Applications of WS_2 (MoS_2) inorganic nanotubes and fullerene-like nanoparticles for solid lubrication and for structural nanocomposites

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Nanoparticles of WS_2 and MoS_2 with a closed cage structure (fullerene-like) that are termed *IF* phases are synthesized in large amounts in a pure form. These nanoparticles were shown to play a favorable role as solid lubricants under severe conditions where fluids are unable to support the heavy load and are squeezed away from the contact area. Various tribological scenarios are presented for these superior solid lubricants, demonstrating the large scale potential for applications of these materials. The mechanism of action of these solid lubricants is briefly discussed. Various other potential applications of *IF* phases for nanocomposites with high impact resistance; in rechargeable batteries and in optical devices are discussed in short.

1. Introduction

Numerous inorganic compounds, like MoS_2 or CdI_2, crystallize in a quasi 2-D layered structure. In these compounds the metal atom is sandwiched between two anionic planes with strong covalent metal–anion bonds. Weak van der Waals interactions are responsible for the staking of the molecular layers into a crystal, which often appears in a platelet-form (deck of cards mode of packing). Fig. 1 shows a depiction of the MoS_2 crystal. It can be noticed that in the minimum energy configuration of the layers they are not aligned one on top of the other. Therefore often layered compounds crystallize in different polytypes. In the case of MoS_2 (WS_2), the low temperature stable polytype is 2H, *i.e.* a hexagonal unit cell consisting of two layers. Other 2-D compounds with different structural motifs and larger number of atoms in the unit cell are known.

It was shown first in 1992 that nanoparticles of layered (2-D) compounds, like WS_2, are unstable in the planar form and they fold on themselves giving rise to polyhedral fullerene-like nanostructures and nanotubes, termed *IF*.[1] This field has been intensively investigated in recent years and a number of review articles were published on this topic.[2] The advent of research on *IF* provided a great stimulus to explore their detailed structure and their properties, offering thereby a plethora of new potential applications, which address real

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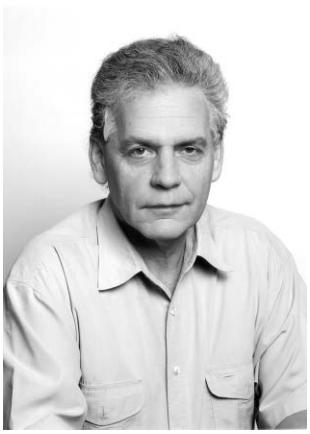

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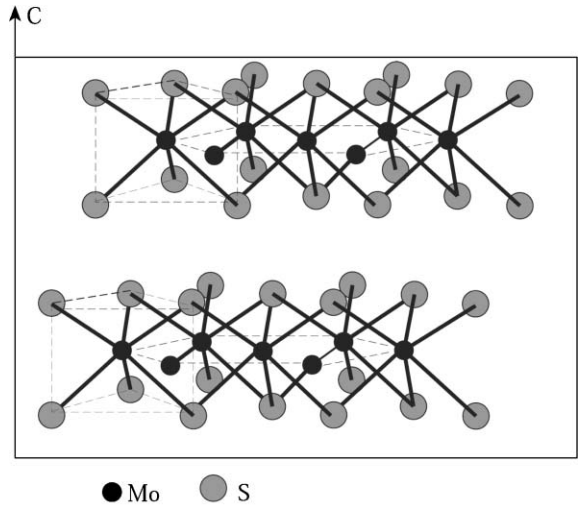

Fig. 1 Schematic rendering of the MoS_2 lattice.

