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Effect of surface films on tribologically induced metallurgical transformations of steel in oil lubricated contacts

Shoufan Cao [a,*], François Sarasin [b], Marco Cantoni [c], Stefano Mischler [a]

[a] Ecole Polytechnique Fédérale de Lausanne (EPFL), Tribology and Interface Chemistry Group, Station 12, CH-1015 Lausanne, Switzerland
[b] Micro Tech Lubes SA, 1207 Geneva, Switzerland
[c] Ecole Polytechnique Fédérale de Lausanne (EPFL), Interdisciplinary Center for Electron Microscopy (CIME), Station 12, CH-1015 Lausanne, Switzerland

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ABSTRACT

This study was initiated with the aim to assess the influence of boundary films on the tribologically induced metallurgical transformations and deformations of metals in lubricated contacts and their effect on wear. For this, the tribological behavior of a carbon steel contact was studied in two commercially available oils expected to form boundary films of quite different chemistry and structure. Surface analysis by AES and XPS revealed that under the investigated conditions the first oil led to the formation of an iron–zinc oxide surface film while the second to a calcium–carbon–oxygen rich film. The results show that, without influencing the coefficient of friction, the nature of the formed films significantly affected the metallurgical transformations (characterized by electron microscopy of focused ion beam cross sections) occurring in the near surface region of the metal and the corresponding wear response. The effect of boundary films on wear was attributed to their capability to influence the plastic flow of the nano-grained structures generated in the studied tribological contacts.

1. Introduction

Anti-wear additives used in oil lubricants are designed to generate, by chemical reaction, surface films acting as boundary lubricants to protect the underlying metal against wear. One of the most studied anti-wear additives for oil is the family of ZDDP (zinc dialkyl-dithiophosphate), which is effective under a variety of tribological conditions [1,2]. ZDDP forms boundary films of complex structure that may include several layers: a metal oxide or sulfide layer interfacing the metal, a layer of short chain phosphates, a layer of long chain poly(thio)phosphates and finally with a soft surface layer of alkyl phosphates [2]. Other additives react differently. For example, Minami et al. [3] reported that over-based calcium sulfonates introduced into base oil generated an efficient wear protective boundary film composed of $CaCO_3$ and CaO.

It is generally accepted that anti-wear boundary films constitute a mechanical protective barrier that acts by different mechanisms. Their effectiveness is usually attributed to their low shear strength that reduces friction and to their capability to avoid direct metal on metal contact, thus preventing adhesion, and to digest hard abrasive particles [1,2].

However, other mechanisms can in principle play a role. Surface films can affect the tribological behavior of metals by directly interfering with the plastic deformation mechanism of metals. Indeed, surface oxide films were observed to render certain metal more brittle and thus more prone to wear. This effect was first observed in the early 20th century by Roscoe [4] who investigated the mechanical properties of cadmium oxidized at different levels. Recently, in water lubricated contacts (tribocorrosion) passive films, i.e. nanometer thin oxide surface films spontaneously formed by reaction of the metal with water, were found to promote strain accumulation in the near surface zone of rubbed metals such as carbon steel [5], stainless steel [6], CoCr alloys [7] and NiCr alloys [8] and to promote wear. The strain accumulation manifested itself in hardening and in extended grain refinement leading to the formation of nano-sized grains in the near surface metal layer [6–8]. As a consequence of strain accumulation, the material became more prone to mechanical failure and wear than the same metal without the passive film. This tribo-metallurgical effect was tentatively attributed to the blocking action that surface films can have on dislocation motion and their annihilation at the surface [6,9]. Büscher et al. [10] found that during the rotation of the nano-grains in the near surface zone under the frictional stress field, surface active species can react with the exposed grain boundaries and thus reduce intergranular adherence and overall surface cohesion resulting in enhanced wear.

* Corresponding author.
E-mail address: shoufan.cao@epfl.ch (S. Cao).

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This work was initiated with the aim to verify whether surface films generated on steel in oil lubricated contacts may indeed modify the tribo-metallurgical response to friction. For this, a bearing ball vs. carbon steel disc contact was evaluated in a reciprocating sliding wear rig lubricated using two different oils. The first one is a fully formulated commercial oil containing among other additives ZDDP (zinc dialkyl-dithiophosphate). In order to modify the nature of the boundary film without affecting the other oil properties, a fully miscible commercial calcium sulfonate and PAO (poly alpha olefin) based additive package was added to the first oil to form the second oil. According to literature [1–3], these two lubricants are supposed to produce boundary films of different nature. Although these lubricants are specifically designed as engine oil for higher temperatures, tribological tests were carried out at room temperature, the goal of this study being comparing different boundary films, not testing the efficiency of oil formulations. Surface chemistry was assessed using Auger Electron Spectroscopy (AES) and X-ray Photoelectron Spectroscopy (XPS). Focused Ion Beam (FIB) cross sections were analyzed by Scanning Electron Microscopy (SEM) to reveal metallurgical transformations induced by rubbing in the near surface region.

