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Slow Release of Fullerene-like WS_2 Nanoparticles from Fe–Ni Graphite Matrix: A Self-Lubricating Nanocomposite

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ABSTRACT

Densified iron–nickel–graphite blocks were prepared by powder metallurgy processes and subsequently impregnated with a few percent of fullerene-like WS_2 nanoparticles (<150 nm), synthesized in a fluidized bed reactor. Using the disc-block setup, the friction coefficient; critical load for seizure, and wear rates were measured. Substantial improvements in all of the tribological parameters were measured with the addition of the fullerene-like nanoparticldes. This behavior is attributed to a slow release of the nanoparticles from the porous matrix onto the block surface and their excellent tribological behavior.

Fullerene-like WS_2 (MoS_2) nanoparticles (*IF*) have been studied in the past.[1−3] Their efficacy as additives for lubrication fluids has been demonstrated.[4] Unfortunately, the slippery nature of these nanoparticles leads to their fast displacement from the contact area, and consequently the efficacy of their lubrication is maintained so long as they can be replenished to the contact area. In a recent work, *IF*-MoS_2 films were found to exhibit excellent tribological properties, even in a humid atmosphere, where sputtered MoS_2 films deteriorate very rapidly.[5] In an alternative approach, *IF*-WS_2 nanoparticles were confined inside a porous and densified bronze−graphite matrix, prepared by the powder metallurgy (PM) technique. Slow release of the *IF* nanoparticles onto the metal surface was shown to alleviate both friction losses and wear, while ensuring the mechanical integrity of the nanocomposite.[6,7] A multiscale tribological model was proposed, according to which the *IF* nanoparticles reside in the pores of the metallic matrix and are slowly furnished to the surface, where they serve as both lubricant and a spacer. In the current work, which is an extension of the previous ones, this concept is taken one step further by using a much harder iron−nickel−graphite porous matrix, which was prepared by powder metallurgy (PM). *IF*-WS_2 nanoparticles were impregnated into the porous matrix and a series of tribological measurements were performed. Substantial reduction in both friction and wear, and an increase in the critical load were observed. The results are rationalized in terms of a multiscale model, which distinguishes between the long residence time of the nanoparticles in the large pores, and their fast sliding (rolling) on the metal surface, with intermittent capture by submicron surface cavities.

Advances in PM technology offer various types of self-lubricating bearings. Examples of this technology are the oil-impregnated bronze (Cu−Sn) bearings, or the much harder iron−nickel bearings. Graphite is often added to improve the tribological properties of these bearings. One of the main advantages of PM technology is the possibility to provide controlled porosity for self-lubrication.[8] The lubricating fluid flows through the interconnected network of pores and is furnished to the metal surface, thereby providing permanent lubrication. Friction coefficients in the range of 0.005−0.09 are observed in the case of oil impregnation. Notwithstanding the temperature limitations of liquid lubricants, these self-lubricating bearings are used only in the low load/high velocity range. At the same time, the addition of oil is prohibitive for various applications, such as vacuum systems and electrical motors. The graphite particles are fixed and their beneficial effect is confined only to its close vicinity. For most applications, the porosity of self-lubricating bearings lies between 25 and 35%.[9] This porosity is sufficient

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to provide connectivity of the pores, and imparts mechanical stability to the matrix.

The growth mechanism of WS_2 fullerene-like nanoparticles has been studied in quite detail.[10,11] Here, H_2S and H_2 react with WO_3 nanoparticles at 850 °C. A closed WS_2 monatomic layer is formed instantaneously, and the core of the nanoparticle is reduced to WO_{3-x}. The enfolding sulfide layer prevents the sintering of the nanoparticles. In the ensuing step, sulfur diffuses slowly into the oxide core and reacts with the oxide. The oxygen atoms outdiffuse, and progressively closed WS_2 layers replace the entire oxide core. After a few hours reaction, nested and hollow WS_2 nanoparticles of a diameter <150 nm are obtained. For the synthesis of *IF*-MoS_2 nanoparticles,[12] MoO_3 powder is vaporized first at 780 °C. The vapor is carried to a hotter reaction zone containing H_2 gas. Reduction of the vapor by H_2 gas at 840 °C leads to the formation of MoO_{3-x} nanoparticles, which subsequently react with H_2S gas. It must be emphasized that this purely chemical synthesis of the nanoparticles lends itself to a scale-up and does not produce byproducts, which saves the costly processes of separation and purification. Once the growth mechanism of the nanoparticles was well understood, a fluidized bed reactor for the synthesis of 30 g/day of the *IF*-WS_2 nanoparticles was conceived.[13] The current production rate of *IF*-MoS_2 nanoparticles (ca. 60 mg/day) does not permit detailed studies of this kind, yet.

