''self-lubrication'' of oils, greases, coatings, polymer composites, bearing powder materials, etc.

In the present work, a novel brand of nanomaterials—inorganic fullerene (IF)-like solid lubricant nanoparticles of WS_2 and MoS_2 (IF)—is considered. Friction and wear properties of IF nanoparticles are compared with commercially available layered WS_2 and MoS_2 solid lubricants. IF solid lubricant nanoparticles were added to oil, grease, and impregnated into the pores of powdered materials. Polymer nanocomposite with IF nanoparticles and alumina covered by thin IF film showed superior tribological properties in comparison to the reference materials. The mechanisms of IF self-lubrication are discussed.

INORGANIC FULLERENE-LIKE SOLID LUBRICANT MATERIALS

Inorganic layered compounds are abundant, in particular, among the transition-metal chalcogenides (sulfides, selenides, and tellurides), halides (chlorides, bromides, and iodides), oxides (hydroxides), and numerous ternary and quaternary compounds. Layered materials such as graphite, MoS_2 and WS_2 (platelets of the 2H polytype) are used both as solid lubricants[1,2] and as additives in liquid lubricants.[3,4] Minimum tangential resistance is commonly associated with shearing of the weak interlayer (typically van der Waals) bonds in these materials.[5,6] Unfortunately, the 2H platelets tend to stick to the mating metal pieces through the reactive dangling bonds on the prismatic edges ($10\bar{1}0$), which lead to their rapid annihilation through burnishing and oxidation. The friction coefficient of MoS_2 solid lubricant particles is more than 0.1 at humid and oxygen-containing environments.

Recently, the tribological properties of C_{60} and C_{70} fullerenes were described.[7–9] It was speculated that the nearly spherical fullerenes might behave as nanoscale ball bearings. Intuitively, fullerene molecules are thought to be too small to separate between asperities of the mating metal surfaces and, therefore, they tend to enter into crevices or valleys. Experiments by Campbell et al.[10] with C_{60} molecules dissolved in dry toluene tend to substantiate this hypothesis, but comparison of this result with macroscopic friction measurements does not yield a conclusive outcome. Further work of this group has demonstrated that, whereas the adhesion energy of smooth C_{60} films is very low, the friction coefficient is rather high in this case. The tendency of the fullerene powders to clump and compress into a high shear strength layer was demonstrated to be a main cause of the high friction coefficient.[11]

Using a reasoning similar to that of carbon fullerenes[12] and carbon nanotubes,[13] several groups proposed[14–16] that their formation is not unique to carbon and is, in fact, a genuine property of 2-D (layered) compounds, such as WS_2 and MoS_2. However, in contrast to graphite, each molecular sheet consists of multiple layers of different atoms chemically bonded to each other. The initial discovery of IF materials elicited a substantial effort of many groups, which has been recently reviewed by a number of authors.[17,18] These nanomaterials were termed under the generic name inorganic fullerene-like (IF) materials. The results of a detailed study of inorganic fullerene-like nanomaterials are considered in this book, in a separate chapter.[19]

The analysis of IF nanoparticles showed that the most, if not all, nanoparticles were closed and hollow, and their shape was found to be irregular with a small fraction of the particles (<10%) having nearly spherical shape. The hollow cage structure of the IF imparts a high elasticity, which augments their resilience in a specific loading range.[20] Dislocations, which have deleterious influence on the chemical stability and the tribological behavior, were abundant in these nanoparticles. A typical assortment of such nanoparticles is shown in Fig. 1. The tilting of the samples in the TEM suggests that the IF-WS_2 nanoparticles have a spherical shape. Atomic force microscopic (AFM) image of an IF-WS_2 nanoparticle, confirming a spherical shape, is presented in Fig. 2. The average size of the IF-WS_2 particles was close to 120 nm, while it was about 50 nm for IF-MoS_2. High elasticity of the IF-WS_2 nanoparticles was confirmed by the analysis of the IF-WS_2 nanoparticle ensemble under hydrostatic

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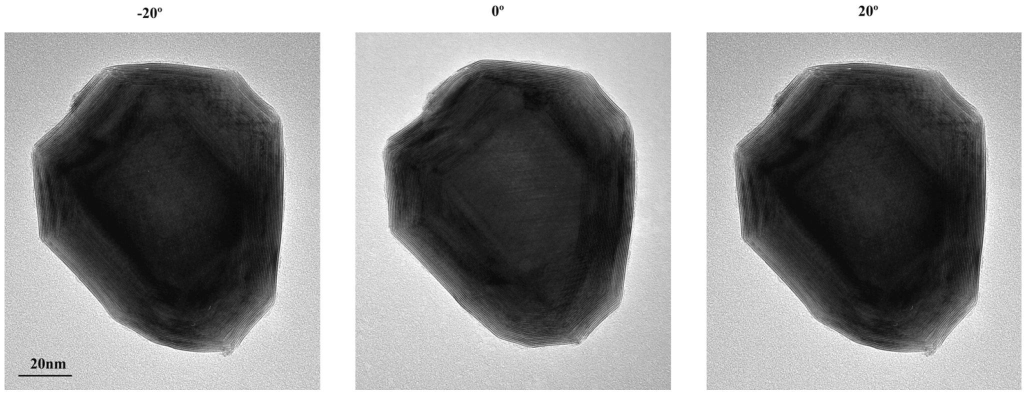


