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# Wear mechanism of Mo–W doped carbon-based coating during boundary lubricated sliding

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## Abstract

The high temperature tribological applications of state-of-the-art diamond-like-carbon (DLC) coatings in automotive industry are often compromised due to their poor adhesion strength and low thermal stability. A molybdenum and tungsten doped carbon-based coating (Mo–W–C) is developed in order to overcome these limitations and to enhance tribological performance during boundary lubricated sliding at ambient and elevated temperature. The coating was deposited utilising HIPIMS technology. Mo–W–C coating showed lowest mean friction coefficient ( $\mu=0.033$ ) compared to a number of commercially available state-of-the-art DLC coatings when pin-on-disc experiments were carried out at ambient temperature. Similarly at 200°C, a significant reduction in friction coefficient was observed for Mo–W–C coating with increase in sliding distance unlike DLC coating. Raman spectroscopy revealed importance of combined Mo and W doping and *tribochemically reactive* wear mechanism of Mo–W–C coating during sliding. The significant decrease in friction and wear rate was attributed to the presence of graphitic carbon particles (from coating) and 'in-situ' formed metal sulphides ( $WS_2$  and  $MoS_2$ , where metals from coating and sulphur from oil) in transfer layer.

## 1. Introduction

Diamond-like-carbon (DLC) coatings are extensively used as tribological coating in various automotive engine parts (such as piston, piston rings, piston pins, gearbox and valve train components), however poor adhesion strength and degradation of the coating properties at higher working temperature often compromise their commercial applications. A standard technique to increase the thermal stability is to incorporate different metal and non-metal dopants into the DLC coating. Among them, addition of Si, Mo or W improves the thermal stability of DLC coating whereas doping with Ti, Mo or W significantly reduces the friction coefficient during lubricated sliding. Thus the attention is drawn to both W-DLC and Mo-DLC coatings because of their higher thermal stability and low friction coefficient during lubricated sliding where engine oil with friction modifier is used as lubricant. A significant reduction in friction value of W-DLC coating was observed due to formation of  $WS_2$  in the transfer layer during sliding when pure and low additive PAO [1] and PAO with EP based additives [2] were used as lubricants. It is a common practice to use formulated oils containing MoDTC and ZDDP additives, which leads to formation of another lubricious compound such as  $MoS_2$  due to chemical reactions in the oil during sliding [3]. This information provides the idea of synergizing the benefits of simultaneous doping of carbon-based coating with Mo and W where the coating itself provides species, which form lubricious compounds via tribochemical reactions during sliding. This work describes the tribological behaviour of Mo–W–C coating in boundary lubricated condition using commercially available engine oil without friction modifier at ambient and elevated temperature.

## 2. Experimental details

The Mo–W doped carbon-based coating (Mo–W–C) was deposited on polished M2 grade HSS disc samples in an industrial sized Hauzer HTC 1000–4 PVD coating machine using combined HIPIMS and UBM techniques. The ~2.2  $\mu\text{m}$  thick coating architecture contained a HIPIMS treated interface [4], a thin Mo – W – N base layer followed by a dense and columnar Mo – W – C layer on the top [5]. Moreover this coating showed good adhesion ( $L_c \sim 80.8$  N), high hardness (1677.5 HV) [5] and high thermal stability. A pin-on-disc tribometer (CSM) was used to study the friction behaviour of Mo–W–C and state-of-the-art DLC coatings against uncoated 100Cr6 steel ball under a static load of 5 N in boundary lubricated condition at ambient ( $\sim 25^\circ\text{C} - 30^\circ\text{C}$ ) and at elevated ( $200^\circ\text{C}$ ) temperature. Commercially available engine oil without friction modifier (Mobil1 Extended life<sup>TM</sup> 10W-60) was used as lubricant, in which the coated disc and the steel ball were fully immersed during sliding. The tribological performance of Mo–W–C coating was compared with different state-of-the-art DLC coatings named as *DLC-A*, *DLC-B*, *DLC-C* and *DLC-D*. The scanning electron microscope (FEI NOVA NANOSEM 200) coupled with EDX analysis module (Oxford instruments X-max detector with INCA analysis software) was used for topographical imaging and X-ray mapping analyses. Raman spectrometer (Horiba-Jobin-Yvon LabRam HR800) fitted with a green laser ( $\lambda = 532$  nm) was used to collect the spectra from the as-deposited coating, adhered debris on the counterpart and within the wear track. The collected spectra were averaged over 5 acquisitions in the wavelength range of  $50 - 2250$   $\text{cm}^{-1}$ . The background of spectrum was corrected using a 2<sup>nd</sup> order polynomial and a multi-peak Gaussian-fitting function was used to deconvolute the spectrum and identify the Raman peaks.

