**WS2 Fullerene-like Lubricant Nano-Additives – A Review**

M. Ratoi1)

1) national Centre for Advanced Tribology at Southampton, School of Engineering Sciences, the University of Southampton, SO17 1BJ, UK

\*Corresponding author: m.ratoi@soton.ac.uk

# Introduction

Much of the current excitement about nanotechnology is driven by the integration of the nanoscale materials

into complex systems. Within lubricant applications, such as engine oils, transmission fluids, gear and bearing oils, the potential exists for lubricants containing nanomaterials to significantly reduce friction and wear of moving parts and enhance machine durability. This can contribute to substantial energy savings, reduced equipment maintenance and longer machine lifetime. For engine oil (crankcase) applications, the lower friction can assist in reducing fuel consumption and accordingly reduce emissions of greenhouse effect gases. It also offers a roadmap to eco-friendly technology with potential for low sulphated ash, phosphorus and sulphur (SAPS) vehicle emissions and extended durability and performance of the exhaust-treatment devices.

Within lubricant nano-additives, the inorganic fullerene tungsten disuphides (IF-WS2) nanoparticles (NPs) have shown the potential to reduce wear and friction significantly better than conventional lubricants. This paper reviews the published research findings and the proposed mechanism of action in tribological contacts. It also suggests further investigations necessary to understand the behavior of nano-additives in tribological contacts and improve their performance.

# Results and Discussion

A large number of experimental studies [1-7] have shown that NPs penetrate the tribological contacts forming a boundary film which has a strong influence on tribological parameters such as friction coefficient and wear. From all the novel NPs, fullerene-like WS2 have stirred a large interest as potential friction modifiers due to their excellent tribological properties.

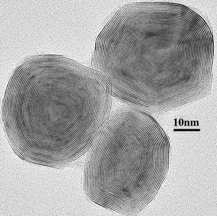


Figure 1. TEM image of nested IF-WS2nanoparticles

IF-WS2 NPs have a layered nested structure and the layered materials such as graphite, WS2 and MoS2 have shown superior lubricating abilities in both forms: as solid dry powder or as additives in greases or liquid lubricants. The weak interlayer bonds in these materials shear with a minimum tangential resistance providing the contacting surfaces with layers of protective boundary material.

The studies which investigated the nested IF-WS2 NPs as additives in oils used NPs with a particles size between 50 and 200 nm. The NPs were dispersed by stirring and bath sonication in non-polar oils, such as mineral base-stock and PAOs, without using surfactants or dispersants.

The effect of the NPs concentration on the tribological performance has been studied by using concentrations between 0.1-8 wt%. An optimal concentration of 1 wt% has been found to be the most efficient in terms of friction coefficient values. Increasing the concentration above this value has not been effective because of the difficulty to disperse the NPs in the base oil [2].

In order to assess the range of operational conditions when NPs are most effective at reducing friction and to understand the mechanism of action in the lubricated contact the tribological tests were performed at different speeds, temperatures and contact loads. All measurements were carried out in sliding contacts of diverse geometries.

A wide range of contact pressures (0.33-1.72 GPa) have been tested and the results showed that the increase in contact pressure has a lowering effect on the friction coefficient up to a value (0.83 GPa) and remains constant above this value [3].

An increase in temperature did not influence the efficiency of the IF-NPs. The higher values of coefficients of friction in the boundary and mixed lubrication regime have been explained by the reduction of viscosity of lubricants with the increase in temperature [3].

The published studies investigated all the lubrication regimes but the attention has been focused on the mixed and boundary regimes where the IF-WS2 NPs proved to be especially effective at reducing friction.

The mechanism of action of IF-WS2 has been ascribed to the adherence of the delaminated nano-sheets of WS2 to the lubricated surface. This has been demonstrated by the presence of the structurally modified WS2 sheets on the wear debris collected and analyzed in the TEM. Video imaging of the lubricated contact during the test showed the formation of tribo-film is progressive and continuous. It has also been found that a critical pressure must be reached to delaminate the IF-NPs and if this is not achieved the decrease in friction is less significant [3].

The anti-wear properties of the IF-WS2 were shown to depend less on the contact load. NPs are equally effective at low pressures because they can fill the asperities gaps and avoid the direct contact of asperities.