market needs in a number of areas. Thus three conditions had to be fulfilled in order to address these opportunities. 1. A systematic investigation was needed in order to elucidate the growth mechanism of such nanoparticles. These developments led to a synthetic strategy which yields pure *IF* phases at affordable costs, and is also scalable to bulk quantities. 2. Once available in sufficient amounts, some unique properties representing a real market need had to be identified. Indeed *IF*-WS_2 and MoS_2 were found to be excellent solid lubricants,[3] especially under high loads where lubricating fluids are squeezed out of the contact region giving rise to high friction and wear. Furthermore, the same nanomaterials were found to have the rare combination of being mechanically very strong and flexible,[4,5] suggesting a large number of different applications. 3. Once identified, extensive research was needed in order to test this nanotechnology under realistic conditions. This process would entice the industry to go into development processes, which could eventually lead to commercial products. The first two conditions have already been fulfilled for *IF*-WS_2 (MoS_2) and although the last step is in progress, it is safe to say at this point that *IF* materials are heading for large-scale commercial exploitation. Perhaps the main obstacle for achieving that goal at this point is the need to scale-up the production to at least a few tons per day, which is expected to be accomplished in a few years time. On the other hand, technologies which require lesser amounts of *IF* materials, like self-lubricating surfaces, are still in their early development and testing stage. The present paper summarizes the observations that led to the development of these viable technologies, emphasizing the unique structure–functionality relationship occurring in these nanomaterials. The last section of this paper is devoted to a short overview of emerging technologies based on *IF* nanomaterials, besides lubrication, in electronics, catalysis, solar cells, *etc*.

2. Synthesis of *IF*-MS_2 nanomaterials

The structure and the physical behavior of *IF* nanomaterials, and hence their applications, are intimately related to their synthesis. Therefore, a very short overview of the synthetic approaches is due at this point. Fig. 2a shows a transmission electron microscopy (TEM) image of a typical nested fullerene-like nanoparticle of WS_2, while Fig. 2b shows a nested MoS_2 nanoparticle. Both kinds of fullerene-like nanoparticles are multilayer closed structures. They are produced by the reaction of H_2S with the respective metal-oxide nanoparticles at elevated temperatures and under a reducing atmosphere. The reaction mechanism to obtain both kinds of nanoparticles has been studied in some detail.[6,7] In these reactions, the oxide nanoparticles serve as a template, and the reaction proceeds from outside inwards. After the first closed MS_2 layer is formed by a fast sulfidization of the oxide nanoparticle, the next steps are a slow indiffusion of sulfur and outdiffusion of oxygen. This reaction occurs in a concerted fashion with a single growth front progressing inwards into the core of the nanoparticle, and a layer by layer reaction mechanism. This quasi-epitaxial growth mode gives rise to a quite perfectly crystalline structure of the *IF* nanoparticle. While the tungsten oxide nanoparticles are synthesized in a separate reactor, the molybdenum oxide nanoparticles are obtained *in-situ* in the same reactor, by reducing MoO_3 vapor with hydrogen.[7] There are a number of advantages and drawbacks to each of these

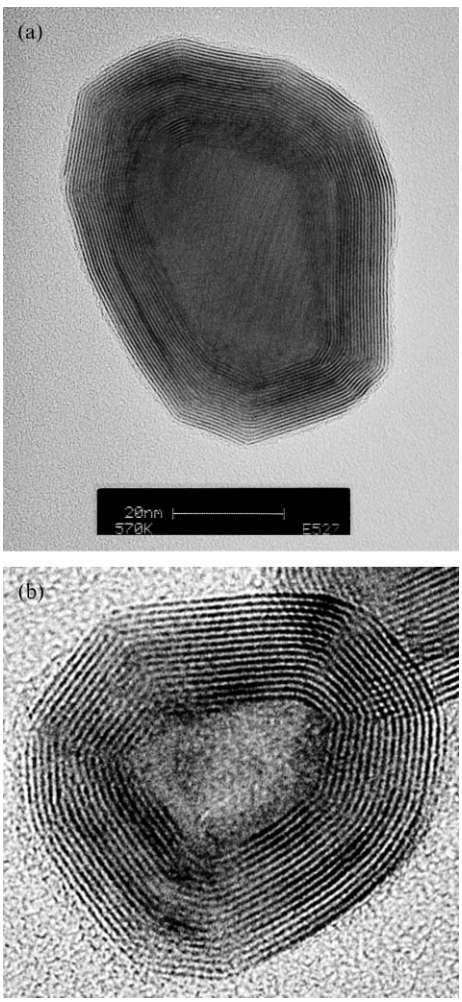

Fig. 2 (a) TEM image of a WS_2 nanoparticle with nested fullerene-like structure. (b) TEM micrograph of an *IF*-MoS_2 nanoparticle. The distance between the layers is 0.02 μm.