## 3. Results and Discussions

Figure 1 shows the friction behaviour of Mo–W–C and state-of-the-art DLC coatings at ambient temperature. The mean friction coefficients ( $\mu$ ) of state-of-the-art DLC coatings were observed in the range of  $0.043 - 0.092$ , with the lowest friction value achieved by *DLC-A* ( $Cr/Cr - WC/W : C - H / a : C - H$ ) coating, used as a benchmark further on in this work. In comparison, further reduction in friction was observed for Mo–W–C coating ( $\mu=0.033$ ). Similarly, *DLC-A* showed a shallow wear track having a wear coefficient of  $7.96 \times 10^{-19}$   $\text{m}^3\text{N}^{-1}\text{m}^{-1}$  whereas no measurable wear in the conditions of the test was observed for Mo–W–C coating.

The wear behaviour of Mo–W–C coating was further investigated using Raman spectroscopy as shown in figure 2. After deconvolution of the spectrum collected from the as-deposited coating (fig. 2a), distinct disordered (D) and  $\text{sp}^2$  bonded graphitic carbon (G) peaks were observed at  $1387.04$   $\text{cm}^{-1}$  and  $1574.32$   $\text{cm}^{-1}$  respectively along with  $\text{Mo}_2\text{C}$  peaks at two consecutive shoulders of the spectrum. The  $I_D/I_G$  ratio was calculated as 1.96 indicating coating's graphitic nature [5]. The Raman spectrum was collected within the wear track after careful removal of the oil film (fig. 2b). The peaks found at  $1390.85$   $\text{cm}^{-1}$  and  $1572.61$   $\text{cm}^{-1}$  corresponded to the D and G bands respectively. The  $I_D/I_G$  ratio was found as 2.72 indicating an increase in disorder of carbon–carbon bonds in the coating due to the sliding. The  $\text{Mo}_2\text{C}$  peaks were observed within the wear track similar to the as-deposited coating. The peak centred at  $\sim 993$   $\text{cm}^{-1}$  indicated possible overlapping of  $\text{Mo}_2\text{C}$  and WC phases as the leading Raman peaks of  $\text{Mo}_2\text{C}$  and WC were reported in the

literature at  $\sim 995\text{ cm}^{-1}$  [6] and  $\sim 960\text{ cm}^{-1}$  [7] respectively. The sharp peak centred at  $\sim 133\text{ cm}^{-1}$  belonged to  $\text{WS}_2$ , which was clearly absent in the spectrum of as-deposited coating.

