Influence of Steel Surface Composition on ZDDP Tribofilm Growth Using Ion Implantation

Mao Ueda*, Amir Kadiric** and Hugh Spikes**

*Shell Lubricants Japan K.K., **Imperial College London

1. Introduction

The role of lubricant antiwear additives, especially ZDDPs, has become increasingly important because of the introduction of very low viscosity oils to reduce power losses from hydrodynamic friction, churning and pumping, and thus increase machine efficiency. Effective tribofilm formation relies on the interaction of ZDDP with a rubbing, solid surface, and to understand and improve the antiwear performance, it is essential to consider the additive and surface in combination. However, the effect of chemical composition of steel on ZDDP tribofilm formation is not yet well understood. This work examines the influence of steel surface composition on ZDDP tribofilm formation by ion-implanting typical steel alloying elements, Ni, Mo, Cr, V and W, into steel surfaces. Such implantation changes the chemical composition of the steel surface but has relatively little effect on its mechanical properties or topography. The mechanism by which implanted ions affect ZDDP tribofilm development is suggested [1,2].

2. Test methods

A MTM ball on disc tribometer with a SLIM was employed to observe ZDDP tribofilm growth.The contact conditions used in the MTM-SLIM tests are shown in Table 1. Under these conditions, the lambda ratio was calculated to be 0.1, thus these rubbing conditions were in the boundary lubrication regime. The development of ZDDP tribofilm on balls was monitored by SLIM measurements performed at set intervals throughout the 4 h test. Standard and ion-implanted AISI 52100 steel discs and balls were studied. The following metals were implanted in steel discs and balls; nickel (Ni), molybdenum (Mo), chromium (Cr), vanadium (V) and tungsten (W). Table 2 shows the chemical composition of the specimens measured by SEM–EDX. Ion implantation increased the concentration of implanted ions in the discs and balls by approximately 1.5 at.% and 1.3 at.%, respectively. A solution of ZDDP in a polyalphaolefin (PAO) base oil was studied. The base oil was PAO 4 having viscosity 18.5 mm2/s at 40 °C and 4.1 mm2/s at 100 °C. The secondary C6 ZDDP was used at a concentration of 800 ppm P. Selected tests were performed at ZDDP concentrations of 200, 400 and 1600 ppm.

Table 1 Scuffing test conditions using MTM

Mean (entrainment) speed; $U = (U_{ball} + U_{disc})/2$	35 mm/s
Slide-roll-ratio (SRR); $SRR = 100*(U_{disc} - U_{ball})/U$	100%
Applied load	34.6 N (max Hertz pressure 1.0 GPa)
Temperature	80 ℃
Rubbing time	4 h
Lambda (minimum EHD film thickness / composite Rq roughness)	0.1

Table 2 Measured chemical composition of MTM discs and balls (at.%)

Material		Fe	Mn	Si	Cr	Ni	Mo	V	W
AISI 52100 steel	Disc	96.4	0.7	0.8	2.1				
	Ball	96.4	0.6	1.1	1.9				
Ni-implanted	Disc	95.1	0.6	0.8	2.0	1.5			
	Ball	95.4	0.7	1.0	1.7	1.2			
Mo-implanted	Disc	95.3	0.7	0.8	1.6		1.6		
	Ball	95.5	0.7	1.0	1.5		1.3		
Cr-implanted	Disc	95.0	0.7	0.8	3.5				
	Ball	95.0	0.8	1.0	3.2				
V-implanted	Disc	94.6	0.8	0.9	2.2			1.5	
	Ball	94.7	0.8	1.1	2.1			1.3	
W-implanted	Disc	94.7	0.7	1.2	1.9				1.5
	Ball	95.0	0.7	1.1	1.9				1.3

3. Results

3.1 Effect of Ion Implantation on Tribofilm Formation

Figure 1 shows the evolution of ZDDP tribofilm thickness on the original and ion-implanted steel balls over 4 h rubbing time, determined using SLIM. Tribofilms on unimplanted steel gradually grew to approximately 150 nm over the first 3 h and then remained stable at this thickness for the remaining hour. Interestingly, implanted Ni ions considerably promoted tribofilm growth, with tribofilm in this case reaching 150 nm after only 1 h of rubbing, and then stabilizing. By contrast, implanted Mo and Cr ions deterred tribofilm growth; tribofilms grew much more slowly and reached only. about 50 nm at the end of the 4-h tests. V and W implantations did not significantly affect ZDDP tribofilm growth. These results suggest that the chemical composition of steel can have a significant influence

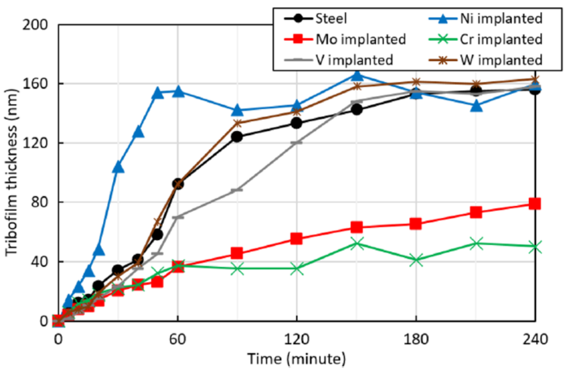

Fig. 1 The evolution of ZDDP tribofilm thickness on the original unimplanted and ion-implanted steel ball