routes. The *IF*-WS_2 synthesis has been scaled-up to produce many kilograms and in the future will undergo further scale-up to produce tons of the nanoparticles. As Fig. 2a indicates, the nanoparticles are 50–100 nm in size with a relatively wide size distribution. The MoS_2 nanoparticles are expected to reveal improved mechanical properties, but scaling-up of the current reactor[7] for the *IF*-MoS_2 is more difficult than was the case for *IF*-WS_2. Furthermore, both reactions occur at elevated temperatures (840–950 °C) and they are slow. A new process, which addresses some of the above drawbacks and may result in nanoparticles with improved tribological behavior, has been recently described.[8]

Inorganic nanotubes belong to the canon of polyhedral structures of the *IF*. Various synthetic strategies to obtain different inorganic nanotubes are described in the literature. Fig. 3 shows a TEM image of a WS_2 nanotube obtained also by sulfidization of WO_3 nanoparticles in substantial amounts.[9]

3. Tribological behavior of *IF*-WS_2 (*IF*-MoS_2) and related materials

The friction between mating couples can be described using a generic behavior, *i.e.* the so-called Stribeck curve. Here the friction coefficient of the reciprocating pair as a function of the velocity of the moving surface, the viscosity of the lubricating fluid and the inverse of the normal load applied on the contact surface, are described. Under small loads and high velocities the pair is considered to operate under hydrodynamic conditions, where the spacing between the surfaces of the reciprocating pair is large. The friction coefficient is influenced mainly by the rheological properties of the lubricating fluid, *i.e.* it increases with increasing viscosity of the fluid. Under very high applied loads and small velocities, the spacing between the mating pair is small (<0.1 micron) and the friction coefficient increases with increasing load, or decreasing velocity. The range of conditions between these two extremes is denoted as boundary lubrication. The *IF* nanoparticles were expected to exhibit a major influence on the tribological behavior of a pair under mixed and boundary lubrication conditions, which was indeed the case.

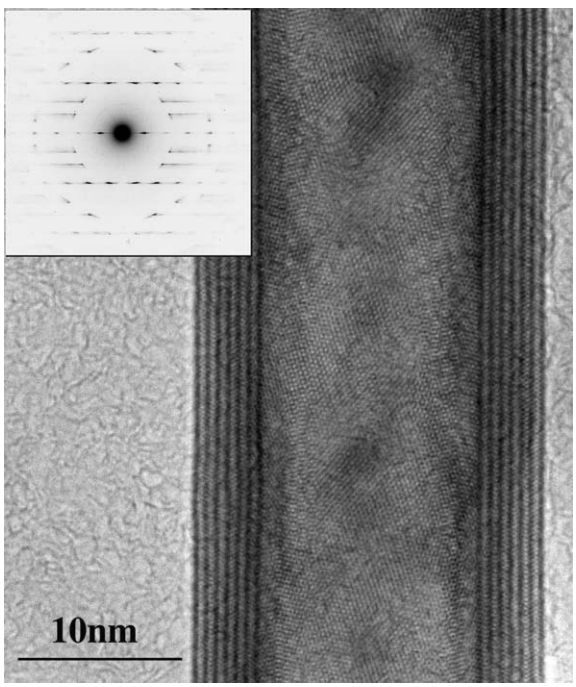

Fig. 3 TEM image of a WS_2 nanotube with its electron diffraction in the inset.