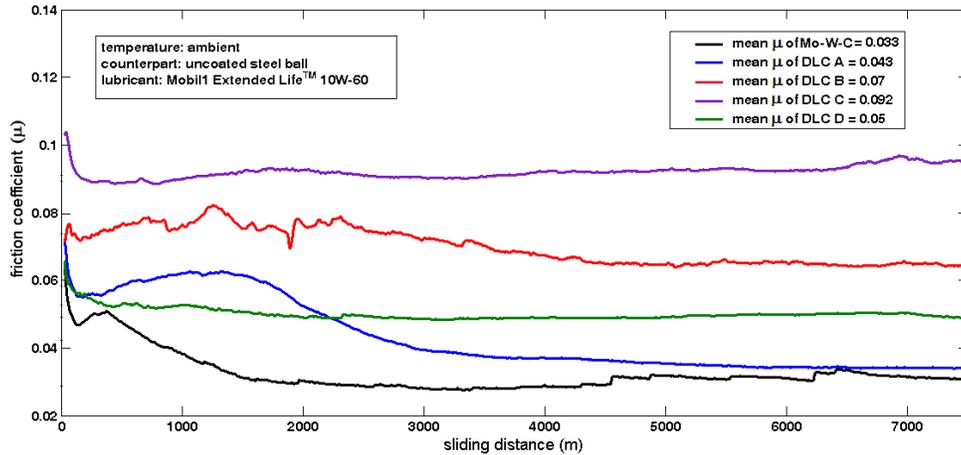


Figure 1: Friction behaviour of Mo–W–C and state-of-the-art DLC coatings at ambient temperature

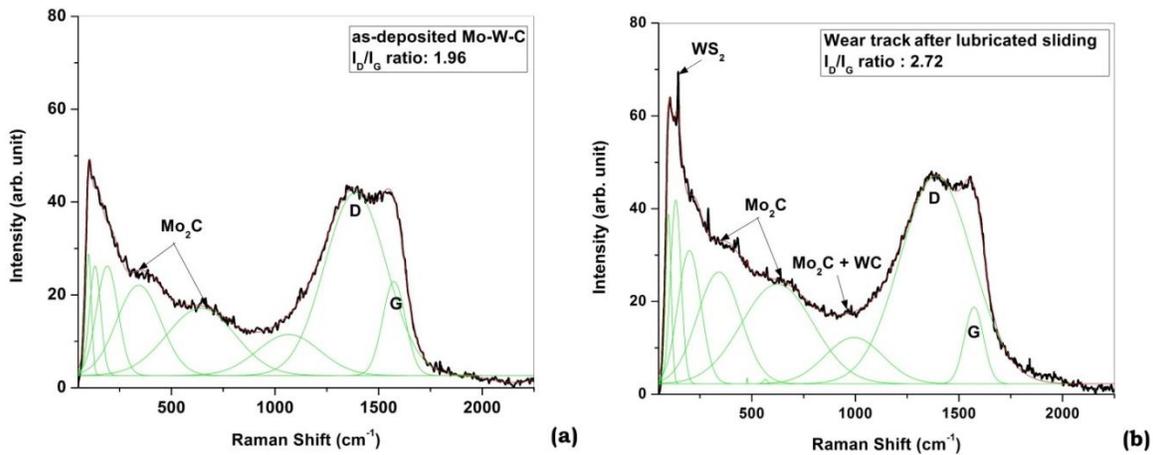


Figure 2: Raman spectra collected from (a) as-deposited coating and (b) within the wear track at ambient temperature

Raman analyses of the wear track revealed the **tribochemically reactive** wear mechanism of Mo–W–C coating during boundary lubricated sliding at ambient condition. The continuous rubbing action between the coating and the steel ball increases the flash temperature at the asperity contacts and the sulphur-containing compounds of the engine oil react with the coating elements at that high temperature. As a result, reaction products like  $\text{WS}_2$  is formed, where W comes from coating and S comes from EP additives present in the engine oil.  $\text{WS}_2$  is a well-known solid lubricant and its structure consists of layers in which tungsten atoms are linked with six sulphides and form a trigonal prism rather than the usual octahedron structure. The layered structure promotes easy slipping between the layers and provides graphite-like lubricating properties [8]. Similar to  $\text{WS}_2$ ,  $\text{MoS}_2$  was formed during sliding however it was not detected in the Raman spectrum possibly because of its small amount. Thus very low friction coefficient and wear rate of Mo–W–C coating during boundary lubricated sliding at ambient temperature are attributed to the formation of transfer layer containing  $\text{WS}_2$  and graphitic carbon particles.

