Nanomaterials for tribological applications in the aerospace

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Summary

In this project we strive to develop new lubrication technology suitable for space applications. The technology is based on new nanoparticles synthesized in the Weizmann Institute laboratory (RT). At the same time a new set-up for tribological measurements in space conditions is mounted in the laboratory of LR at the Holon Institute of Technology. The newly synthesized nanoparticles of MoS_2 have fullerene-like (closed cage) structure and are doped by either rhenium or niobium atoms, which makes them negatively or positively charged at their surfaces. The extremely challenging synthesis of these nanoparticles is briefly delineated. The characterization of the nanoparticles and the determination of the doping level (<200 ppm), which was found to be extremely difficult in this case, is briefly mentioned. The new set-up for tribological measurements under vacuum and cryogenic conditions is nearing completion and will be tested and run in the next few months. A new series of tribological measurements investigating the effect of added WS_2 nanotubes on the friction and wear of aerospace grade epoxy resin are reported.

Main report

1. Forward

Space environment is harsh and requires technologies which are sometime very different from the ones used in terrestrial applications. Typically, aerospace systems encounter rapid temperature variations from cryogenic to very high temperatures, strong and erratic variations, radiation damage, etc. New tribological technologies are required to respond to the challenges of long and far trips of unpopulated and human populated missions to the outer space. To respond to these needs we propose to use solid-state nanoparticles which offer improved lubrication under harsh conditions. These nanoparticles are based on (Re, Nb)-doped MoS_2 (WS_2) nanoparticles with fullerene-like structure.

The WIS PI group has demonstrated some 24 years ago that nanoparticles of WS_2 and MoS_2 form hollow closed structures, dubbed inorganic fullerene-like (IF) structures and multiwall inorganic nanotubes (INT).[1] These nanoparticles were used as additives to fluid lubricants and were shown to exhibit superior tribological behavior.[2] The technology was licensed to NanoMaterials (N.I.S.-www.nisuscorp.com) which manufactures and sells “NanoLub” oil-additive based on “industrial grade” IF-WS_2 nanoparticles.

The synthesis of IF/INT nanoparticles/nanotubes doped with very small amounts (<100 ppm) of rhenium (Re) atoms, was reported by us.[3] These nanoparticles were found to be superior to the undoped nanolubricants.[4,5] These new additives to lubricants show great promise to space technology.

2. Synthesis of advanced IF/INT for (aerospace) tribological applications (WIS): Here, much of the effort was focused on developing a new synthetic strategy for obtaining Nb-doped IF/INT of MoS_2 (WS_2). This high-temperature synthesis is extremely challenging. The doping of the semiconductor nanoparticles by extrinsic dopant atoms is intended to tune their Fermi level and control their

surface charge (zeta potential). To achieve the uniform Nb doping of IF/INT-MoS_2 (WS_2), which will produce positively charged (p-type doping) nanoparticles, we have synthesized first a new Nb_xMoO_3-x phase and subsequently sulfurized this oxide at elevated temperatures (about 900 °C). The nanoparticles were characterized by SEM-EDS, TEM-EDS, XRD. Their shape was quite perfect as indicated by TEM analysis (see **Fig. 1**). Determination of the low doping level of the nanoparticles was found to be extremely challenging. Attempts to use ICP-MS, which has been used successfully for the determination of the loading level of rhenium atoms in IF-MoS_2,[3] were not successful for technical reasons. The loading (doping) level of the Nb was determined by X-ray fluorescence and was found to be < 1000 ppm (<0.1 at%). EXAFS-XANS measurements of the Nb-doped samples done in the synchrotron light source of the Brookhaven National Laboratories (US), showed that, as expected, the Nb occupies (Mo) substitutional site in the MoS_2 lattice, i.e. Nb_{Mo}. Kelvin probe measurements with AFM showed that the Fermi level of the doped IF-MoS_2 nanoparticles is 400 meV below that of the undoped ones, i.e. their work function is larger than 5 eV. Zeta potential measurements of aqueous dispersions of Nb-doped IF-MoS_2 were carried out as a function of the pH of the dispersions. These measurements demonstrated that the surface potential of the Nb-doped IF-MoS_2 is less negative and the isoelectric point shifted to higher pH's as compared to the dispersions of undoped and Re-doped nanoparticles. Thus, larger [OH^-] ion concentrations are required to neutralize the positive charge induced by the Nb-doping of the nanoparticles. These findings will be summarized into publications during the second year of the project. Extensive tribological measurements[4,5] have demonstrated that the Re-doped IF-MoS_2 nanoparticles with ca. 100 ppm are superior solid lubricant to the undoped IF nanoparticles and appreciably better than the neat oil or oil formulated with microscopic MoS_2 platelets. Similar measurements will be carried out for the Nb-doped nanoparticles once sufficient amount is available. Incidentally, the Re-doped IF-MoS2 nanoparticles were found to be very good electrocatalysts for hydrogen production.[6]

