

# Comparative Wear Behavior of MoS<sub>2</sub> and WS<sub>2</sub> Coating on Plasma-Nitrided SG iron

Aravind Vadiraj and M. Kamaraj

(Submitted September 12, 2008; in revised form March 7, 2009)

**The dry sliding wear behavior of MoS<sub>2</sub> and WS<sub>2</sub> was studied with plasma-nitrided SG iron. Both the lubricants were effective in preventing wear loss of the sliding material due to low friction. The specific wear rate of coated material was 10 times lower than uncoated material. The coefficient of friction of MoS<sub>2</sub> and WS<sub>2</sub> was 0.1 and 0.03, respectively. Wear damage was observed to be significantly lower for lubricant-coated material compared to uncoated part.**

**Keywords** cast iron, coatings, tribology

## 1. Introduction

Mineral oil-based fluid lubricants (oil and grease materials) function properly, where the designed surface areas and shaft speeds allow for the effective formation of an oil film, as long as the machine operating temperature envelope falls within the allowable range. The only absolute limits that apply for fluid lubricants, regardless of the base oil type, are conditions that cause a change in the state of the fluid that prohibits fluid film formation. Dry sliding is invariably experienced in oil-starved conditions in various industrial applications where dry lubricants show improved resistance to seizure or galling. Molybdenum disulfide (MoS<sub>2</sub>) (Ref 1) and tungsten disulfide (WS<sub>2</sub>) (Ref 2) have proven ability to withstand extreme conditions in operating environments. They can be applied on the component through spray blasting, buffing, or blending with the existing liquid lubricants which gets gradually coated over the mating surface during service. They have a layered lattice structure with weak bonding between individual layers that allows sliding over each other to provide the desired lubricity.

MoS<sub>2</sub> is a naturally occurring mineral mined as molybdenite ores and refined to achieve high purity for lubrication purposes. The hexagonal crystalline structure allows for easy shear to occur at the interface between the sulfur atoms. The particle size and film thickness are important parameters that should be matched to the surface roughness of the lubricated component. Particle size is much larger for rough cut surfaces, such as hobbled open gears, than for highly finished surfaces, such as those found on bearings. Improperly matched particle sizes may result in excessive wear by abrasion. The temperature limitation

of MoS<sub>2</sub> at 450 °C is imposed by oxidation and formation of molybdenum trioxide and sulfur dioxide. Great improvements in the scuffing resistance of gears have been obtained from these coatings (Ref 1, 3). The wear behavior seems to also depend on the relative humidity of the atmosphere (Ref 4). Morimoto (Ref 2) reported that MoS<sub>2</sub> coatings were more effective than oil lubricants in reducing wear and friction of ceramic ball on steel disc.

Tungsten disulfide is a dry film lubricant developed by Stanford University in 1960 for NASA. Following its initial debut, it found its way into industrial applications, primarily in aerospace and defense applications. It is produced from a direct reaction between tungsten particles and sulfur powder and found to offer superior wear resistance as a dry lubricant or as an additive in paraffin (Ref 2). It is known to improve wear and enhance lubricity and has an affinity for lubricants, resulting in oil retention properties in wet applications. WS<sub>2</sub> is one of the most lubricious materials known to science. With coefficient of friction at 0.03, it offers excellent dry lubricity unmatched to any other substance (Ref 5, 6). It can also be used in high-temperature and high-pressure applications. Load bearing capacity of coated film is extremely high at 2000 MPa. Coefficient of friction of WS<sub>2</sub> was found to reduce at higher loads.

In new IC engines, there is a critical period known as break-in period during which the asperities between the mating parts contact and wear to finally conform to one another. During this period, they are highly susceptible to scuffing wherein the metal-to-metal contact between piston ring and cylinder wall will wear out the materials to form a gap for leaking the combustion products thereby reducing the efficiency and overall useful life of the engine. WS<sub>2</sub> coating on the contact area of the ring is known to reduce scuffing to a large extent.