Porous metal pieces, which are similar in size and shape to commercially available sliding bearings, were manufactured according to a standard PM procedure. Iron−nickel−graphite powder was mixed with a low melting point organic material, such as carbomethyl cellulose, which contribute to the pore formation, and then were compacted at room temperature. The pressed samples were sintered in hydrogen atmosphere at 1100 °C. Due to the difference in size between the Ni and Fe particles, a wide distribution of pore sizes, between 20 and 150 μm, was obtained. Subsequently, impregnation of oil−2H−WS_2 (6.5%) and oil−*IF*-WS_2 (4−8.4%) suspensions into the porous metal parts was carried out under low vacuum. Afterward, the samples were dried at 150 °C (2 h) under a vacuum of 10^{-2} Torr, to release the fluid from the porous metal piece. Finally, the samples were re-pressed (400−500 MPa) in order to bring them into the required shape and porosity (25−30%). The reference sample, which did not contain any solid lubricant, was soaked with oil, dried at 150 °C in a vacuum and re-pressed. A run-in period of between 10 and 30 h was performed, during which the load was slowly increased to 300 N, until most (ca. 70%) of the concave surface of the metal piece was in contact with the convex surface of the steel disk. Intermissions for examination of the bearing surface with optical and scanning electron microscopes (SEM) with energy dispersive (EDS) analyzer were taken from time to time during the run-in period and in the experiment itself.

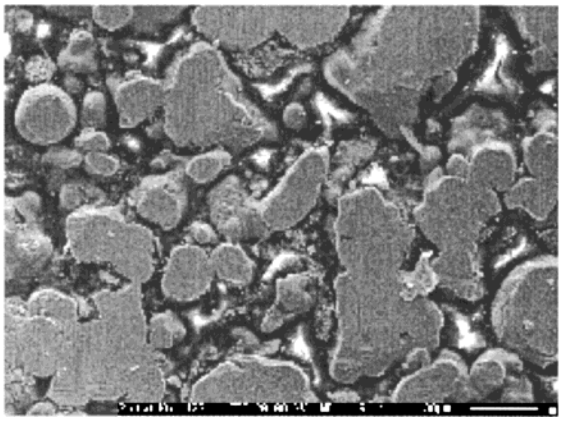

Figure 1. SEM image of the surface of an Fe−Ni−C metal piece after a 10 h run-in period under 300 N and a velocity of 1 m/s. Agglomerates of the *IF*-WS_2 nanoparticles reside in the pores as confirmed also by EDS analysis. Scale bar is 30 micron.

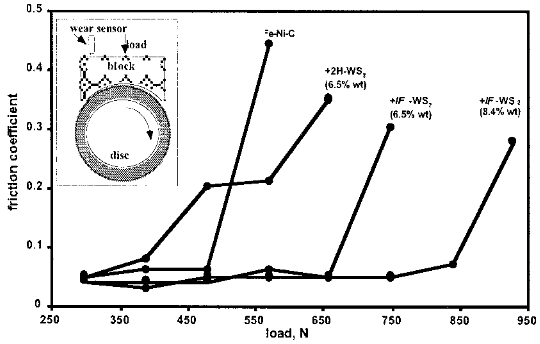

Figure 2. Friction coefficient vs load (in N) of porous iron−nickel−graphite block against hardened steel disk (HRC 52). In these experiments, after a run-in period, the loads were increased from 30 kg with an increment of 90 N and remained 1 h under each load. The graph shows the iron−nickel−graphite sample without added solid- lubricant; iron−nickel-graphite sample with 2H−WS_2 (6.5%); the same sample with (6.5%) and 8.4% hollow *IF*-WS_2 nanoparticles. Velocity is 1 m/s.