2H-MoS_2 powder serves in various tribological applications, either on its own, or as an additive to fluid lubricants.[10] Solid lubricants are used in areas where lubrication fluids can not be used, for example lubricating high vacuum systems, or in space applications. Alternatively, they are used as additives to enhance fluid lubricants which are tuned for heavy duty applications. Two main mechanisms were evoked to explain the low friction coefficients and wear resistance of contact surfaces lubricated with 2H-MoS_2 powders. 1. The fact that the basal (00*l*) planes of MoS_2 platelets consist of sulfur atoms which are fully bonded and non-reactive entails that the crystallite exhibits low reactivity towards the underlying surface leading thus to low absorption of water vapor. Moreover, the surface energy of the terminal sulfur atoms is rather low allowing them to easily shear with respect to the metal surface. The weak van der Waals type sulfur–sulfur interaction between adjacent layers permits easy shearing of the layers with respect to each other, which provides another efficient lubrication mechanism. 2. More recently however,[10] the role of material transfer from the MoS_2 platelets onto the metal surfaces (third body[11,12]) was discussed. Here gradual peeling-off of molecular layers from the MoS_2 crystallite and their deposition on the asperities of the opposing metal surfaces, provides low friction of rubbed surfaces.

However, the 2H-MoS_2 crystallites are known to be highly anisotropic and reactive. While the sulfur atoms of the basal (00*l*) planes are fully bonded and consequently non-reactive, the Mo and S atoms on the prismatic (*hk*0) faces are not fully bonded and are consequently very reactive. Therefore, instead of the crystallites aligning their basal (00*l*) plans parallel to the underlying surface, they tend to stick to the surface through the pending atoms of the prismatic (*hk*0) surface, actually disturbing the easy shear and thus the effective lubrication. The platelets are therefore burnished and oxidized quite rapidly during the friction of the two mating surfaces. This fact explains the relatively short lifetime of the lubricant due to fast deterioration of the 2H-MoS_2 particles.

Fullerene-like MoS_2 (WS_2) nanoparticles were hypothesized to improve the tribological behavior of the pair under the scenarios of boundary and mixed lubrication. The small size and quasi-spherical and seamless shape was thought to provide an effective means for rolling friction, and reduced wear. Furthermore, the closed cage structure means that these molecules are mechanically very stable. However, in contrast to 2H-MoS_2 platelets, shearing between the closed layers in the seamless fullerene-like structure is believed to be ineffective. Following the synthesis of the first macroscopic amount of *IF*-WS_2 a series of tests were undertaken in which small amounts of the *IF* powder were added to lubricating oils.[3] These experiments vindicated the hypothesis that *IF*-WS_2 outperforms any other solid lubricant under harsh conditions.

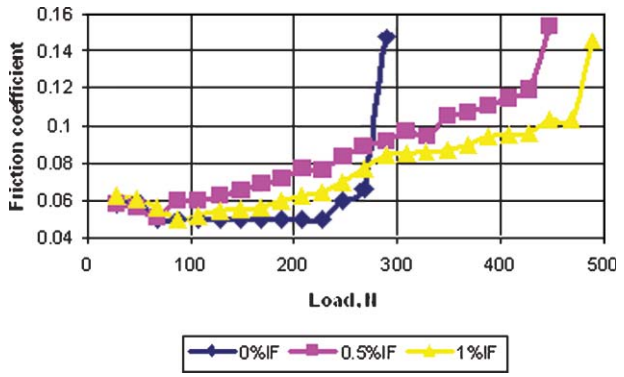

Fig. 4 The effect of load on friction coefficient of ball-on-flat pairs rubbed with paraffin oil and paraffin oil mixed with 0.5 and 1% of *IF*-WS_2 nanoparticles.

Fig. 4 shows typical results from ball on flat test, in which the performance of pure paraffin oil and that of oil mixed with *IF*-WS_2 were compared. It may be seen that the addition of only 0.5% of the *IF*-WS_2 nanoparticles improved remarkably the load capability of friction pairs as indicated by the rise in the critical load to seizure (deflection point of the curve), which increased from 270 to 430 N.

Another potential application of *IF* nanoparticles is as an additive to improve the performance of metal working fluids. The nanosize of the nanoparticles makes them particularly well suited to act as solid lubricants even in small tolerance drilling. In addition, the very low friction coefficients reduce temperature rises due to the metal working process which means that less fluid is needed to cool the work pieces. As the *IF* material also reduces wear, the lifetime of the cutting tools can be extended.