Spheroidal graphite cast iron, also known as nodular or ductile iron, is used in several engineering applications such as automobile, earthmoving, railways, mining equipment, switch-gear, machine tools, power transmission, textile machinery, heavy equipment, etc. It has higher mechanical strength, ductility, and increased shock resistance compared to gray cast iron. Plasma nitriding produces hard wear resistant layer and an adjacent nitrogen-diffused layer which improves antiwear properties along with its corrosion resistance (Ref 7-9).

**Aravind Vadiraj**, Advanced Engineering, Ashok Leyland Technical Center, Vellivoyalchavadi, Chennai 600103, India; and **M. Kamaraj**, Metallurgical and Materials Engineering Department, Indian Institute of Technology-Madras, Chennai 600036, India. Contact e-mails: aravindmail@yahoo.com and kamaraj@iitm.ac.in.

In this study, sliding wear performance of commercially available MoS<sub>2</sub> and WS<sub>2</sub> powder coating on plasma-nitrided SG iron has been investigated to understand the influence of these coatings in preventing wear loss of plasma-nitrided layer on SG iron.

## 2. Experimental Details

Commercially available SG iron slab was procured, and cylindrical pins of 10 mm diameter and 15 mm height were made by wire-cut EDM. Plasma nitriding was performed at Ionbond Coatings, Chennai, India. The details of the process are proprietary and not disclosed here. Vickers microhardness was measured along the cross section of the nitrided pins.

Commercially available MoS<sub>2</sub> (0.65 μm) from Dow Corning and WS<sub>2</sub> (0.6 μm) from MK Impex, Canada were procured. The tribological evaluations of the samples were made in standard pin-on-disc test rig according to ASTM G99-05.

The disc used was through-thickness hardened steel of diameter 55 mm and 10 mm thick with the following composition: 1.08C + 0.4Mn + 0.026P + 0.046S + 1.34Cr. The steel disc composition was determined by optical emission spectroscopy. The average surface hardness was 752 VHN (62 HR<sub>C</sub>). Tests were conducted with sliding speed of 0.4 m/s, and three specimens were tested for each condition and the average was recorded.

Alumina ball of 10 mm diameter was used for the initial experiments for sliding on lubricant-coated discs for 100 m. This experiment was conducted just to identify the efficacy of dry lubricants used under point contact loading. The wear loss was calculated from differences in initial and final weights of the worn disc with a digital balance (max 310 g) of 0.0001 g precision after the test.

The second set of experiments was conducted with the plasma-nitrided pins. Both the disc and the pin flat end were smeared with similar lubricant before sliding for 450, 1000, and 1500 m. The normal load used was 160 N. Each test would take 1 h approximately. The wear loss of pins was calculated from the differences in weights before and after each sliding test and specific wear rates were identified. Wear damage was recorded at ×50 using a digital CCD camera fitted to optical microscope interfaced with an image analyzer.

## 3. Results and Discussion

### 3.1 Materials and Microstructure

Plasma-nitrided SG iron with clear distinction between hard layer (4.35 μm) and the substrate is shown in Fig. 1. Figure 2 shows hardness profile from the surface to the interior of the sample, indicating decrease in hardness values toward the substrate. This indicates the presence of diffused nitrogen layer below the compound layer which would also provide load support to the hard top layer.

### 3.2 Ball-on-Disc Sliding Test

Friction coefficient during sliding shows a gradual increment to a steady state value of 0.6 for uncoated and 0.4 and 0.3 for MoS<sub>2</sub> and WS<sub>2</sub>, respectively, as shown in Fig. 3.