Fig. 1 Transmission electron microscopic (TEM) image of typical IF-WS_2 nanoparticles at different tilt angles. Results demonstrate the spherical shape of these nanoparticles.

compression.[21] This experiment was performed to evaluate the behavior of IF solid lubricant nanoparticles as a self-lubricating medium. It was found that these nanoparticles are capable of withstanding a severe hydrostatic pressure, caused by compression. Detailed structural studies revealed that no phase changes were observed during compression. With increasing load, some IF-WS_2 nanoparticles were found to be damaged (Fig. 3). Frequently observed defects can be associated with the breakout of the outer shells of the nanoparticles. The layer-to-layer distance of 0.62 nm was preserved in the broken sheets. The inner layers of these nanoparticles seem to remain intact. The broken outer layers are expected to be transferred to friction surfaces, providing superior tribological properties of rubbed surfaces. The 2H-WS_2 particles with platelet shape suffered severe damage under the same loading conditions.

The behavior of the IF nanoparticles has been compared with layered 2H-WS_2 and 2H-MoS_2. Preliminary friction experiments showed that IF added to oil possess lubricating properties superior to those of 2H platelets in a definite range of operating conditions.[22] The weak van der Waals forces operating between the layers leading to easy shear of the films likely cannot control the tribological properties of spherical IF-WS_2 nanoparticles. We attributed the recently reported outstanding tribological behavior of IF-WS_2 to its chemical inertness and to the hollow cage structure, which leads to high elasticity and allows the particles to roll, rather than slide (rolling friction), in appropriate loading regimes. It was realized that the addition of small amounts of quasi-spherical WS_2 or MoS_2 nanoparticles with fullerene-like structure to various kinds of lubricant greatly improves their tribological characteristics. Thus a systematic study of the tribological behavior of such nanoparticles under different contact conditions was undertaken. Based on this study, some applications for these nanoparticles are offered.

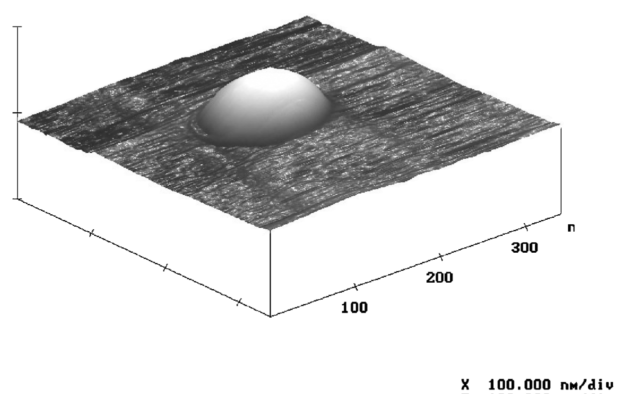


Fig. 2 AFM image of spherical IF-WS_2 nanoparticles. (*View this art in color at www.dekker.com.*)

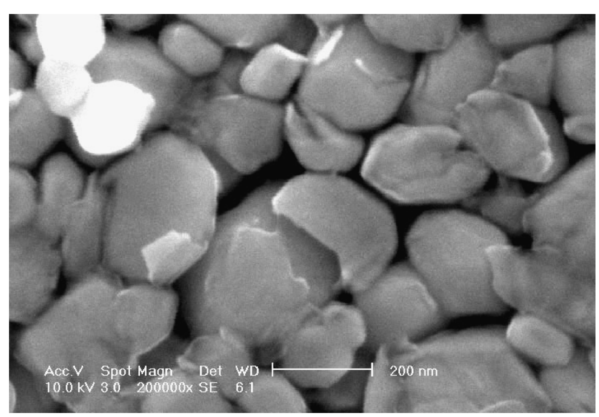


Fig. 3 Scanning electron microscopic (SEM) micrograph of ensemble of the IF-WS_2 nanoparticles after compression with a pressure of 500 MPa.

Hereinafter, some recent highlights of this progress will be delineated.