2. Experimental

2.1. Materials and lubricants

Disks of 20 mm diameter and 5 mm thickness made of 1.6582 carbon steel (V155 from Böhler Steel, Austria) were used as flat samples. The chemical composition is 0.34% C, 1.5% Cr, 1.5% Ni, 0.2% Mo, 0.5% Mn, 0.3% Si and balance Fe. According to the manufacturer, the V155 steel is delivered in tempered state with yield strength of 900 MPa. Fig. 1 shows the metallurgical structure of the metal used for the disks. A very fine and homogeneous annealed martensitic structure was found. The balls, with diameter of 6 mm, were made of 1.3505 bearing steel (100Cr6 from Bossard AG, Zug/Switzerland). According to the supplier, the surface roughness of the bearing balls is 60 nm. The disks were polished down to mirror grade. Prior to tests, the balls and disks were ultrasonically cleaned in acetone and ethanol for 5 min respectively and dried with oil free compressed air.

The oil used was an industrial fully synthetic motor oil (Mobil 1 0W-40), hereinafter referred to as “Oil A”. The PAO/calcium sulfonate additive package Engine Treatment commercialized by BestLine Research Inc. was blended with Oil A (15 vol%) in order to obtain the second lubricant called hereinafter “Oil B”. According to the manufacturers, the Oil A contains 1100 ppm of zinc and the additive package contains group III and group IV PAOs (including aliphatic spirits, 1-decene hydrocarbon and cycloparaffins), liquid fluorocarbon resins and synthetic antioxidant calcium sulfonates. Both the oil and the additive package were supplied by Micro Tech Lubes SA (Geneva, Switzerland). The viscosity of Oil A and B was measured at room temperature (22 ± 1 °C) using a viscometer (Model RI:1:L from Rheology International Shannon, Ireland). Spindle 2 was used and five rotating speeds (20, 30, 50, 60, 100 rpm) were applied to obtain the viscosity, respectively. At the above different rotating speeds, no big difference of the viscosity was found. The viscosity of the Oil A is 171 ± 2 mPa · s and the Oil B has a very close viscosity of 169 ± 1 mPa · s.

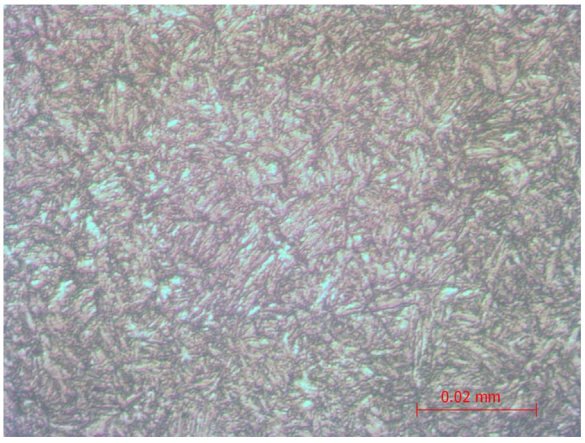

Fig. 1. The metallurgical structure of the metal (V155) used for the disks.

Table 1
Experimental parameters of the wear tests.

Motion	Reciprocating
Load	3.9 N or 5.7 N
Average Hertzian contact pressure	692 MPa or 785 MPa
Stroke length	5 mm
Frequency	4 Hz
Sliding velocity	40 mm/s

2.2. Tribology tests

Ball-on-disc configuration was adopted to carry out the tribology tests. The reciprocating motion tribometer used is described in more details in [11,12]. Before sliding, the loaded ball and disc were left in the lubricant for 5 min. Then the sliding started and lasted for 120 min. After sliding, the loaded ball and disc were left in the lubricant for another 5 min. Table 1 shows the experimental parameters for the tests. The coefficient of friction was recorded during the whole rubbing period as the ratio between the frictional and normal force when the ball was in the middle of the stroke. After the test, the disc and the ball were ultrasonically cleaned first in petrol and then in ethanol for 10 min, respectively and dried by compressed air.

2.3. Characterization

The topography of wear tracks was observed under optical microscope (Leitz), SEM (Phillips XLF30) and 3D white light interferometer (GBS smartWLI). The volume of the wear track on the disc was calculated by multiplying the area of the cross section of the wear track by its length.

Micro-hardness was measured using a Vickers micro hardness tester (Leitz) inside and outside of the wear tracks. Average values were calculated from five individual tests. The applied load was 0.98 N and the dwell time was 15 s.

Cross section images of the wear tracks (perpendicular to the sliding direction) were obtained from serial high-resolution SEM images in a combined FIB-SEM system (Zeiss XB540). A Ga^+ ion beam was used in the FIB system to mill the cross section surfaces. 3D reconstruction was implemented using an open-source image processing software (Fiji). 300 cross section images at 10 nm spacing obtained from the FIB system were employed and then aligned and segmented by Fiji. The plugin “3D Viewer” was used to acquire the 3D images.

The chemical composition of the surfaces (inside and outside of the wear track) after the wear tests was analyzed by AES and XPS. AES was carried out using a PHI 680 Scanning Auger Microscope (Physical Instruments AG, Germany) operated with a primary beam of 10 nA at 10 keV. AES sputtering depth profiles were measured using a 1 keV Ar^+ ion beam rastered over an area of 2×2 mm corresponding to a sputtering rate of 2 nm/min as calibrated on SiO_2 films. XPS measurements were carried out using a