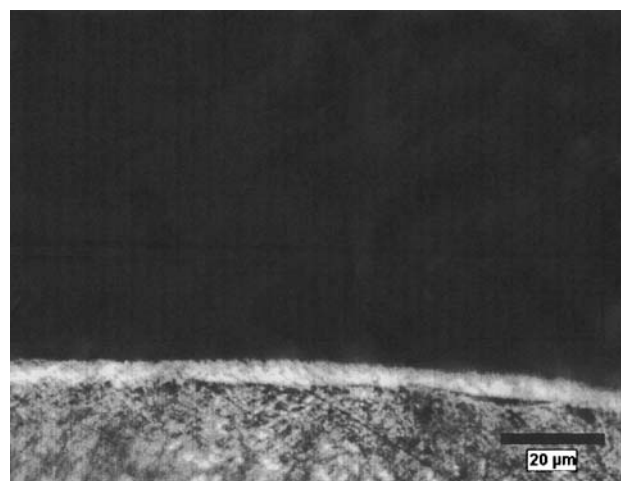


Fig. 1 Hard nitride layer (4.35 μm) on plasma-nitrided SG iron

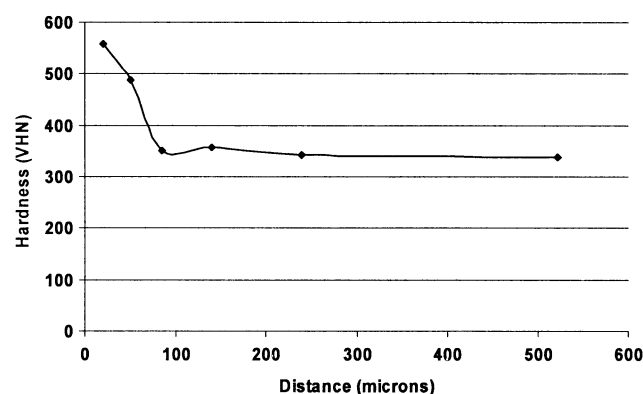


Fig. 2 Hardness profile of plasma-nitrided SG iron

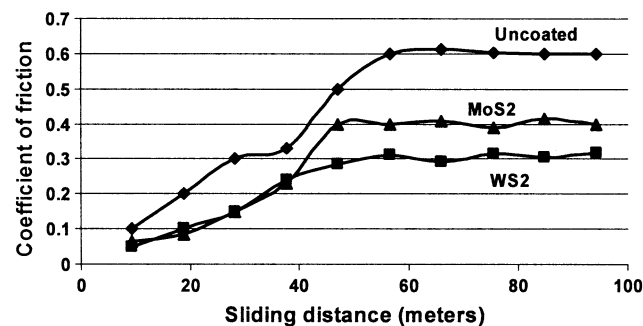


Fig. 3 Friction coefficient profile of lubricant-coated and uncoated disc

The gradual increment indicates the time required to pass the break-in period where the mating parts achieve conformance with each other before achieving steady-state friction. Friction reaches a steady state after a certain sliding distance and the coated material has maintained slightly less friction indicating the retention of the coating within the point contact. Steady-state friction coefficient of WS<sub>2</sub> is half that of uncoated disc indicating the superior lubricating property of the powder. The wear loss of the disc after 450 m of sliding is as shown