More recently, *IF*-MoS_2 films were synthesized by a high pressure arc-discharge technique, and their tribological behavior was compared with sputtered 2H-MoS_2 films in both dry and 45% humid atmospheres and a load of 1.1 GPa.[12] Whereas the sputtered MoS_2 films showed a friction coefficient higher than 0.1 and were rapidly deteriorated, the *IF*-MoS_2 films exhibited friction coefficients no larger than 0.01 and much better longevity. The *IF*-MoS_2 nanoparticles collapsed under high contact pressure and were transfered as small molecular sheets onto the two matting surfaces. In another series of experiments *IF*-MoS_2 films were prepared and tested using a pin on flat tribometer under ultra high vacuum conditions and high loads (0.7–1.1 GPa).[13] Under these conditions the gap between the two mating surfaces in the contact region is smaller than the size of the *IF* nanoparticles themselves, *i.e.* <0.1 micron, and the nanoparticles squeezed to the contact region suffer mechanical deformations and they start to peel-off (*vide infra*). The beneficial effect of these *IF* coatings suggest numerous applications for the aerospace industry. With the same purpose in mind, *IF*-MoS_2 nanoparticles were synthesized by an arc-discharge system where the electrodes are immersed in water.[14] The hydrophobic nanoparticles, which floated on the water surface, were collected and deposited as thin films on a metallic substrate. They were found to provide low friction and wear in comparison with macroscopic 2H-MoS_2 particles and sputtered films.

IF-WS_2 powder has significantly surpassed the minimum requirements of an outgassing screening test for space applications. This aerospace qualification test was done in accordance with international specifications (ASTM E-595). This test measures the total mass loss (TML) and the collected volatile condensed material (CVCM) under vacuum at 125 °C for 24 hours. The criteria of TML < 1% and CVCM < 0.1% are used for certification of materials for space applications. The total mass loss and volatile mass loss of the *IF* powder under these conditions was several times lower than the specified target values, *i.e.* 0.4% and 0.02%, respectively.

Solid lubricants are required in several types of space applications since in such low pressure environments conventional liquid and grease lubricants are generally not stable. Besides aerospace, the high stability of *IF* nanoparticles and their low vapor pressure suggest that they will be excellent lubricants for other ultra clean environments as well such as for semiconductor fabrication facilities and in food and pharmaceutical manufacturing equipment. Preliminary data indicate that *IF* materials can provide excellent lubricity in space applications.

The behavior of *IF*-WS_2 nanoparticles was also studied under fretting friction conditions.[15] Here a ball was moved back and forth in a small (180 micron) amplitude on top of a stainless steel flat surface. Fretting friction conditions occur in various systems subjected to small mechanical vibrations. The applied loads (0.4–0.85 GPa) imply that the contact pairs lubricated with oil + *IF*-WS_2 nanoparticles were tested under mixed (moderate loads and sliding velocities) and boundary (high loads and low sliding velocities) lubrication conditions. A very favorable effect of the solid lubricant additive (reduction of friction by more than 50%) was obtained under mixed lubrication conditions, but under higher loads, *i.e.* boundary lubrication conditions (> *ca.* 0.5 GPa), the friction coefficient increased to a point close to that of the system lubricated with *IF*-free fluid.

The mechanical properties of *IF*-WS_2 under compression were studied.[16] The nanoparticles were shown to be mechanically very robust and they did not collapse instantaneously under high loads (*vide infra*). Theoretical analysis showed that *IF* nanoparticles 60 nm in diameter become unstable and yield under a pressure of 1GPa.[17] Friction and wear experiments with *IF* nanoparticles under severe contact conditions (high loads and sliding velocities) showed that these nanoparticles are destroyed in the interface with formation of smooth well adhered thin layers.[12,13] Although the nanoparticles collapse at the interface they provide a remarkably low friction and wear rate. The above analysis suggests that the abrupt increase in the friction coefficient in the fretting friction experiment[15] under high loads should be attributed to the particular conditions used in this experiment.

