AN INITIAL EXAMINATION OF NANO-FULLERENE COATINGS AS POTENTIAL SPACE LUBRICANTS

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ABSTRACT

The tribological properties of the well-established space lubricant MoS_2, and other metal dichalcogenides, are excellent in vacuum conditions but are comparatively poor in air. It has been postulated that fullerene films based upon MoS_2 and WS_2 could be less sensitive to the effects of moisture and offer the possibility of low friction (and wear) even when operated in air.

To determine whether this is the case, ESTL carried out a test programme to evaluate the friction and wear characteristics of WS_2-based fullerene films in vacuum, dry nitrogen and air. A pin-on disc test apparatus was used to evaluate their tribological properties as a function of load, speed and dwell.

The results of these tests showed that the fullerene films performed well in vacuum and dry nitrogen but relatively poorly in air. There was no indication that these particular WS_2-based fullerene films were more resistant to the effects of moisture in humid air than sputtered MoS_2 films.

1. BACKGROUND

Since the discovery of the soccer ball shaped C60 buckminster-fullerene carbon molecule in the mid 1980s [1], it has been speculated that it, and similar rounded cage structures, will exhibit lubricating action involving the rolling of the molecules. Tribological studies have shown that whilst useful in lowering friction when used as an additive in fluid lubricants, carbon fullerenes themselves are actually poor solid lubricants [2].

Subsequently, a range of other non-carbon based materials with fullerene-like atomic structures (referred to as inorganic fullerenes, IF) have been synthesised and investigated. This field of research started with the discovery in 1992 of fullerene-like tungsten disulphide (WS_2) by researchers at the Weizmann Institute, Israel who later formed NanoMaterials Ltd. [3]. Since the familiar form of metal dichalcogenides such as WS_2 is similar to the layered graphite form of carbon, it is unsurprising that fullerene-like structures should exist.

It has now been shown that several metal dichalcogenide materials, including MoS_2 [4] as well as WS_2, can be produced in the form of fullerene-like nanospheres. In their conventional layered forms, both materials (particularly MoS_2) are well established as lubricants for vacuum and space, but their tribological properties remain poor in the presence of moisture [5, 6, 7]. This is generally accepted to result from the adsorption of water molecules on exposed edge sites resulting in higher shear strengths.

The results of several studies show that IF metal dichalcogenide materials may represent a new class of lubricants, with improved behaviour in both vacuum and ambient air conditions. The atomic structure of these fullerene-like materials generally consists of nested rounded hollow cages [4]. Thus, in the case of isolated nanoparticles, the lubrication properties are inherently isotropic, unlike the case of layered hexagonal MoS_2 for example, which only acts as a lubricant in the direction of the basal planes [8]. The nanoparticles' closed-sphere structure has an additional advantage in that it is chemically inert, with no exposed reactive edge sites [9]. As such, IF materials may be less sensitive to the effects of moisture and offer the possibility of low friction (and wear) even when operated in air.

In early studies of the use of IF materials as lubricants, adhering nanoparticles to a surface proved difficult due to the lack of chemically binding edge sites [10]. Consequently much of the research has been based around either adding the nanoparticles to lubricant oils [11], use as a dry powder on a substrate [12], or impregnation of the IF in composite materials [13], rather than the formation of a solid thin film coating, as is the preferred option for many space tribology applications [6].

One method which may be used to form thin film coatings on a metal substrate is high-pressure arc-discharge deposition, which has been successfully used by researchers at Cambridge University, UK to deposit IF-MoS_2 [4]. High-resolution electron microscope

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images, such as that in [Fig. 1], show that the coatings consisted of curved S-Mo-S planes and nano-particles with a nested (onion-like) structure.

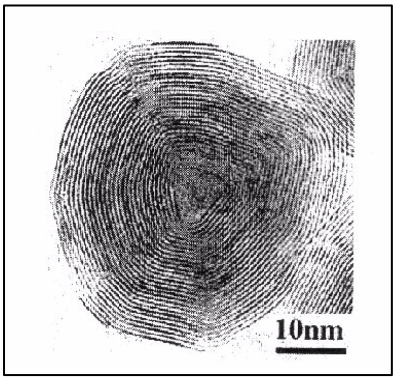

Figure 1. High resolution electron microscope picture of a typical nano-sphere

This work offered compelling evidence that thin films of IF-like metal dichalcogenides may offer improved lubricant behaviour, particularly in air, over the conventional layered forms. Friction and wear measurements indicated that low friction was obtained in both dry nitrogen gas and air (at an RH of 45%). Furthermore the friction coefficient observed of the films in air was lower, and the lifetime longer, than that of a sputtered MoS_2 in dry nitrogen [4].