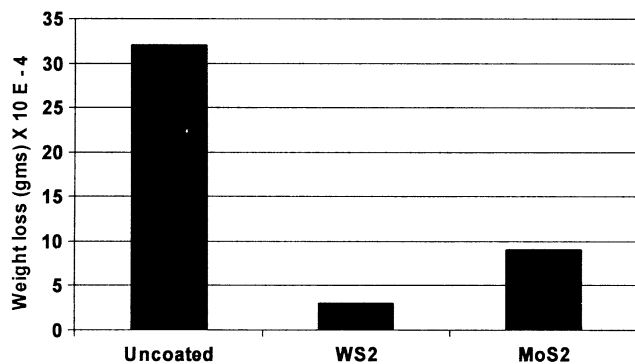


Fig. 4 Wear loss comparison trend for lubricant-coated and uncoated disc

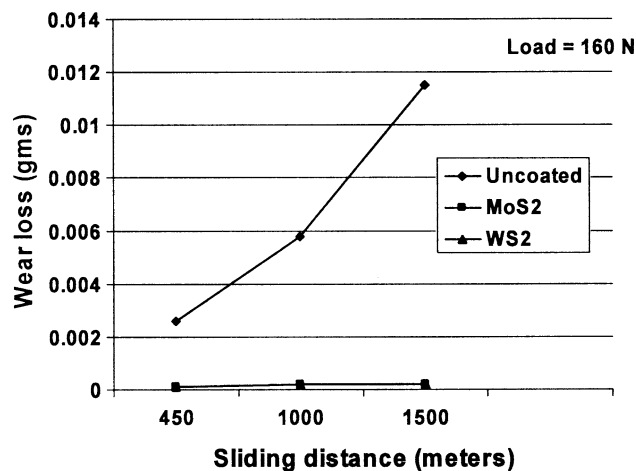


Fig. 5 Wear loss with sliding distance for lubricant-coated and uncoated sample

in Fig. 4. It can be observed that  $WS_2$ -coated disc shows 10 times reduced wear loss while  $MoS_2$ -coated disc shows 3 times reduced wear loss compared to uncoated counterpart.

The sintered alumina ball had been observed to retain some of the coating material within the contact to provide low friction and wear loss of the disc. Lubricant retention was also observed along the wear tracks during sliding and even after completion of the programmed sliding distance indicating the good adherence of the coating on the disc. Nano particulate coating powders used would always be available within the small undulations on the disc preventing the wear and/or seizure of the contacts.

### 3.3 Plasma-Nitrided Pin-on-Disc Test

Wear loss characteristics between uncoated and lubricant-coated samples are compared in Fig. 5, indicating the superior effect of powder coatings. The sample without lubricants show high wear loss compared to sample coated with lubricants. The powder coatings were retained within the contact for a long sliding distance preventing the wear of the samples. After 450 m sliding distance, the wear rate of uncoated sample was more acute when the plasma-nitrided layer was no longer present to protect the substrate. Specific wear rates of coated with uncoated samples is compared in Fig. 6 indicating

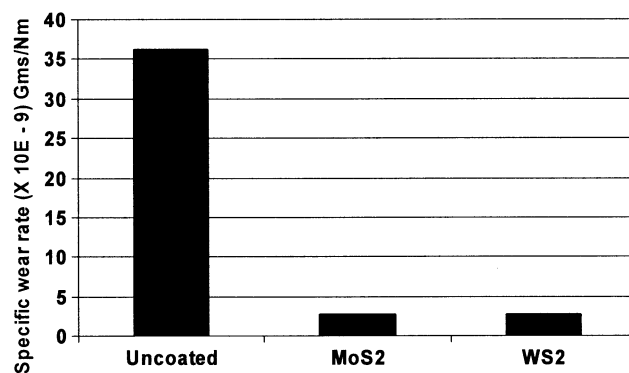


Fig. 6 Specific wear rates trend showing contrasting differences in wear rates between uncoated and lubricant-coated sample