The beneficial effect of *IF* was not limited to metal pairs, but was observed also in ceramic pairs.[18] Fig. 5 shows the effect of adding *IF* nanoparticles in the contact region between the surfaces of a ceramic Si_3N_4 ball and an alumina flat. Whereas severe wear damage could be observed on the ball tested without the solid lubricant, no damage whatsoever was observed when the *IF* nanoparticles were applied at the interface. The overwhelming effect of the *IF* nanoparticles in

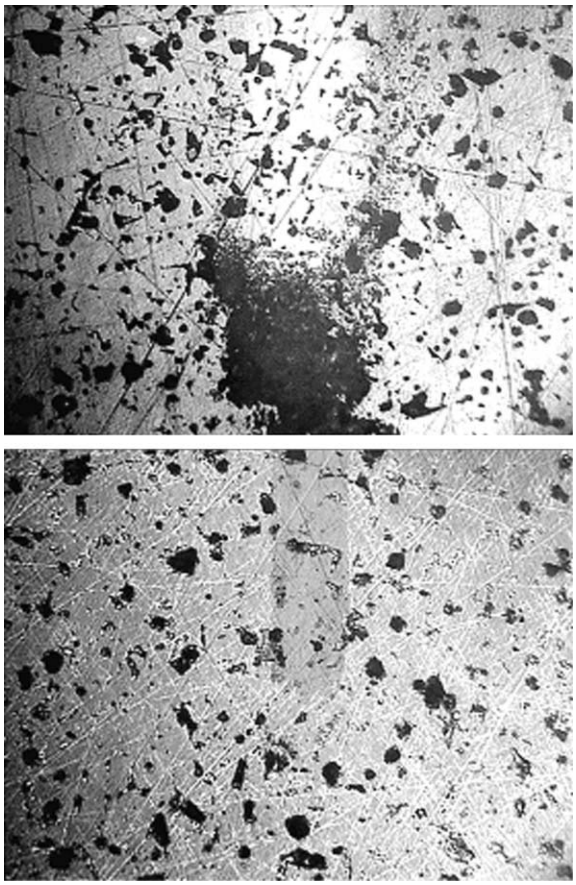

Fig. 5 An SEM micrograph showing the wear track on the surface of alumina produced by reciprocating Si_3N_4 ball. Large amount of wear debris were observed for the non-lubricated pair (top). Narrow, practically wear-free track is observed on the surface of alumina, which was burnished with *IF*-WS_2 nanoparticles prior to the tribological test (bottom).

alleviating friction and wear of the ceramic pair suggests numerous potential applications.

Early discussions of the lubrication mechanisms of the *IF* nanoparticles emphasized the fact that their quasi-spherical shape confer them rolling friction behavior. More recently however, substantial evidence has been accumulated also in favor of a third body transfer. This mechanism involves the transfer of exfoliated molecular sheets from the multi-walled nanoparticles (there may be 20–40 such layers depending on the diameter of the nanoparticle) onto the asperities of the mating surfaces, especially under severe contact conditions. Early on, three different mechanisms for the alternation and gradual destruction of *IF* nanoparticles during tribological tests were described:[19] a. puncturing of the nanoparticles; b. mechanical deformation into a rugby-ball shaped structure and c. peeling-off of a few layers from the nanoparticles surface. It was also argued that once deformed or punctures, *IF* nanoparticles are more prone to further damage by oxidation, or ripping of molecular layers. This phenomenon can also be considered as self-healing. The peeling-off of a few external layers from the nanoparticles' surface reveals new layers of close quasi-spherical nanoparticles that can roll and support the contact load.