THE EFFECT OF THE IF NANOPARTICLES IN OIL

Ring-block test of a steel pair at sliding velocities V=0.22–1 m/sec and loads of 150–1200 N was performed.[23] To simulate typical industrial conditions, only 5 wt.% of the solid lubricants (IF or 2H-WS_2) were dispersed in oil. It was observed that IF showed superior friction and wear properties under relatively low values of the loads and sliding velocities. Analysis of the solid lubricant particles showed that a substantial number of the 2H platelets were destroyed, whereas IF particles were found to remain undamaged under these conditions. With increasing load, three mechanisms of IF particle damage could be discerned: plastic deformation of the quasi-spherical nanoparticles into ovoid shape; peeling-off of external sheaths; and splitting.[23] The quantity of damaged particles increased with increasing load. The amount of the oxide was found to be substantially larger on the surface of the wear track in contact with the 2H-WS_2 platelets compared to IF nanoparticles. The chemical reactions that are relevant to the wear of platelet materials occurred predominantly at the prismatic edges, where reactive dangling bonds exist. The presence of unsaturated or dangling bonds in metal dichalcogenides led to oxidation of the surface in the surrounding environment, especially at elevated temperatures which may occur as a result of friction. For instance, a switch from an environment of dry nitrogen to humid air led to an increase of the friction coefficient of 2H-WS_2 from 0.03–0.04 to 0.15–0.20, and a decrease in its resistance to oxidation by several orders of magnitude.[24] Therefore, the absence of dangling bonds may be one of the prime advantages of IF nanoparticles over the crystalline platelet (2H) particles for reduction of friction and wear.

Mixed lubrication is an extremely important regime of liquid lubrication when both fluid film and boundary lubrication take place.[25] Mixed lubrication region is the transition to scuffing and seizure. The behavior of IF-WS_2 solid lubricant in oil has been compared with pure oil.[26] The kinetic of the friction force change between two feedings of lubricants has been analyzed. Based on this analysis, it was concluded that the addition of IF nanoparticles to oil induces protection for the contact surface, decreases the fraction of straight asperity contact, and thus improves the tribological properties of pin-on-disk contact pair under mixed lubrication. It was found that the wear of the pin rubbed with oil+IF lubricant is lower in comparison to the pin lubricated by a pure oil. This effect grows with increasing load, suggesting that the favorable role of the IF increases with the load. Damage and destruction of IF-WS_2 was usually observed over a pressure of 0.5 GPa. The main damage incurred to the IF nanoparticles was the exfoliation (delamination) of external sheets (Fig. 4). Thin nanosheets of delaminated IF are also observed. Usually, only a few external molecular sheets of the IF are damaged. Appreciable damage occurred for the small number of fullerene-like nanoparticles. The surface of the pin rubbed with oil+IF was found to be covered by a film. X-ray photoelectron spectroscopy (XPS) analysis revealed that this film consisted of WS_2.

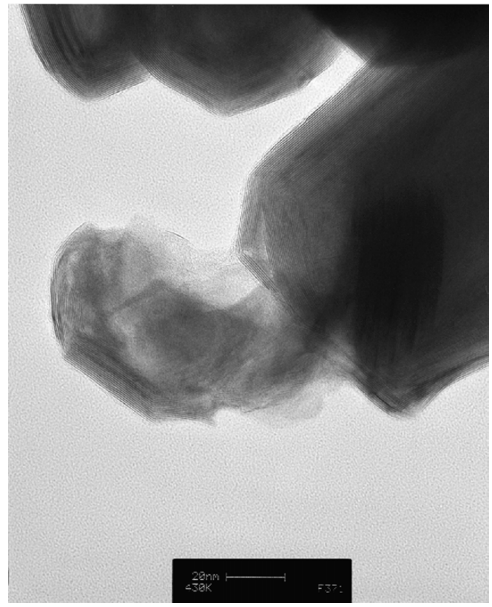


Fig. 4 TEM image of the IF nanoparticles after the pin-on-disk test.

IF agglomerates are compressed and penetrate into the surface layers of the soft pin (Fig. 5). As a result of this effect, the surfaces rubbed with oil+IF were rougher compared to the surfaces lubricated with a pure oil. The main friction mechanism for IF nanoparticles in the range of mixed lubrication is the transfer of exfoliated thin sheets to the contact surface. The transfer is probably responsible for the self-lubrication of the IF solid lubricant nanoparticles in the mixed range of lubrication.

After the friction test, the loaded pin was etched lightly with 3% HNO_3 in alcohol, which dissolved the wear debris impregnated onto the metal surface and revealed the wear damage. SEM analysis of the etched surface showed that, while the oil-lubricated surface was heavily damaged with deep scratches and grooves occurring, the surface of the metallic pin lubricated with oil+IF remained almost unchanged.

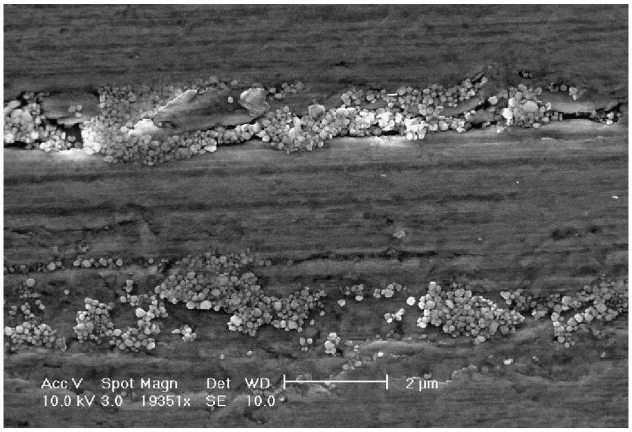


Fig. 5 Penetration of the IF nanoparticles and their agglomerates into the surface layers of hard disk.