To make the NPs dispersion in base oils more stable to aggregation and assess the influence on the tribological parameters some studies used surface functionalized NPs. Hydrophobic IF-WS2 NPs coated with silanes showed a lower tendency to form aggregates and therefore an improved stability in oils [4]. The length of the alkyl chain (C6, C12, C18) in the silane coating had a large influence on the NPs agglomerates sizes and their sedimentation time. The tribological measurements taken immediately after dispersion by sonication showed similar friction reducing abilities for the uncoated and silane-coated NPs. However, later measurements (taken after 65/110 hours) showed that the non-coated NPs became totally ineffective at reducing friction (having a friction coefficient of the same value as the base oil) while the silane-coated, stabilized NPs largely maintained their friction reducing ability. The friction coefficient was influenced as well by the length of alkyl chain in the silane coating. The authors concluded that the agglomeration of NPs has a deleterious effect on the stability of NPs and their tribological properties and the functionalization of the NPs can improve the long-term tribological behavior of the IF-WS2 dispersions.

NPs dispersability and stability in base oils are very important parameters for the achievement and maintenance of the long-term tribological effectiveness of NPs. In order to have a good stability to aggregation, NP dispersions should be characterized by low average particle sizes and narrow size distributions. The published research studies have used electron microscoply (TEM, SEM) to measure the size of the NP aggregates in oils. The stability of the NP dispersions has so far been determined by the visual observation of the sedimentation process. More work is necessary to measure the particle size distribution (PSD) of NPs in their dispersion medium and the stability to aggregation. To reach this objective, appropriate state-of-art techniques must be identified and their capabilities investigated for different NP morphologies (spherical, tubes, rods) and sizes.

The dispersability and stability to aggregation of the NP colloidal dispersions are influenced by many factors and some of the most important ones are: the techniques and times used for dispersion, NP surface charge and chemistry, the type of surfactant/dispersant or functionalization used and the type, chemistry, temperature and pH (for aqueous dispersions) of the dispersion medium [8].

An important area to investigate is the effect of NP surface functionalization and of surfactants/dispersants on the dispersability, stability and lubricating ability of NP dispersions.

The type and chemistry of oil used as a dispersion medium also influences the stability of NP dispersion and its tribological ability. In all the published research studies the IF-WS2 nanoadditives were dispersed in non-polar oils such as mineral basestock or poly-alpha-olefins (PAOs). These oils have none or very low polarity and do not compete with the NPs for attraction to the polar lubricated surfaces. It is important to find out if NPs are also effective at reducing friction when dispersed in more polar oils (esters, PPGs) and how the oil chemistry influences the NP dispersion stability and lubricating ability.

# Conclusions

IF-WS2 NP colloidal dispersions in oils of low polarities can reduce the friction coefficient up to 70% and are especially effective in the mixed and boundary lubrication regimes. IF-WS2 NPs can act immediately (t=0) in all temperature ranges and are supplied continuously into the lubricated contact.

The values of the friction coefficient indicate that the mechanism of action is by film transfer from the NPs to the contact surface by exfoliation of IF-NPs under pressure.

For a colloidal dispersion to be a good lubricant candidate it needs to fulfill two main requirements: a long-term stability to aggregation and an excellent friction reducing ability.

More research studies are necessary to identify techniques able to measure the dispersability and stability of NPs in oils and correlate these results with the tribological performance.

The chemistry and polarity of the NP surface and the base oil are important parameters which need to be investigated in more detail.

Sustained efforts have been made so far for the development of novel lubricant nano-additives. However, more work is necessary for a better understanding of the NPs behavior in tribological contacts and to be able to improve NPs dispersion, stability to aggregation and lubricating performance in lubricants (aqueous and oil-based).

The future studies hopefully will provide a superior insight into the NPs potential applications in lubrication.

# References

[1] R. Greenberg, G. Halperin, I. Etsion and R. Tenne *Tribology Letters* **17, 2** (2004)

[2] F. Abate, V. D’Agostino, R. Di Giuda, A. Senatore *Tribology* **4, 2** (2010)

[3] L. Joly-Pottuz, F. Dassenoy, M. Belin, B. Vacher, J.M. Martin, N. Fleischer *Tribology Letters* **18, 4** (2005)

[4] C. Shahar, D. Zbaida, L. Rapoport, H. Cohen, T. Bendikov, J. Tannous, F. Dassenoy and R. Tenne *Langmuir* **26, 6** (2010)

[5] J.M. Martin and N. Ohmae *Nanolubricants*, New York Wiley (2008)

[6] L. Rapoport, O. Nepomnyashchy, I. Lapsker, A. Verdyan, A. Moshkovich, Y. Feldman and R. Tenne *Wear* **259** (2005)

[7] L. Rapoport, V. Leshchinsky, I. Lapsker, Yu. Volovik, O. Nepomnyashchy, M. Lvovsky, R. Popovitz-Biro, Y. Feldman and R. Tenne *Wear* **255** (2003)

[8] M. Ratoi, A.J.A. Crossley, P.J. Dobson, NANOSAFE2 Final Report (2009)