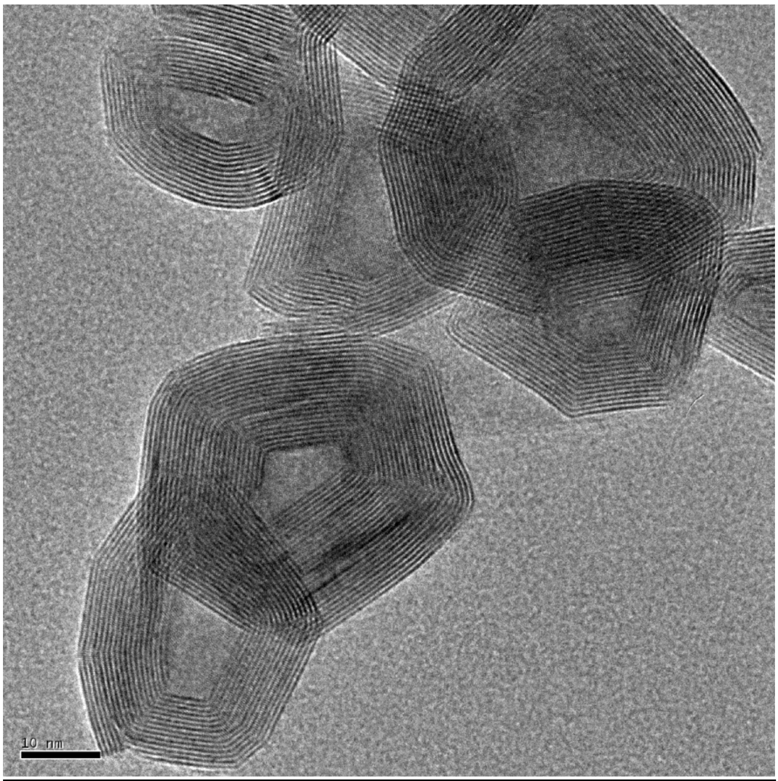

Fig.1. Transmission electron micrograph (TEM) of an assortment of typical Nb-doped (200 ppm) IF-MoS_2 nanoparticles.

<u>3. Setting-up a new tribological apparatus for aerospace applications (HIT)</u>: a new set-up for tribological measurements under controlled atmosphere and variable temperatures (from cryogenic to 300 °C) has been constructed and will be used to study lubricating technologies under space-

simulated conditions. For the manufacturing of the cryotribometer the analysis of the literature concerning the test machines for the study of friction and wear at high vacuum (10^{-6} Torr) and low temperatures (up to -200C) was undertaken (see e.g. Ref. 7). Based on the analysis of the literature, the friction scheme -3 balls against disk has been chosen. The sliding velocity can be varied up to 300 rev/s; the applied load can reach up to 50 N. **Fig. 2** shows a schematic rendering of the cryogenic tribometer and **Fig. 3** shows a photograph of the set-up

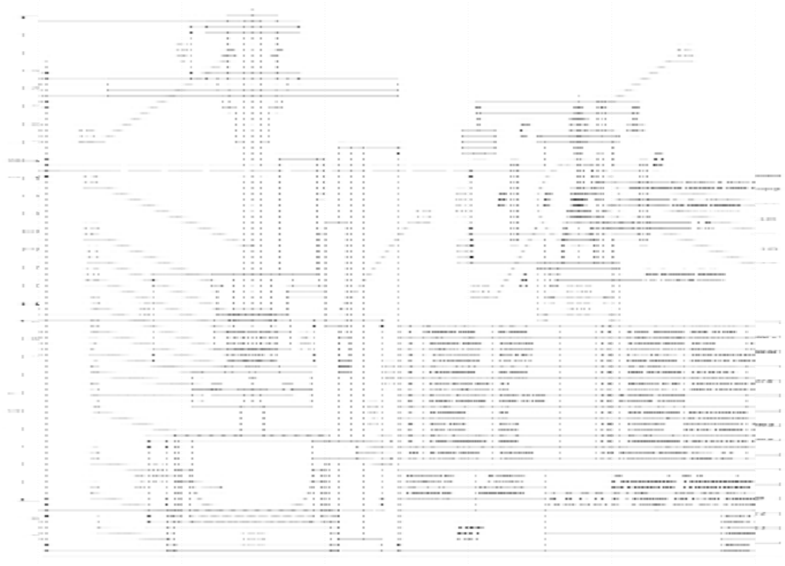

Fig. 2. Schematic rendering of the cryogenic tribometer fabricated in Rapoport's laboratory