The thickness of the lubricant film depends on contact conditions (viscosity of lubricant, load, and sliding velocity). Using the analysis of mixed lubrication for the surface with a real roughness,[25] the mean film thickness was found to be smaller than the size of IF nanoparticles. When film thickness is smaller than the size of nanoparticles, IF-WS_2 have to delaminate or, they can be preserved in the valleys of the roughened surfaces, or the two processes can occur together. Identification of WS_2 on the contact surface (XPS and etching), preservation of the full shape of IF nanoparticles (TEM analysis), and the formation of a rough surface under steady friction prove that a part of the IF-WS_2 is preserved in valleys of the contact surface while another portion of the IF nanoparticles is delaminated and transferred to the rubbed surfaces.

IF nanoparticles in the valleys and delaminated transferred nanosheets on the surface decrease the straight asperity contact under mixed lubrication. Thus the IF-WS_2 film protects the contact surface and enhances the wear resistance of contact surfaces. We suppose that sliding/rolling of the IF nanoparticles in the interface between rubbed surfaces is the main friction mechanism under loads, when the shape of nanoparticle is preserved. It was found that the efficacy of IF nanoparticles was increased with the load. It may be expected that, under friction with very high loads (>1 GPa), a considerable number of nanoparticles will be delaminated and consequently, transfer of thin nanosheets a few nanometers in size may be a dominant friction mechanism. Recent results confirm this assumption.[27] Also, this study underscores the importance of size control for the IF nanoparticles.

Using the surface force apparatus, the friction behavior of IF nanoparticles was investigated in detail.[28–30] It was revealed that IF nanoparticles are gradually exfoliated, leaving molecular sheets of WS_2 on the mica surface, thereby reducing the shear resistance of the matting pairs in tetradecane suspension. Therefore the interplay between the rolling/sliding of the nanoparticles and their slow exfoliation seem to play an important role in the self-lubricating of mating tribological surfaces with IF. In contrast, 2H-WS_2 particles did not show favorable tribological properties.[30]

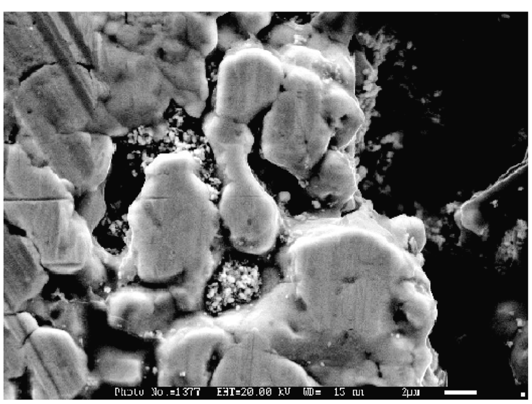
IMPREGNATION OF IF NANOPARTICLES INTO POWDER MATERIALS

Modern powder metallurgy (PM) technologies are used to produce low-cost, high-quality bearings and gears with long-term performance and reliability in critical applications (high loads and sliding velocities). Interconnected system of pores renders the supply of oil impregnated throughout the entire metal piece, thereby providing self-lubrication of these bearings. The lubricating fluid flows through the porous structure and is furnished to the metal surface. However, the addition of oil is prohibitive for various applications, such as aerospace, vacuum systems, and electrical motors. The impregnation of solid lubricants platelets, such as powders of WS_2 and MoS_2, into the powder matrix allows for an increased loading of the bearings. Unfortunately, the friction coefficients encountered in bearings stuffed with solid lubricants are invariably higher (0.1–0.3) than in oil-impregnated bearings.