Examination of the metal piece with the SEM revealed that the surface of the metal matrix is nonuniform and contains a wide distribution of micron-size pores and submicron cavities. Furthermore, the impregnated 2H−WS_2 platelets are observed to be "glued" edge-on onto the metal surface through their reactive prismatic edges. This orientation is unfavorable for the tribological action of this lubricant, and in fact is expected to "glue" the asperities of the two mating metal surfaces. On the contrary, spherical agglomerates of the *IF*-WS_2 nanoparticles, which are trapped in the cavities and pores on the metal block surface, were clearly discernible (see Figure 1).

These agglomerates are very soft, and they decompose into separate *IF* nanoparticles under light loads and shear movement.

Figure 2 shows the friction coefficient as a function of the load exerted on the composite metal matrix (the inset of Figure 2 displays a schematic of the tribological setup).

Under relatively low loads, all of the sintered samples exhibited a relatively low friction coefficient (ca. 0.05). Beyond a certain critical value, the friction coefficient increased abruptly, signifying the seizure of the mating metal pair. Most remarkably, while the addition of 2H−WS_2 platelets does not lead to a significant increase of the critical load (470 N), if any, compared to the unlubircated sample, the uptake of hollow WS_2 nanoparticles increases this point, substantially. The critical grip (seizure) load was found to increase quite monotonically with the *IF* content: from 600 N for 4% *IF* to 660 N (6.5%) and 850 N (8.4%).

The time evolution of the friction coefficient, under a load of 300 N and velocity of 1 m/s, was examined as well. The friction coefficient of the reference sample (without any solid lubricant added), and also that with 2H−WS_2 particles impregnated, decreased over the first few hours and then stabilized at the value of 0.048 for the rest of the experiment (37 km or >10 h). The friction coefficient of the *IF*-impregnated sample was 0.04 throughout the entire experiment. The measured wear coefficient for the reference metal piece after 10 h of experiment was 76.4×10^{-11} mm^3/mmN. For the 2H−WS_2 impregnated porous metal piece this coefficient was 41.9 and it went down to 16.9×10^{-11} mm^3/mmN for the *IF*-impregnated metal matrix. These experiments demonstrate, in fact, very significant improvements in both lifetime and performance of the iron−nickel−graphite sample with *IF*-WS_2 nanoparticles incorporated into the porous matrix.

The main favorable benefits of the hollow WS_2 nanoparticles in oil were attributed previously to the following three effects: (a) rolling friction;[4] (b) the *IF* nanoparticles serve as spacers, preventing the contact between the asperities of the two mating metal surfaces;[4] (c) third-body material transfer,[14] i.e., mono or diatomic layers of WS_2 are gradually transferred from the nanoparticles onto the metal surfaces during the experiment, providing a reduced sliding friction between the two mating metal surfaces. This effect was discussed before in connection with the lubrication provided by 2H−MoS_2 powder.[15]