on ZDDP tribofilm growth. To examine the ability of ZDDP to adsorb on ion-implanted steels, the effect of varying ZDDP concentration on tribofilm formation on (a) steel, (b) Ni-, and (c) Mo- and (d) Crimplanted steels was studied. The part of results is shown in Fig. 2. On 52100 steel, tribofilm formation rate increases with P concentration from 200 to 800 ppm, with the 135 nm and 155 nm maximum tribofilm thickness, respectively, after 4 h rubbing. However, 1600 ppm of P forms a tribofilm at a similar rate and to a similar thickness as 800 ppm P. On Ni-implanted steel, while tribofilm forms faster at 400 ppm P than at 200 ppm P, behaviour at 800 ppm P is similar to that at 400 ppm P. On Mo- and Cr-implanted steels, tribofilms grew faster and thicker as P concentration increased from 800 to 1600 ppm. These results show that the concentration of ZDDP above which tribofilm formation saturates varies with the presence of different elements in the surface, being no more than 800 ppm P for unimplanted steel, 400 ppm P for Ni-implanted steel, and greater than 1600 ppm P with Mo- and Cr-implanted steels. This suggests that ZDDP may adsorb most easily on Ni-implanted steel, and least easily on Mo and Cr-implanted steels.

3.2 Surface Analysis

Cross-sections of tribofilms on Ni- and Mo-implanted discs were analysed using STEM-EDX. Fig. 3 shows the EDX line spectra of tribofilms on Ni and Mo-implanted steels after 4 h rubbing tests. The peak intensity was adjusted by scaling to the same phosphorus peak intensity to easily compare the ratio of other elements to phosphorus. Note that the vertical dashed lines in the figure show only approximate extent of the tribofilm since the exact boundaries are difficult to ascertain in the EDX spectra. Zn and P were detected in both tribofilms, suggesting the formation of zinc phosphates. The peak of Fe was present in the tribofilm near the steel substrate, and this decreased towards the tribofilm surfaces. This suggests that Fe was transferred into tribofilms from steel substrates. The peaks of implanted Ni and Mo were clearly detected in both substrates while within the tribofilm, they only appear to be present in the immediate vicinity of the tribofilm-substrate interface and at relatively low concentrations. Aside from STEM-EDX, the analysis using XPS and TEM was carried out to understand the ZDDP tribofilm property on ion implanted steels.

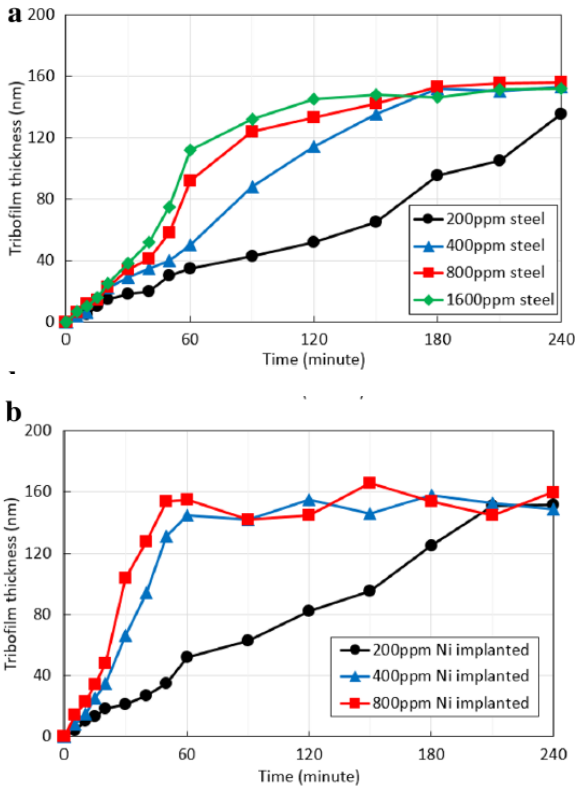

Fig. 2 The effect of ZDDP concentration on tribofilm thickness on **a** original 52100 steel, **b** Ni-implanted steel

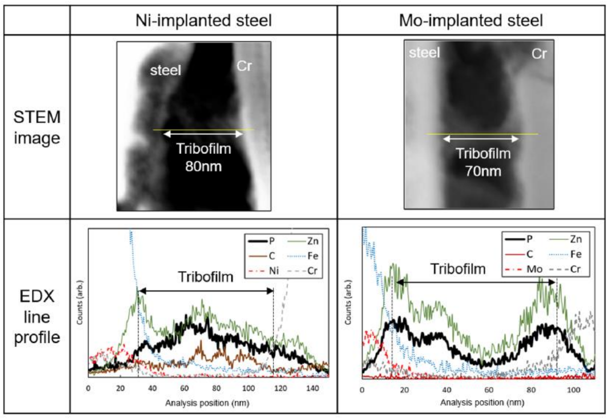

Fig. 3 STEM images and EDX line profiles of the tribofilms on Ni-and Mo-implanted steels.

4. Conclusions

ZDDP tribofilm formation on Ni, Mo, Cr, V and W ion implanted steel has been studied. The implantation of different metal ions into steel surfaces results in variations in the rate of ZDDP tribofilm growth. This suggests that the observed variation in ZDDP tribofilm formation with different implanted ions may originate from differences in surface reactivity, and thus the ease of adsorption of ZDDP on the surfaces, resulting from different ion implantation. The fact that alloying metals in steels affect tribofilm formation has practical implications for optimizing lubricants and the composition of substrate surfaces to protect components from wear.

5. Reference

[1] M. Ueda, A. Kadiric, H. Spikes, Influence of Steel Surface Composition on ZDDP Tribofilm Growth Using Ion Implantation, Tribol. Lett. (2021) 1–14.

[2] K. Pagkalis, H. Spikes, J. Jelita-rydel, M. Ingram, A. Kadiric, The Influence of Steel Composition on the Formation and Effectiveness of Anti-wear Films in Tribological Contacts, Tribol. Lett. 69 (2021) 1–20.