For most applications, the porosity of self-lubricating bearings lie between 25% and 35%. It is clear that such high porosity diminishes the mechanical properties of the porous material. On the other hand, reducing the porosity to increase the strength of the matrix would restrict the permeation of the solid lubricant into the pores. It was hypothesized that IF-WS_2 nanoparticles will benefit self-lubricating bearing technology in a number of ways. First, being small (0.005–0.2 μm), they could be easily impregnated into bearings of substantially smaller porosity. Such bearings will have appreciably higher mechanical strength combined with an improved tribological behavior, especially under extreme loads and velocities. Second, their seamless character and spherical shape will allow their facile impregnation throughout the entire bearing matrix. Also, being stocked in microscopic pores, these slippery nanoparticles would not be removed at once from the contact area. Instead, a slow release of the nanoparticles from the matrix pores will provide steady flux of lubricants and easy shearing of the metal–metal interface, even under extreme loads. It was also expected that the spherical shape of IF nanoparticles impregnated inside a porous solid matrix will lead to an easy flow from the pores to the contact surface, thus alleviating both friction losses and wear. The continuous supply of solid lubricant nanoparticles to the sliding contact is of great importance in this case. Therefore, it is expected that impregnation of spherical nanoparticles into the densified powder matrix will lead to a nanocomposite with superior mechanical and self-lubricating properties. Porous metal pieces, which are similar in size and shape to commercially available sliding bearings, were manufactured according to a standard PM procedure. The details of preparation PM parts were described in Ref. [31]. Bronze, iron, and iron–nickel matrices were been used in this work. Subsequently, impregnation of oil–2H-WS_2 and oil–IF-WS_2 (10 wt.%) suspensions into the porous metal parts was carried out under low vacuum. IF-WS_2 nanoparticles and layered platelets 2H-WS_2 with size close to 4 μm were used as solid lubricants. The density of IF nanoparticles is about 15–20% smaller than that of the bulk (2H) particles. Afterward, the samples were dried at 150°C (2 hr), under a vacuum of 10^{-2} Torr, in order to release the fluid lubricant from the porous metal piece. The hollow IF nanoparticles were 5 wt.% of the powder bronze, compared with 6% for the 2H-WS_2.

Fig. 6a shows SEM micrographs of the virgin bronze surfaces after impregnation of the 2H-WS_2 platelets has taken place. As shown by the micrograph, the surface of the metal matrix is nonuniform, and the 2H-WS_2 platelets are ''glued'' edge-on onto the metal surface through their reactive prismatic $(10\bar{1}0)$ faces (Fig. 6b). This orientation is unfavorable for the tribological action of this lubricant, and is, in fact, expected to ''glue'' the asperities of the two mating metal surfaces. Contrarily, the IF-WS_2 nanoparticles are scattered quite randomly on the porous metal matrix surface. Spherical agglomerates of the IF nanoparticles, which are trapped in the cavities on the metal block surface, are discernible. The SEM image of the powder nanocomposite showed that the penetration of IF-WS_2 nanoparticles is close to150–250 μm, and it depends on the matrix density.

(a)



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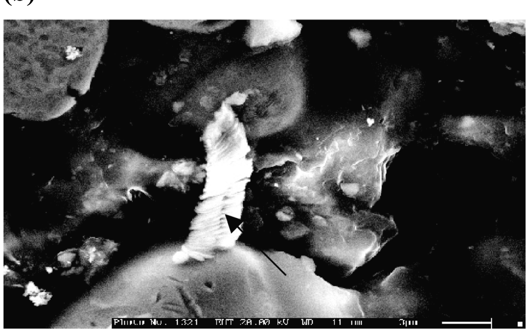

Fig. 6 SEM micrographs of the virgin bronze surfaces after the impregnation of the solid lubricant particles: a) IF-WS_2 nanoparticles distributed in the pores; b) 2H particles glued onto the metal surface (noted by arrow).

The study of friction and wear was performed by using a ring-block tester at wide range of sliding velocities and load.[32] Samples that were oil-impregnated and dried (hereafter designated as reference) were studied first. It was established that the surface pores of this sample are rapidly filled with agglomerated wear particles already under the low load. The agglomeration and compaction of the wear particles in the pores led to a formation of smooth surfaces. With increasing load, severe plastic deformation of the surface layers was obtained. In this case, delamination of thin surface plates was observed. The fast agglomeration and compaction of the wear particles within the pores and the severe plastic deformation of the surface layers led to an increase of the friction coefficient, contact temperature, and wear rate. With increased loading, the pores became completely closed, and a smooth surface of the densified powdered block is obtained. Upon transition to seizure, the wear particles adhere to the contact surface, leading to the formation of a rough surface. The friction coefficient and temperature increase abruptly, which finally leads to seizure of the matting surfaces.

The friction coefficient and temperature for bronze part impregnated with oil+IF and reference sample were very low ($\mu = 0.006$) over a large range of contact conditions, while it was higher ($\mu = 0.06$) for reference sample. In this case, a lot of small pores were preserved on the surface of powdered bronze impregnated with IF under steady friction conditions. With increasing load the detached and trapped wear particles fill the pores, but a fraction of the pores nevertheless remained opened. Friction and wear of the samples impregnated with IF nanoparticles associated with their release from the interconnected system of pores in the metal matrix and a furnishing to the contact interface. Supply of the solid lubricant from the pores to the surface requires the preservation of an open porosity at the surface. Furthermore, IF nanoparticles facilitate the dislodging of the agglomerated wear particles from the pores and thus preserve the porosity and the supply of IF nanoparticles to contact surfaces. Thus the impregnation of IF nanoparticles into the pores enables the improvement of the self-lubricating properties of powder materials, thereby considerably decreasing the friction coefficient and wear rate. Diminution of the friction coefficient with the IF nanoparticles can be attributed to the following effects:[33–36]

1. The slow release and furnishing of nanoparticles from the open pores to the contact surface prevent the direct contact between the first bodies.
2. The sliding/rolling of IF nanoparticles in the boundary of the first bodies and in between the wear particles (third body) facilitate the shear of the lubrication film.
3. The adhesion of IF nanoparticles to the agglomerated wear particles facilitates their dislodging from the pores, keeping the pores to remain open during loading.