There have also been a number of reports on the tribological behaviour of IF-WS_2, including a presentation by Niles Fleischer of NanoMaterials Ltd. of Israel at the 10th ESMATS conference [9, 13, 14]. A study of the stability of inorganic fullerenes showed that IF-WS_2 is more stable than IF-MoS_2, which in turn is more stable than IF-NbS_2 [15]. IF-$TiWS_2$ has also recently been prepared, and initial studies show it can have a friction reducing effect when used as an additive in conventional lubricant oils [16]. In a slightly different application, MoO_3 nanocrystals, produced by the thermal oxidation of an MoS_2 surface have been used as 'molecular bearings' confined between two MoS_2 surfaces - it is speculated that such an arrangement may be useful in the development of nano- and micro-machines [17].

It has been claimed that the mechanism of lubrication in IF-like metal dichalcogenides may not be due to low shear strength (as is conventionally the case) but rather due to the ability of the nano-spheres to act as microscopic ball bearings, by rolling rather than sliding contact [11]. It has also been shown that the 'onion' surfaces undergo 'exfoliation' during sliding, and transfer conventional MX_2 sheets to the other contacting surface [13]. High contact pressure and sliding may result in the nano-spheres being flattened or sheared open, but it has been reported that when this happens, friction is still reduced by the rolling of flattened cages, or the formation of the familiar MoS_2 sheets if the cages are sheared open completely [18].

An assessment of the lubricating behaviour of these new materials, particularly in vacuum, was considered highly desirable. In this way the potential of these lubricants for space applications could be assessed. ESTL's approach was to carry out fundamental friction and wear measurements in vacuum, air and dry nitrogen.

2. TESTING

This work was carried out using pin-on-disc (POD) tribometers in which an uncoated 7.14mm diameter steel (52100) ball was loaded against a fullerene-coated hardened steel (52100) washer (type INA WS81102, with dimensions 28 mm OD, 15 mm ID and 2.75 mm thick).

2.1. Sample Details

Nanomaterials Ltd, based in Israel, produced the fullerene surface coating by an in-house burnishing technique. The coating thickness of the samples provided was approximately 2 - 3 µm, [Fig. 2] shows one of the discs after testing and [Fig. 4] shows the coating surface viewed under a Scanning Electron Microscope (SEM).

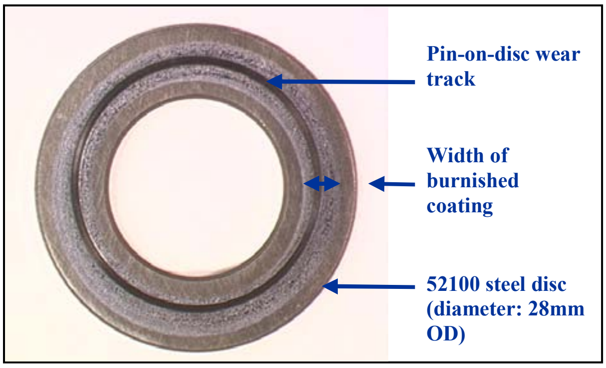

Figure 2. Plan View of Fullerene Coated Disc (after testing)

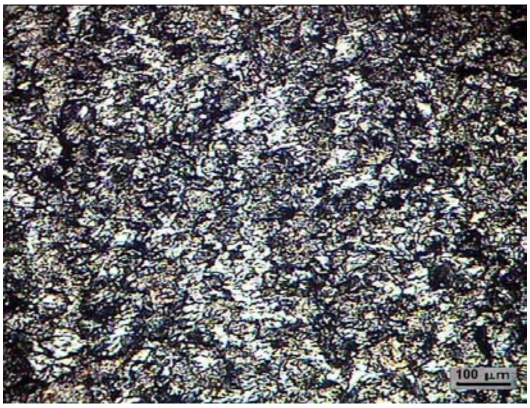

Figure 3. SEM micrograph of burnished coating

2.2. Test Set-up and Test Conditions

Testing was performed on two separate pin-on-disc (POD) tribometers. The vacuum tribometer [Fig. 4] for vacuum and air tests and the CSEM nitrogen purge tribometer [Fig. 5] for the nitrogen and air tests.

Friction was monitored to determine the performance of the coating. Tests were carried out until the friction co-efficient exceeded 0.3 (signifying metal on metal contact) at which point motion was terminated.