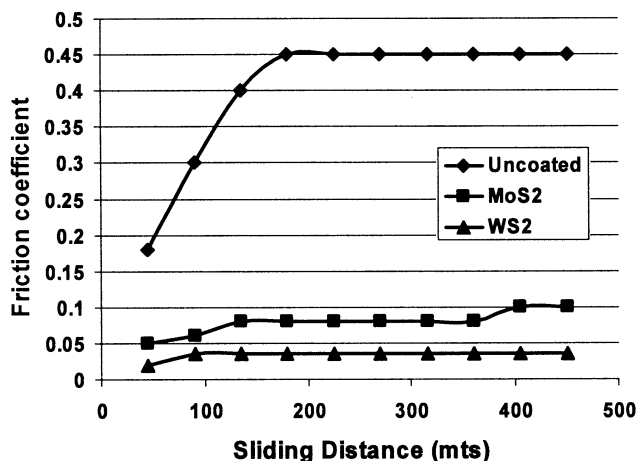


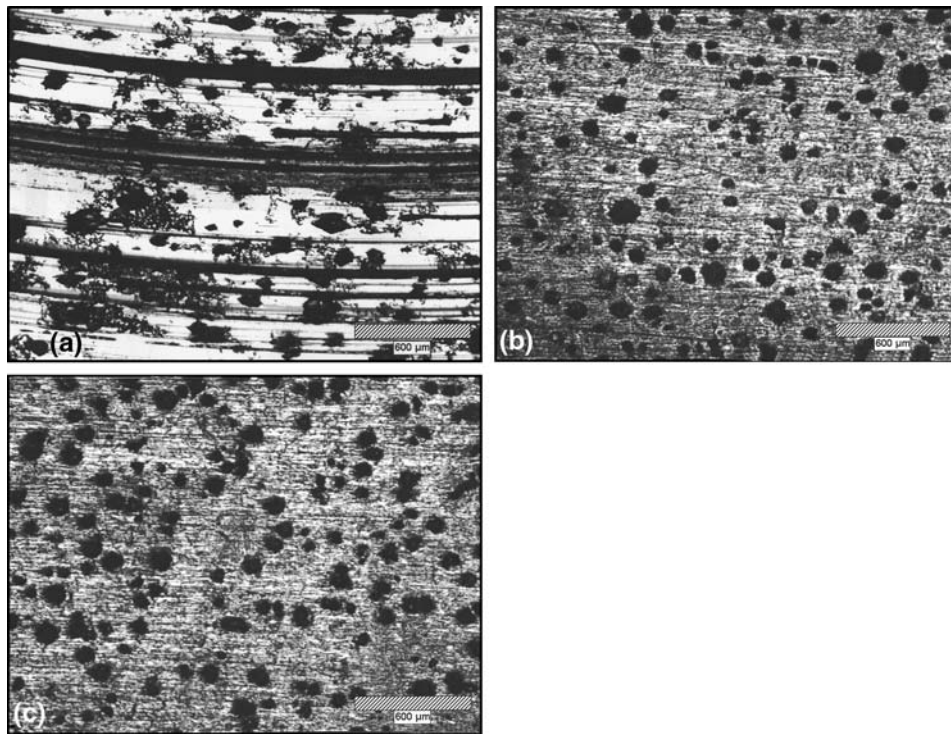
Fig. 7 Friction curves with sliding distance indicating superior effect of dry lubricant-coated samples

contrasting differences in the values. The wear rates were equal for both the coated samples and were almost 10 times less than the uncoated counterpart. The particulates are small enough to accommodate within the undulations of the surface to reduce surface exposure and adhesion. The squeak noise characteristics of adhesive wear was absent indicating favorable mode of operation during sliding.

Friction coefficient profile of the coated and uncoated samples is compared in Fig. 7, indicating high friction for uncoated sample. The friction coefficient of lubricant-coated sample was more uniform ( $<0.1$ ) than sample without lubricants. The  $WS_2$  coating showed friction coefficient of 0.03 while  $MoS_2$  showed 0.1. This conforms to the literature values (Ref 2, 7). High friction of uncoated sample generated scouring sound during sliding while the coated samples were silent indicating reduced contact and friction between mating parts.

### 3.4 Wear Damage

Wear damage comparison between uncoated and lubricant-coated samples, as shown in Fig. 8, indicates far reduced damage for coated samples even after longer sliding distance. All the samples were observed with uniform sliding marks across the contacting surface indicating full contact with the



**Fig. 8** Wear damage of (a) Uncoated (after 450 m), (b) MoS<sub>2</sub>-coated (after 1500 m), and (c) WS<sub>2</sub>-coated (after 1500 m) samples for similar testing conditions

disc. Uncoated samples are observed with deep grooves (Fig. 8a,  $R_a = 1.34 \mu\text{m}$ ) indicating abrasive mode of wear possibly from hard nitrided particulates ejected from the surface during sliding. The ejection most probably occurs from the interface between graphite nodules and matrix combined with high friction at the contact. The ejected hard nitride particles abrade both the contacting surface leaving deep scoring marks before leaving the contact. Even the presence of graphite cannot help reduce the wear and friction in this case due to severe effect of hard particles. The oxidized wear debris ejected from the disc also adds to the abrasive wear. The hard layer seems to have worn out completely within the short sliding period. The exposed substrate then would have higher wear loss than the nitride layer as seen from Fig. 5 from the increased slope of the curve.