It was shown that 2H particles are ‘‘glued’’ edge-on to the underlying metal surface through their reactive prismatic faces $(10\bar{1}0)$.[32] The sticking (‘‘gluing’’) of the prismatic edges of the 2H platelets to the metal surface averts their permeation deep into the metal piece and leads to their accumulation at the metal surface. The accumulation of 2H particles in the superficial pores leads to the formation of a thin WS_2 film on the surface of the sample. Under low load, this film provides the low friction coefficient and a reduced wear rate. However, with increasing load, the WS_2 film is cracked and its favorable tribological properties are diminished. The transition to seizure occurs under a load much lower than with IF nanoparticles.

The supply of solid lubricant from the pores to the surface requires the preservation of an open porosity at the surface. In the case of powdered materials impregnated with 2H-WS_2, the large delaminated wear debris filled the pores. This effect led to smoothing of the rubbed surface and clogging of the pores. In contrast, the IF-WS_2 nanoparticles, which are dispersed throughout the entire porous metal reservoir, are forced to proceed gradually to the metal surface, and some of them are even picked up by the disk.

The efficacy of the IF is considerably increased when an oil film is supplied to the interface. The application of oil allowed the considerable increase in the load-bearing capacity of powdered bearing samples impregnated with oil+IF nanoparticles.[34] It is likely that the release and furnishing of the solid lubricant from the interconnected system of pores to the contact surface is also facilitated by the oil.

ADDITION OF THE IF NANOPARTICLES INTO THE GREASE

The effect of IF nanoparticles added to a heavy-duty (lithium-based) grease was studied by using a ring-block tester.[37] Here, the friction behavior of the base grease (containing 5 wt.% IF-WS_2 nanoparticles) and a commercial grease [containing 5 wt.% 2H-MoS_2 particles (platelets) as additives] were compared. SEM examination of the tested grease shows that IF nanoparticles remained intact, but partially agglomerated. The fibrelous structure of the grease is preserved after the tribological experiments with the added IF nanoparticles, suggesting that grease does not decompose, or react, with either the nanoparticles or the metal surfaces, even under the heavy loads employed in the present experiment (Fig. 7a). The delamination of thin layers is observed on the surface of the 2H-MoS_2 (Fig. 7b). The friction and wear behavior of the base grease, the same state-of-the-art grease formulated

(a)

(b)

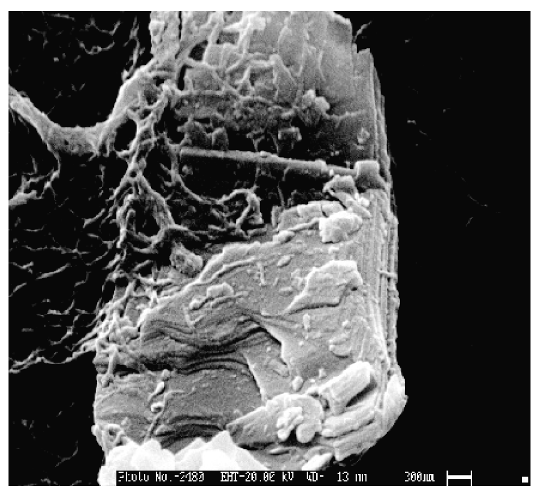

Fig. 7 SEM micrograph showing the thickener fibers with IF a) and 2H b) particles of solid lubricant.

with 2H MoS_2 platelets, and the grease formulated with IF tungsten disulphide nanosphere material were compared. Notably, the addition of only a small amount - (5 wt.%) of the IF-WS_2 nanoparticles to the grease leads to very low friction coefficient under very high loads, largely surpassing the critical loads for seizure of the pristine grease, or the grease with 5 wt.% 2H-MoS_2, added. While the temperature of the grease with 2H-MoS_2 particles rises to 75°C under high load of 2700 N load, it does not exceed 55°C under 3300 N for the grease with added IF nanoparticles. The effect of IF nanoparticles in greases on the friction, wear, and the temperature of powdered iron samples was studied. Under low loads, friction coefficients for greases with IF and 2H were close. However, with increasing load, the IF became more effective. Under load of 2700 N, a transition to seizure occurred with 2H particles, while the test with IF was continued up to the maximum possible load of the tester (3300 N). It was found that, in analogy to the friction coefficient, the effect of IF increases with the load. Thus it may be concluded that all the tribological parameters studied were considerably improved for the grease with IF nanoparticles in comparison to commercially available grease with 2H-MoS_2 particles. A large part of the pores was preserved on the surface of the powdered sample lubricated with grease + IF, while most of the pores were found to be clogged on the surface of the sample rubbed with a virgin grease. The study of friction and wear of powdered materials with greases showed high efficacy of the IF in comparison to commercial grease with 2H-MoS_2 particles and the base grease. IF nanoparticles were transferred from the grease to the contact surface. Energy-dispersive X-ray (EDS) and XPS analyses demonstrated that IF nanoparticles are confined in the pores of powdered matrix and are released to the interface even over high contact conditions.