Measurements using surface force apparatus (SFA) provided further evidence on the lubrication mechanism of *IF* nanoparticles and the transfer films in particular. Here, mica surfaces lubricated with pure tetradecane and loaded with 5% *IF* nanoparticles and with 5% 2H-WS_2 particles were studied.[20] A comparison between the lubricants clearly showed the favorable effect of the *IF* nanoparticles in reducing the friction between the reciprocating mica surfaces. Subsequent analysis of the mica using atomic force microscopy (AFM) revealed that the surface was uniformly covered with islands of WS_2 nanoparticles a few molecular layers thick. These nano-islands, which were assumed to be ripped off from the fullerene-like nanoparticles, are believed to have been the main cause for the easy sliding of the reciprocating mica surfaces with respect to each other. These experiments were the first to indicate a new mechanism for friction and wear reduction in interfaces, *i.e.* formation of uniformly distributed islands of thin layers resulting from broken *IF* nanoparticles on the contact surfaces.

Clearly, under boundary or even mixed lubrication conditions the spacing between the asperities of the two mating surfaces is smaller than the size of the nanoparticles themselves. In this case, pristine *IF* nanoparticles are unable to enter the lubricated area and they are partially deformed or even fully collapsed under the exerted heavy mechanical load. This initial structural damage enhances the gradual exfoliation of the *IF*-WS_2 nanoparticles and the transfer of some of its molecular sheets onto the asperities of the two mating surfaces.[21] A similar approach has been proposed also by Joly-Pottuz *et al.*[22] The nature of the transferred film was convincingly verified using a number of analytical techniques, including X-ray diffraction, Raman and photoelectron spectroscopy (XPS).

Another kind of beneficial tribological application of the *IF* nanoparticles was obtained by impregnating it into porous matrices prepared through powder metallurgy.[23] Thus, the powder-based samples which were impregnated with the *IF* nanoparticles exhibited low friction coefficients and wear loss even under high loads. Furthermore, it was established that the impregnation of the *IF* nanoparticles allows a very high load capacity of the powder-based materials, whereas oil-lubricated parts failed under these loads. Various porous matrices of different strengths were prepared and tested, all of them proved to perform better upon impregnation of the *IF*-WS_2 nanoparticles. Irrespective of the exact lubrication mechanism discussed above, a slow release of *IF* nanoparticles from the pores and their furnishing to the contact interface occurred. This can be easily understood as the penetration depth of the impregnated nanoparticles is greater than the wear damage of the matrix. Thus, the motion and vibrations of the mechanical parts lead to a slow release of the impregnated nanoparticles. The released nanoparticles are slowly migrating through the tortuous paths of the porous matrix to the contact area of the reciprocating surface alleviating the friction and the wear. Since the surface of the porous mechanical part is quite rough, the *IF* nanoparticles are not free to slide freely on the rubbed surface and hence they are maintained for relatively long periods of time in the contact area. Such porous self-lubricating mechanical parts are used extensively in sliding bearings, which are found in cars, home appliances, electric hand tools, machines and numerous other applications.

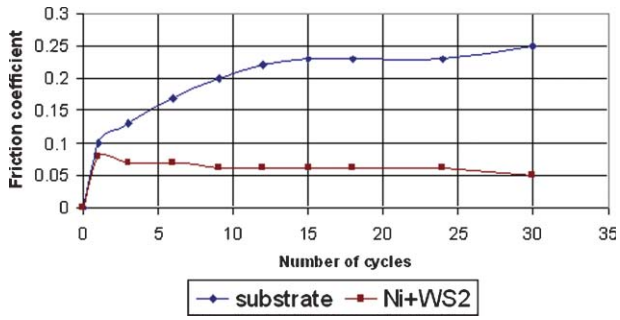

Fig. 6 Typical dependence of the friction coefficient *vs.* time for a Ni–P electroless coating on stainess steel, with and without *IF*-WS_2 nanoparticles incorporated into the layer.