Fig. 3. Photomicrograph of the cryotribometer

4. Tribological measurements of epoxy resin reinforced with WS_2 nanotubes

4.1. Experimental Procedure

The tribology tests were performed using block-on-ring rig (epoxy ring against - steel ring, AISI 52100, Hardness, HV=8.0-8.5 GPa), see schematic rendering of the rig in Fig. 4. The tests were performed with lubricant- synthetic poly-alpha olefin oil (PAO 4-oil, 6 drops/min) at room temperature. The scheme of loading was as follows: 115 N during 0.7 hour, 213 N during 2 hours and 360 N during two hours. The friction coefficient and wear rate were measured during the test.

Inductive sensor with accuracy of 0.1 micron was used for analysis of wear. Sliding velocity is constant (100 rpm). Epoxy resin mixed with INT-WS_2 (1%, 3%, 10%) has been used. The virgin roughness parameter, Rz = 0.6 micron.

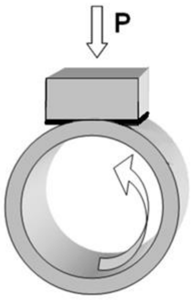

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Fig. 4. Scheme of block-on-ring rig

4.2. Results and discussion of the tests

The results of the analysis of the friction coefficient and wear loss are presented in Fig. 5.

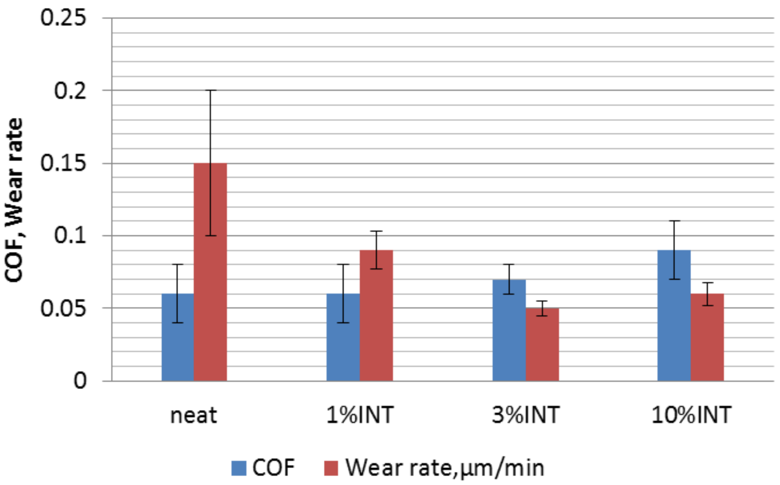

Fig. 5. The effect of the amount of added nanotubes on the friction coefficient and wear rate of the epoxy resin

The variation of the amount of INT-WS_2 in the epoxy resin has practically no influence on the friction coefficient. However, the analysis reveals a strong effect of the INT on the wear rate. The largest effect is observed when 3% of INT are added to the epoxy. With further increase of the amount of INT in the epoxy the effect is diminished. The absence of a favorable effect of the INT on the friction coefficient can be rationalized by the mechanism of lubrication by WS_2 the nanoparticles [e.g. 8,9]. Fullerene-like nanoparticles (IF) are effective when they can be supplied to the surface as free particles, which provides easy shearing between the rubbed surfaces. The INT nanotubes are released to the interface during the wear of the epoxy resin. However, the nanotubes can serve as effective lubricants only when they are oriented perpendicular to the shearing direction. Since the direction of the nanotubes in the epoxy matrix is random, upon release they are also randomly distributed at the interface and hence their effect on the friction is minimized. On the other hand, the INT reinforce the epoxy matrix,[8] increasing its strength and fracture toughness, and hence they favorably affect the wear resistance of the epoxy resin.

5. Future plans: In the second year of the research tribological tests of various lubricants suitable for cryotribometric measurements will be undertaken. Space-tuned lubricants, like Fomblin, will be tested with undoped and Re (Nb)-doped IF-MoS_2 nanoparticles.

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