NEW APPLICATIONS OF IF SOLID LUBRICANT NANOPARTICLES

Thin films of IF nanoparticles were deposited on metal substrates, either in the pure form or embedded in electroless coatings,[30,38,39] and were found to confer low friction and wear to the substrate, even under very high loads, ultrahigh vacuum (UHV), and in a humid atmosphere. It was shown that the frictional and wear properties of MoS_2 thin films deposited by ablating a solid MoS_2 target can be improved by the incorporation of fullerene-like nanoparticles.[38] IF-MoS_2 nanoparticles were tested under boundary lubrication and ultrahigh vacuum (UHV) and were found to yield an ultralow friction coefficient in both cases compared to hexagonal 2H-MoS_2 material.[30] The friction coefficient under high pressure (maximum pressure above 1.1 GPa in oil and 400 MPa in high vacuum) and slow sliding velocities (1.7 mm/sec in oil test and 1 mm/sec in high vacuum), and decreased and stabilized at about 0.04 for 800 cycles in both cases. It was found that 2H-MoS_2 particles are flattened and then break because of the contact pressure. The lamellar structure discovered in wear particles, MoS_2, leads to ultralow friction.

Ceramic materials are very ionic and consequently, are rather tough and brittle, notoriously known for exhibiting very poor tribological behavior. This poor behavior can be also attributed to the high surface roughness of ceramic materials. When rubbed against another surface, asperities of the rough ceramic surface detach and small wear particles are formed, which scratch and damage the mating surface, leading to its rapid deterioration. The surface of an alumina wafer was coated with a thin dry layer of IF-WS_2 nanoparticles, which was stressed under pressure applied by the reciprocating action of a ceramic ball. The added IF nanoparticles were found to decorate the irregularities and scratches on the surface of ceramic materials. Fig. 8a shows the results of a tribological experiment with Si_3N_4 ball and a flat alumina wafer. Here a 1 order-of-magnitude reduction of the friction coefficient is obtained by adding IF-WS_2 to the interface in comparison to a dry friction test. Furthermore, severe wear damage occurs to the surface of the ceramic ball rubbed against alumina (a) in Fig. 8b. Contrarily, almost no wear was incurred to the ceramic ball that was rubbed against the alumina surface coated with IF film (b) in Fig. 8b. This remarkable behavior could potentially be very useful for machine parts in the textile, food, and microelectronic industries, where ceramic components take part in the manufacturing processes. Under very high pressure (>1 GPa), nanoparticles suffer a severe plastic deformation and they gradually exfoliate, producing a continuous film 3–5 nm thick on the underlying surface, which has been studied by AFM.[36] This film is expected to provide easy shear of thin exfoliated sheets of IF nanoparticles under such extreme circumstances. This observation was, in fact, preceded by a theoretical calculation, which predicted that IF nanoparticles 60 nm in diameter will plastically deform under pressures exceeding 1 GPa.[39]

A polymer-fullerene-like–WS_2 nanocomposite was developed by impregnating the epoxy resin with IF-WS_2 nanoparticles. Polymer pin–steel disk test has been performed to evaluate the self-lubricating properties of this composite.[40] The friction coefficient of a disk–pin impregnated with IF-WS_2 is shown to be three times lower than for a pair: epoxy resin–steel disk. The wear rate of the

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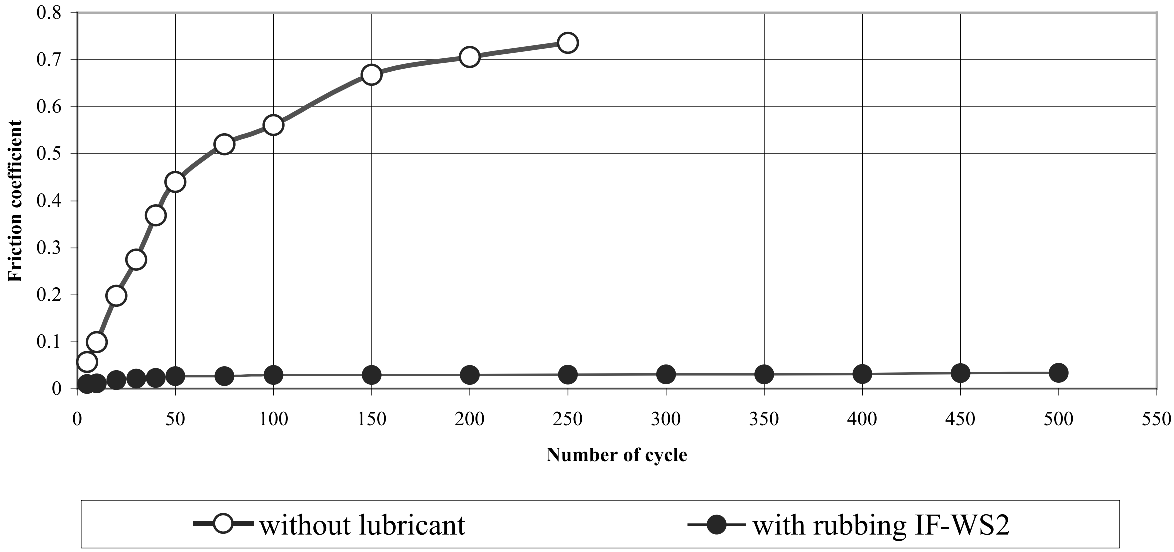
(a)