The effect of load was assessed by varying between 3.3 and 20N.

The effect of speed was assessed by varying between 1 and 200rpm.

The effect of dwell was assessed by varying stop times between 10 and 10,000seconds.

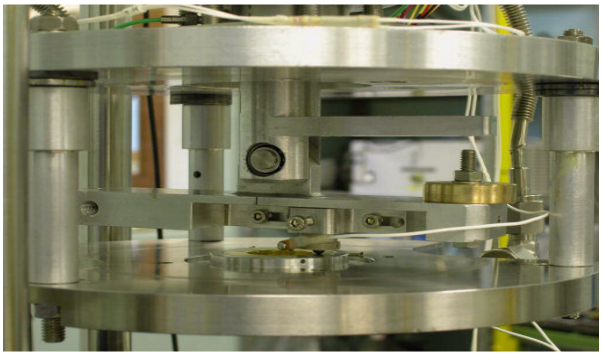

Figure 4. Air and Vacuum Testing Apparatus.

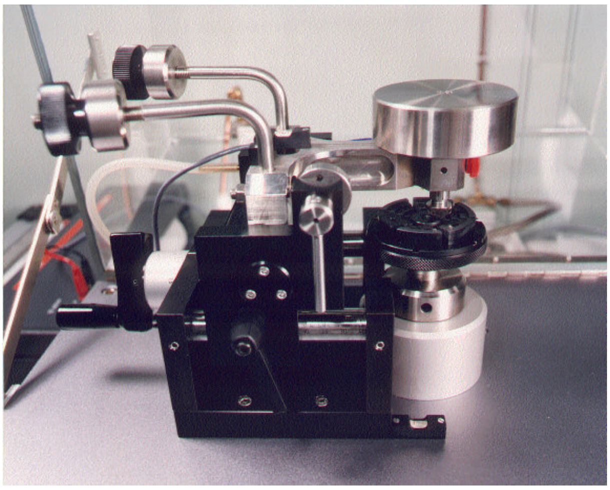

Figure 5. Air and Nitrogen Testing Apparatus.

3. SUMMARY OF RESULTS

3.1. Environment

The fullerene coatings yielded low friction under high vacuum (friction coefficient in the order 0.02 [Fig. 6]) and dry nitrogen gas (friction coefficient in the order 0.03, [Fig. 7]).

Coating life was consistently longer in vacuum than dry nitrogen gas by a factor of at least 2 but up to 10. The example shown in [Fig. 6] and [Fig. 7] with a 10N load shows a life in vacuum of 1,200,000 revs compared to 142,000 in nitrogen.

In laboratory air (RH ~ 50%) the fullerene coatings yielded higher friction (friction coefficent in the region 0.1 to 0.15 at a pin load of 10N). The coating lives were considerably shorter in air (2000 - 5000 revs at 10N load).

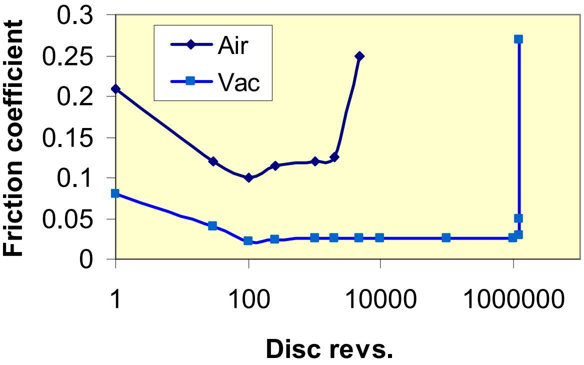

Figure 6. Fullerene in Air & Vacuum POD Tests, (Pin load = 10N; mean contact stress = 824MPa)

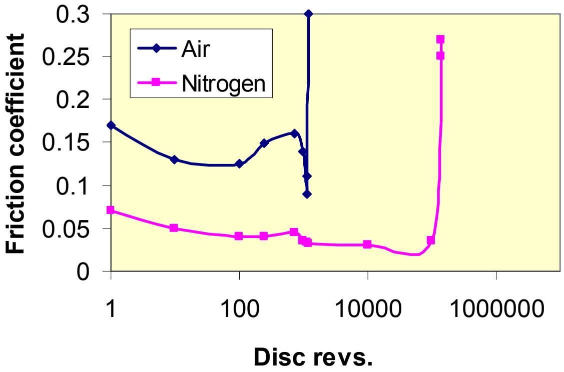

Figure 7. Fullerene in Air & N_2 POD Tests (Pin load = 10N; mean contact stress = 824MPa)

3.2. Load

The friction co-efficient and coating life both tended to reduce with increasing load as would be expected for thin solid film lubrication. An example of the load life relationship is shown in [Fig. 8].