Mild scratches with low surface roughness ( $R_a < 0.3 \mu\text{m}$ ) were observed for all the lubricant-coated samples as seen in Fig. 8(b) and (c). In case of lubricant-coated surface, the chance of hard nitride particle release is less due to low friction and no contact between the sliding surfaces. The lubricant powder film prevents the contact between the materials thereby lowering the chances of wear. As observed in Fig. 8(a) and (b), the original nitride layer is still intact with mild scratches on it. This also indicates the superior tenacity of the lubricants to the surface.

## 4. Conclusions

Plasma nitriding of SG Iron produced a hard nitride layer above the substrate. Dry lubricants were effective in preventing wear damage of plasma-nitrided layer on SG Iron due to low friction between the sliding members. Specific wear rates were

10 times lower than uncoated sample. Steady-state friction coefficient was 0.03 for WS<sub>2</sub> and less than 0.1 for MoS<sub>2</sub> compared to 0.45 for uncoated plasma-nitrided SG iron sliding members. Severe damage was observed for uncoated samples after 450 m sliding compared to minimal wear damage in case of dry lubricant-coated samples even after 1500 m sliding. This proves the superior efficacy of these coatings on plasma-nitrided SG iron.

## Acknowledgment

The authors gratefully acknowledge the experimental assistance provided by Mr. Kesavan and Mr. J. A. Suresh, IIT Madras and Dr. G. Balachandran for suggestions and comments.

## References

1. R. Martins, R. Amaro, and J. Seabra, Influence of Low Friction Coatings on the Scuffing Load Capacity and Efficiency of Gears, *Tribol. Int.*, 2008, **41**(4), p 234–243
2. T. Morimoto, Effect of Molybdenum Disulphide upon the Friction and Wear in Ceramic–Steel Pair, *Tribol. Int.*, 1997, **30**(12), p 871–879
3. R.I. Amaro, R.C. Martins, J.O. Seabra, N.M. Renevier, and D.G. Teer, Molybdenum disulphide/Titanium Low Friction Coating for Gears Application, *Tribol. Int.*, 2005, **38**(4), p 423–434
4. M. Steinmann, A. Müller, and H. Meerkamm, A New Type of Tribological Coating for Machine Elements Based on Carbon, Molybdenum Disulphide and Titanium Diboride, *Tribol. Int.*, 2004, **37**(11–12), p 879–885
5. P.-Z. Si, C.-J. Choi, J.-W. Lee, D.-Y. Geng, and Z.-D. Zhang, Synthesis, Structure and Tribological Performance of Tungsten Disulphide Nanocomposites, *Mater. Sci. Eng. A*, 2007, **443**(1–2), p 167–171
6. T.W. Scharf, S.V. Prasad, M.T. Dugger, P.G. Kotula, R.S. Goeke, and R.K. Grubbs, Growth, Structure, and Tribological Behavior of Atomic



- Layer-Deposited Tungsten Disulphide Solid Lubricant Coatings with Applications to MEMS, *Acta Mater.*, 2006, **54**(18), p 4731–4743
7. Y.-T. Xi, D.-X. Liu, and D. Han, Improvement of Corrosion and Wear Resistances of AISI 420 Martensitic Stainless Steel Using Plasma Nitriding at Low Temperature, *Surf. Coat. Technol.*, 2008, **202**(12), p 2577–2583
8. P. Corengia, F. Walther, G. Ybarra, S. Sommadossi, R. Corbari, and E. Broitman, Friction and Rolling–Sliding Wear of DC-Pulsed Plasma Nitrided AISI 410 Martensitic Stainless Steel, *Wear*, 2006, **260**(4–5), p 479–485
9. Y. Sun, T. Bell, and G. Wood, Wear Behaviour of Plasma-Nitrided Martensitic Stainless Steel, *Wear*, 1994, **178**(1–2), p 131–138