Figure 3 shows the friction behaviour of Mo–W–C and DLC-A coatings during lubricated sliding at 200°C. The friction curve of DLC-A showed a rapid decrease in friction in "run-in" period (segment I), followed by an increase in friction from middle of the segment II to the end of segment III. DLC-A produced wear debris of graphitic nature, which explained the decrease in friction coefficient in "run-in" period. However degradation of coating properties at 200°C increased the friction coefficient of DLC-A later (segment III). On the other hand, Mo–W–C coating showed a high friction coefficient in "run-in" period (segment I), followed by a slow but steady decrease for rest of the sliding distance (segments II and III). This reduction in friction coefficient of Mo–W–C coating was attributed to the formation of the lubricious compounds ( $\text{MoS}_2$  and  $\text{WS}_2$ ) during sliding as revealed by Scanning electron microscopy and Raman spectroscopy.

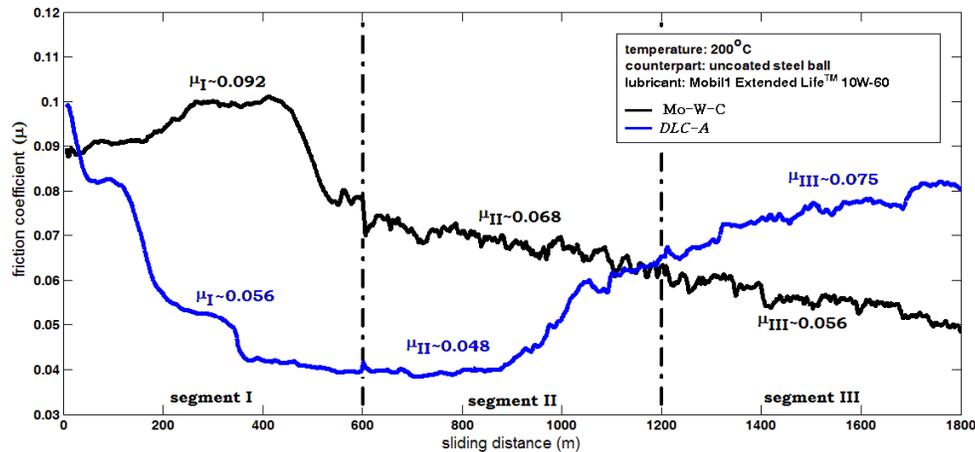


Figure 3: Friction behaviour Mo–W–C and DLC-A coatings during lubricated sliding at 200°C

Figure 4a shows the X-ray mapping results of the debris adhered to the steel ball after sliding against Mo–W–C coating at 200°C. The tungsten, molybdenum and sulphur maps showed their presence only on the adhered debris. Carbon and iron were present all over the wear scar, however the intensity of iron was observed lower within the adhered debris. These maps indicated that the adhered debris was composed of graphitic carbon particles and sulphides of tungsten and molybdenum. The lower intensity of iron within the debris possibly showed the absence of iron sulphides.

Figure 4b shows the magnified image of debris adhered to the steel ball. At *position a*, the debris was smeared over the ball surface whereas the debris was accumulated and thickened on the ball surface at *position b*. The EDX analysis was carried out on these two positions in order to understand the elemental composition. The spectrum collected from *position a* showed strong peaks of Fe, Cr and C and weak peaks of W and S. Thus *position a* was basically the ball surface, which was possibly covered by graphitic carbon and  $\text{WS}_2$  particles formed during sliding. The EDX spectrum collected from *position b* showed strong presence of W, Mo and S, which indicated that the accumulated debris on *position b* was a thick layer consisted of a mixture of  $\text{WS}_2$  and  $\text{MoS}_2$ . It is believed that both  $\text{WS}_2$  and  $\text{MoS}_2$  are formed due to the chemical reactions taking place at the asperity contacts during lubricated sliding and adhered to the ball surface.