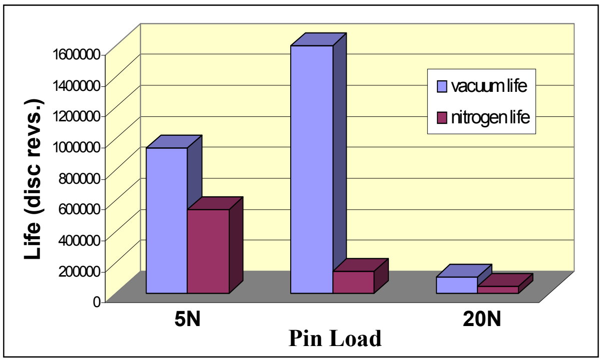

Figure 8. Fullerene Life in Vacuum & Nitrogen Under Varying Load

3.3. Speed and Dwell

In vacuum and dry nitorgen we observed that the film friction was speed-dependent [Fig. 9]and also exhibited a 'dwell' effect [Fig. 10] i.e. after running-in the coating the re-start friction was a function of stop time (such properties have been seen for sputtered MoS_2)

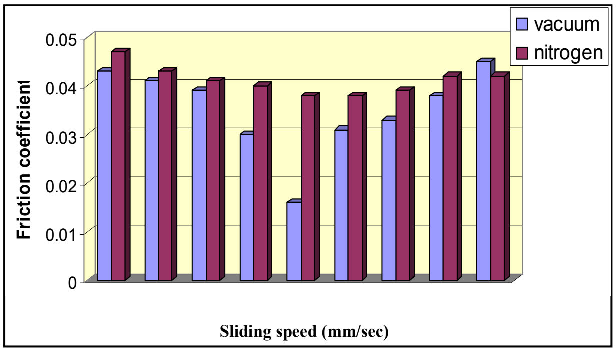

Figure 9. Fullerene in Vacuum & Nitrogen at Varying Speed, 20N Load.

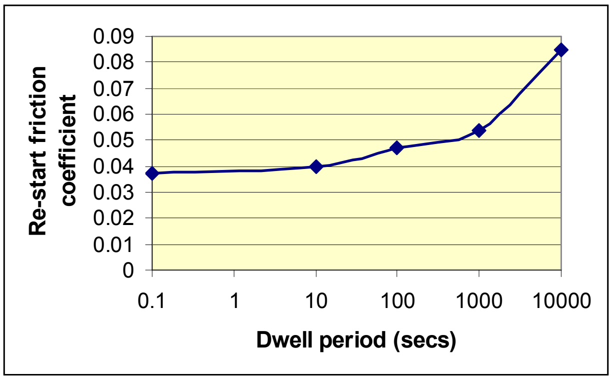

Figure 10. Example of Dwell Effect in Vacuum

4. DISCUSSION

In many ways the tribological properties of the WS_2 fullerene coatings mirror those of molybdenum disulphide. That is to say:

- Friction is low under high vacuum and dry nitrogen and increases significantly in laboratory air.
- Friction is speed-dependent (more so in vacuum than in dry nitrogen).
- The coatings exhibit a significant ‘dwell’ effect in vacuum and dry nitrogen.
- Wear life is appreciably greater in vacuum and dry nitrogen than in air.
- In vacuum and nitrogen both friction coefficient and life tend to decrease with increasing load.

The above observations imply that the lubricating mechanism of lamellar metal dichalcogenides (e.g. sputtered MoS_2) and fullerene-structured metal dichalcogenide (burnished WS_2 fullerene coatings) is the same. It is generally accepted that the in-vacuo lubricating action of conventional MoS_2 and WS_2 is due to their lamellar structure, such that there is easy shear between adjacent lamellae. Additionally, the increase in friction in the presence of water vapour is attributed to adsorption of H_2O molecules followed by oxidation at the exposed reactive sites at the edges of the lamellae (the reactivity at these sites is attributed to the presence of dangling bonds).