Another large field of application for the *IF* nanoparticles is for self-lubricating coatings. Here the *IF* nanoparticles are impregnated into a solid film. Early attempts to impregnate the nanoparticles into polymer matrices,[24] and nickel–phosphorus electroless coatings,[25] were successful, but further work is needed to elucidate the working mechanism and improve the properties of these self-lubricating coatings. Fig. 6 shows the results of a typical tribological test with a Ni–P coating deposited through an electroless process onto a stainless steel substrate. Obviously, the impregnated nanoparticles are unable to freely rotate and provide rolling friction. However, the low friction coefficients observed for these coatings suggests that here transfer of *IF* nanoparticles or layers peeled-off from the nanoparticles play an important role in reducing friction of the coating. Furthermore, the impregnated nanoparticles are not very well dispersed in the matrix and therefore they form agglomerates. Under the load of the mating surface, some pristine *IF* nanoparticles are released to the interface and provide rolling friction. Another mechanism by which the *IF* coatings may alleviate friction at the interface is through concerted vibrational modes of the entire nanoparticle, *e.g.* like that of a tennis ball bouncing from a wall. Another possibility is that due to their symmetrical spherical shape, once exposed at the interface, the *IF* nanoparticles act as an array of points which facilitates sliding action of the reciprocating metal pieces.

Rolling friction is likely to play a larger role if more spherical and smaller *IF* nanoparticles were used. Stated differently, one would expect that rolling friction could prevail under lower Stribeck numbers, *i.e.* higher loads and low sliding velocities. It is expected that the small, more perfect and spherically shaped nanoparticles will provide better tribological properties than the platelets form of the solid lubricants. Such a new process has been described.[8] Preliminary tribological tests with the newly synthesized *IF* nanoparticles indicate that indeed using these nanoparticles the friction coefficient was close to 0.03. Future improvements are likely to lead to even lower friction coefficients.

4. Other potential applications for *IF* nanomaterials

The phase diagram of the pair M–S (M = W, Mo) does not contain any additional high pressure phase other than MS_2. Indeed measurements in a diamond anvil cell showed that 2H-MoS_2 is stable to 30 GPa.[26] The mechanical properties of *IF*-MS_2 nanoparticles, which are being currently investigated,[4,5] show that the average yield strength and strain of WS_2 nanotubes are respectively 22 and 12%. The shockwave resistance of WS_2 nanotubes was determined to be >20 GPa.[27] Fullerene-like MoS_2 nanoparticles were found to withstand shockwaves as high as 30 GPa.[28] These high values suggest that *IF*-MS_2 powders can be formulated into ultra high strength nanocomposites, which can also withstand high impacts, with numerous potential applications in the automotive, aerospace and personal safety and defence industries.

Various other applications are being explored for the inorganic nanotubes. Thus using MS_2 (M = Mo, Ti) nanotubes for catalytic[29] methanation of CO and as cathode materials for Li intercalation batteries[30] have been described by Chen *et al.* VO_x nanotubes were also investigated as host material for Li intercalation batteries.[31] The nanotubes are particularly useful because they can host a large amount of the guest Li atoms in the spacing between the layers. Furthermore, being a stable phase (in the nanoregime, *i.e.* <0.1 micron), they can be reversibly charged/discharged many times without losing their perfectly crystalline structure or changing their composition. Most recently, VO_x nanotubes which were intercalated with Li and iodine atoms were shown to exhibit ferromagnetic behavior at room temperature.[32] Such nanophase materials are likely to be important in the development of spintronics and computer memory.

The electronic and optical properties of various inorganic nanotubes have been investigated through theory and experimental work. It was shown that, in contrast to quantum dots, the bandgap of semiconducting nanotubes, like MoS_2, shrinks with decreasing diameter of the nanotubes.[33,34] This new tunability opens the path for new optical observations. Tunability of the Fermi level and thus the conductivity of semiconducting *IF* nanoparticles by intercalation of alkali metal atoms was also demonstrated.[35] Furthermore, metallic[36] and even superconducting[37] nanotubes were studied, which suggests that various electronic devices could be fabricated using inorganic nanotubes. Optical limiting behavior in VO_x nanotubes was measured,[38] providing further evidence for the large, hitherto barely explored, plethora of optical phenomena which could exist in inorganic nanotubes.

Conclusions

Inorganic nanotubes and fullerene-like materials form a newly established paradigm. They open up a large variety of opportunities for the applications of inorganic compounds in a fashion not hitherto explored.

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