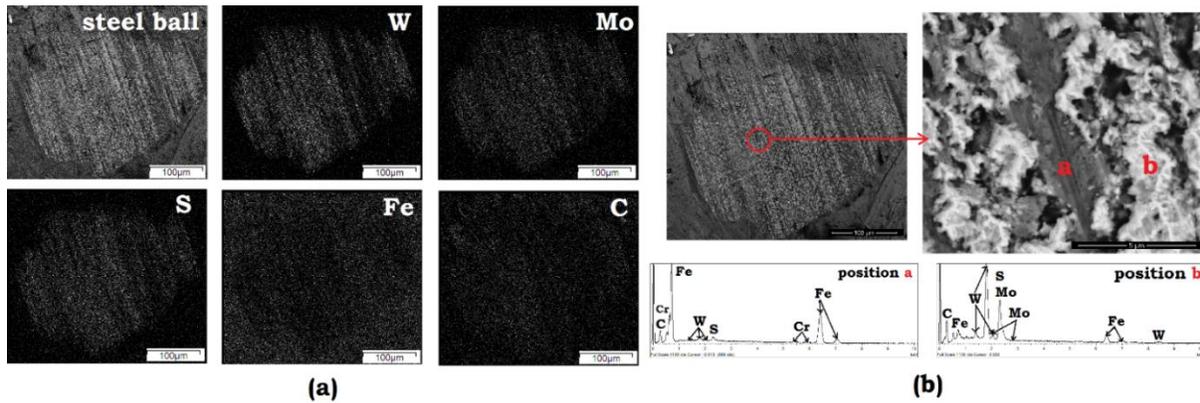


Figure 4: (a) X-ray mapping and (b) EDX analysis of the debris adhered to the steel ball after sliding against Mo–W–C coating at 200°C

Figure 5 shows the Raman spectra collected from the *position a* and *position b* of the ball surface. The positions of spectrum collection were encircled in the image shown in the insets. After deconvolution of the spectrum collected from *position a*, the distinct and dominant graphitic carbon peaks (having an  $I_D/I_G$  ratio of 1.41) and  $WS_2$  peak (centred at  $\sim 323\text{ cm}^{-1}$ ) were observed. Similarly after deconvolution of the Raman spectrum collected from *position b*, very sharp  $WS_2$  and  $MoS_2$  peaks were observed indicating their strong presence in the accumulated debris. The most intense peak centred at  $\sim 406.5\text{ cm}^{-1}$  indicated presence of both  $WS_2$  and  $MoS_2$  phases and the second most intense peak centred at  $\sim 379\text{ cm}^{-1}$  belonged to  $MoS_2$  phase. Thus the Raman analyses completely agreed with the X-ray mapping results confirming presence of graphitic carbon particles and solid lubricants like  $WS_2$  and  $MoS_2$  within the adhered debris.

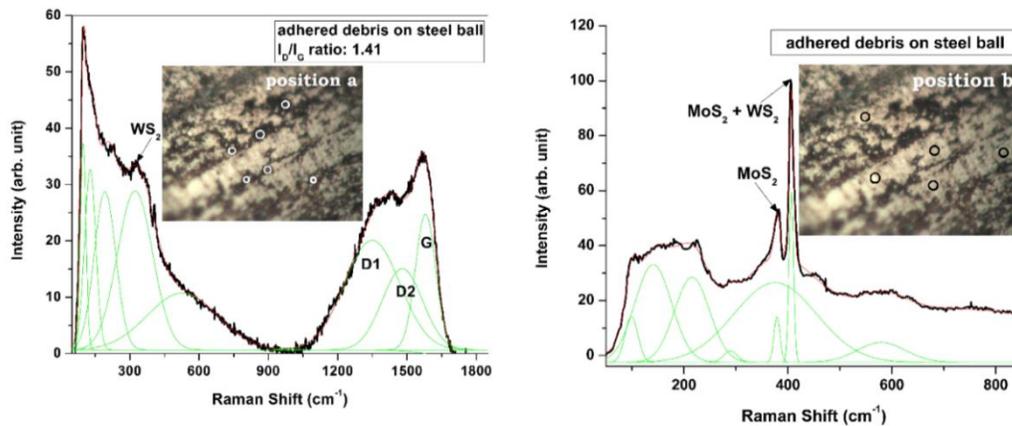


Figure 5: Raman spectra collected from the adhered debris after sliding against Mo–W–C coating at 200°C