The situation in self-lubricating metal surfaces is more complex, however. Following the run-in period, the metal block surface consists of a distribution of large (few tens of microns) pores, and micron-size to nanoscopic surface cavities, separated by relatively flat domains. The size distribution of the cavities has been clearly confirmed by atomic force microscopy (AFM). The *IF* solid lubricant consists of nanosize particles. Therefore, the friction mechanism of the *IF* lubricant has to be considered on a multiscale level, in both space and time domains. The interconnected network of pores can store the nanoparticles for long periods of time and furnish them gradually to the surface (see Figure 3A). Once on the surface, the slippery *IF* nanoparticles slide (role) very fast and they are trapped momentarily by the submicron cavities, which prevents their run-away (Figure 3B). When an *IF* particle is confined in a nanoscopic cavity, it starts to roll under the effect of the shear forces in the system, and reduces the friction at the interface. Momentary confinement of the nanoparticles in larger cavities or channels (pores) does not lead to a reduction in the friction or wear, but prevents the run-away of the nanoparticles from the contact area and protects them against mechanical damage and oxidation. Also, the *IF* nanoparticles, which are confined in nanoscopic cavities, prevent the contact between the asperities of the mating surfaces, serving thereby as spacers. This scenario provides low friction and a long-term protection against wear, which averts the rapid filling of the pores by wear debris. The slow rate of wear in this case allows also for gradual dislodging of the wear debris outside the contact area, leaving the pores open and permitting *IF* nanoparticles, which were initially buried deep beneath the surface, to access the surface. At the same time, the slow wear rate also reveals fresh pores with *IF* nanoparticles stored inside, which maintain the low friction and wear rate for prolonged periods. The driving forces, which dislodge the nanoparticles from the deep pores onto the metal surface, are probably of hydrodynamic and mechanical nature. This unique scenario provides a synergism between the two components of the nanocomposite, which protects the surface against excessive friction and rapid wear under extreme loading conditions.

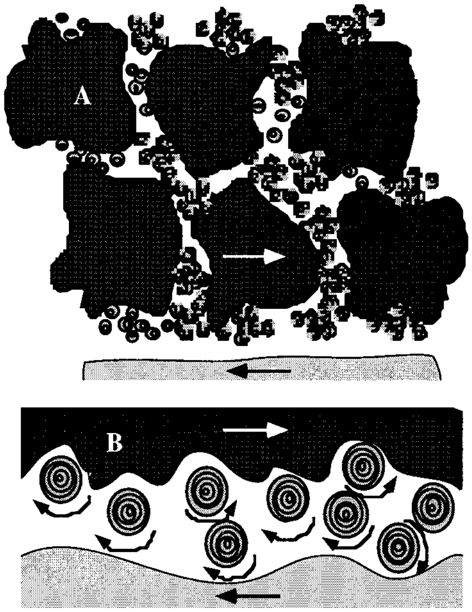

Figure 3. Schematic illustration of the wear protection mechanism of porous metal matrices impregnated by a solid lubricant. The shaded areas are representative of the metal grains; the concentric circles represent the *IF*-WS_2 nanoparticles. Image A shows the *IF* nanoparticles, which are impregnated into the pores and are released to the mating metal surfaces. The exploded view (B) represents the interlocking of the nanoparticles at the metal surface by nanometric cavities and their rolling, which reduces friction and wear.

Sliding bearings are routinely used in places where ball bearings are prohibitive due to weight-saving considerations, such as for car and other automotive engines, transmission systems, pumps, aerospace, appliances, and numerous other applications. Unfortunately, the losses due to friction are higher in sliding bearings than those encountered in ball bearings. The present nanocomposite combines the advantages of the two technologies. Here, the hollow WS_2 nanoparticles serve as nanoball bearings and thereby reduce frictions to levels comparable with those encountered in ball bearings, but with the additional weight savings benefit, typical of sliding bearings and without sacrificing the mechanical strength of the metal part.

To further improve the present technology, additional densification of the metal matrix and use of smaller iron−nickel grains for the PM processing, which will leave smaller pores and thereby improve the mechanical robustness of the metal parts, would be useful if not necessary. Therefore, the relationship between the pore and nanoparticle sizes should be studied in detail in the future. *IF*-MoS_2 nanoparticles are expected to outperform the presently available *IF*-WS_2 nanoparticles.[5] Future efforts to synthesize *IF*-MoS_2 powder in adequate amounts (a few grams) will permit such experiments. It is not unlikely that for the hard metallic matrix, used in the present experiment, stiffer nanoparticles, which can support heavier loads, would be required to prevent the contact between asperities. This can be achieved, e.g. by leaving some of the oxide within the core of the *IF* nanoparticles, or by using the WC core[16] instead of the present hollow core. Further research is necessary in order to unravel the tribological mechanism of this complex interface.

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