Since the fullerene structure is closed, i.e. it does not have any exposed edge sites and dangling bonds, it is assumed that, provided the closed fullerene structure is maintained, there can be little reaction with air molecules. Therefore, the observation that the WS_2 nano-fullerene coatings yield similar frictional properties in air and vacuum to lamellar MoS_2 and WS_2 implies that the fullerene structure breaks down under sliding contacts of high stress to lamellar–like formations. This concept is illustrated in [Fig. 11]. In this scenario the nanospheres are deformed under load and with the continued action of shearing under high contact stresses break open and unravel to yield lamellar particles.

Evidence for this mechanism has been demonstrated for nano-fullerene coatings of MoS_2 [RD18]. In that study TEM images of the contact zone revealed flattened nano-particles and nano-particles which had been broken and unravelled to form lamellar and layered MoS_2 stacks.

It should be noted that our comparison of air and vacuum lifetimes related to tests made under a pin load of 10N - corresponding to a mean contact stress of 824 MPa. This stress level is not untypical of that occurring in ball bearings of spacecraft mechanisms. It may be that at much lower stresses (which are not representative of tribo-components in spacecraft mechanisms) the nano-particles retain their fullerene structure. It would be informative therefore to examine the effect of contact stress/load on the air-sensitivity of such coatings although this would not necessarily be relevant to space mechanism lubrication.

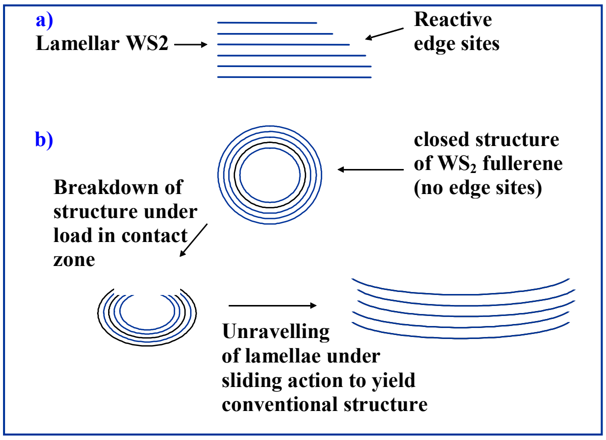

Figure 11. Possible mechanism for breakdown and unravelling on WS2 nanospheres.
(a) conventional lamellar structure (b) nanosphere structure

Whilst it is disappointing that the fullerene coatings did not, in our tests, display an insensitivity to operation in air, a positive outcome is the comparatively long life of the coatings in vacuum. In general, burnished coatings of metal dichalcogenides have relatively short lives. [RD6] reports that that the in-vacuo life of MoS_2 powder burnished onto steel discs is some 3 orders of magnitude less than for sputtered MoS_2. In this context the burnished fullerene WS_2 nano-particles are seen to have yielded an impressively long lifetime in vacuum. On this basis one can make a case for continued study of burnished films of this type with perhaps an emphasis on optimising the burnishing technique further to determine whether further extensions in lifetime are achievable. Additionally, given that coatings produced by PVD (e.g. sputtering) tend to be superior to those produced by other techniques then an examination of methods of producing fullerene by PVD methods might prove rewarding.

The life of fullerene WS_2 coatings was consistently shorter in dry nitrogen, by a factor of at least 2, when compared to that in vacuum. The reasons for this are unknown and contrast with that of sputtered MoS_2 for which the life is at least as good in dry nitrogen as it is in vacuum. More data would be required to determine whether this observation is statistically significant. If it is shown to be the case then this has implications with regard to ground testing in a nitrogen environment – in that such testing would reduce the subsequent in-vacuum life of the coatings.

5. CONCLUSIONS

The following conclusions are drawn relating to burnished, fullerene WS2 coatings.

- The coatings yield low friction in vacuum and dry nitrogen, the friction coefficients measured being comparable to those of sputtered MoS_2 operating under similar test conditions.
- The coatings yield a relatively long life in vacuum. In dry nitrogen coating life is less than in vacuum. This implies that ground testing in nitrogen may subsequently lead to a reduction in the lifetime of the film in space.
- As is the case with sputtered MoS_2, the coatings generated higher friction and had much shorter lives when operated in laboratory air. This sensitivity to air operation suggests that the fullerene structure may be breaking down to yield lamellar particles.
- Qualitatively, the effects of sliding speed, dwell period and load upon friction coefficient are similar to those observed with sputtered MoS_2.
- Although the coatings' friction and life properties are air-sensitive and as such do not offer any advantage over sputtered MoS_2, the performance (particularly life in vacuum) is considered good for a film produced by burnishing. On this basis further work is merited. This should be along the lines of investigating alternative methods of creating nano-sphere coatings, including PVD methods.

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