Figure 6a shows the presence of metal sulphides ( $MoS_2$  and  $WS_2$ ) in the EDX spectrum collected within the wear track of Mo–W–C coating after sliding at 200°C. This is further confirmed by the Raman spectrum collected from the wear track as shown in figure 6b. The deconvoluted spectrum contains  $MoS_2$  peak centred at  $\sim 372\text{ cm}^{-1}$  along with distinct graphitic carbon peaks having an  $I_D/I_G$  ratio of 1.55. The formation of  $MoS_2$  and  $WS_2$  indicates that the wear mechanism at elevated temperature is **tribochemically reactive** similar to ambient temperature. With increase in test temperature from ambient to 200°C, the chemical reactions occurred between the coating and the sulphur-based compounds of the engine oil are promoted and more amounts of metal sulphides ( $WS_2$  and  $MoS_2$ ) are produced leading

to continuous decrease in friction coefficient with increase in sliding distance unlike *DLC-A*. The analytical techniques reveal that these metal sulphides have stronger affinity towards steel ball rather than the coating, thus they adhere to the ball surfaces by forming a thick tribolayer.

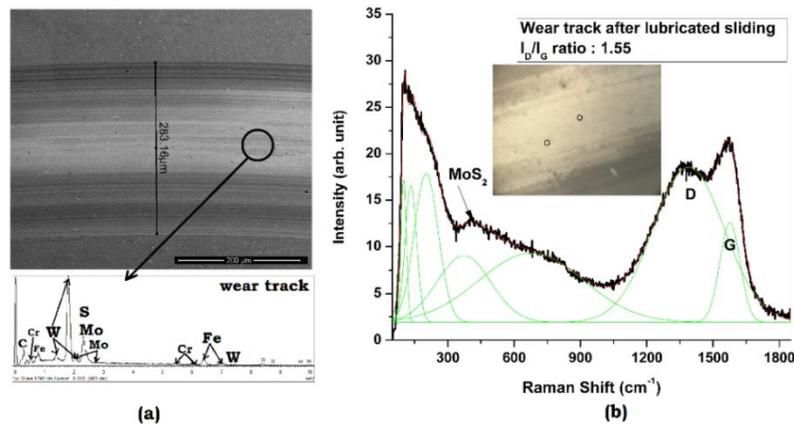


Figure 6: (a) Wear track profile and (b) Raman spectrum collected from the wear track after sliding at 200°C

#### 4. Conclusion

Mo–W–C coating was successfully deposited using HIPIMS technology. A range of surface analyses techniques revealed the "in-situ" formation of solid lubricants such as WS<sub>2</sub> and MoS<sub>2</sub> at the tribo-contacts in boundary lubricated conditions at ambient and elevated temperature. This mechanism is believed to be the key-factor for reduction in friction of Mo–W–C coating. The presence of graphitic carbon particles further benefits the friction behaviour of Mo–W–C coating ( $\mu \sim 0.033$  at ambient temperature and  $\mu_{III} \sim 0.056$  at 200°C) compared to the state-of-the-art DLC coatings. It is observed that low friction is achieved mostly due to formation of WS<sub>2</sub> at ambient temperature, whereas formation of both WS<sub>2</sub> and MoS<sub>2</sub> significantly decreases the friction at elevated temperature. This indicates importance of combined Mo and W doping over single-metal doping in carbon-based coatings.

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