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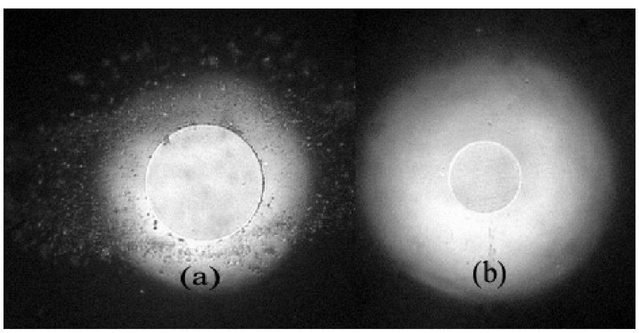

Fig. 8 a) The friction coefficient of a Si_3N_4 ball loaded against Al_2O_3 flat wafer; b) micrographs demonstrating the wear damage on the surface of the balls loaded against alumina wafer: a) without IF film and b) with thin film of IF nanoparticles. (*View this art in color at www.dekker.com.*)

polymer nanocomposite is found to be 10 times lower than for the virgin polymer. It is shown that polymer nanocomposites are transferred to the hard metal surface, releasing slowly the IF nanoparticles, which provides easy shear for the mating surfaces. Analysis of the contact surfaces of the steel disk rubbed with the polymer nanocomposite identified a transferred black film on the surface. To prepare the samples for TEM analysis, the transferred film was carefully delaminated from the surface of the disk. Using EDS analysis, it was observed that, apart from the epoxy matrix, the delaminated particles contain WS_2. It is likely that increasing the strength of nanocomposite, as a result of impregnation of stiff and elastic spherical particles and the formation of the transfer films containing the IF solid lubricant nanoparticles, are the main factors leading to lowering of the friction of the nanocomposite with solid lubricant nanoparticles. The wear coefficient, K_w, for nanocomposites was 0.5×10^{-11} vs. 4.6×10^{-11} mm^3/mmN for the epoxy samples.[40]

CONCLUSION

This description shows a plethora of somewhat unrelated tests and disparate set of data, whereby different interfaces lubricated with IF nanoparticles exhibited invariably significantly better tribological behavior compared with the reference systems, especially under heavy loads. It suggests that the beneficial self-lubricating properties of IF nanoparticles cannot be attributed to a single mechanism alone. Under low loads, the film thickness is close to the size of nanoparticles. In this case, the shape of the nanoparticles is preserved and sliding/rolling of the spherical IF nanoparticles at the interface seems to be the dominant friction mechanism. The agility of IF nanoparticles in the contact region also depends on their shape and size, underscoring the importance of their synthesis. The quasi-spherical shaped nanoparticles produced by the fluidized bed reactor are very suitable in this respect. When the film thickness is smaller than the size of the solid lubricant nanopowder (high contact pressures), deformation and destruction of IF nanoparticles leads to the exfoliation of thin external sheets. The self-lubricating behavior of IF solid lubricant nanoparticles is probably provided by shear of the thin transfer film. Note, that the distorted IF nanoparticles were found to be both in the valleys of contact surface and as transferred sheets at the summits of the asperities. The IF-WS_2 film serves to protect the contact surface and thus enhances the wear resistance of contact surfaces. Nanoparticles confined in the surface irregularities are unable to slide freely away from the contact area and are gradually released from the grooves and furnished to the mating surface, providing easy shearing, temporarily, until they are trapped again in another groove. This mechanism explains the beneficial role of surface roughness on the performance of the IF nanoparticles in tribological contacts. Self-lubricating properties of the powder materials impregnated with IF solid lubricant nanoparticles are explained by their easy furnishing and slow release to the contact surface. Stiffness of IF nanoparticles and their self-lubricating properties impart superior tribological properties to ceramic surfaces coated by IF and polymer nanocomposites with embedded solid lubricant nanoparticles.

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