

Reaction Films Formed Thermally and Mechanically from Lubricants: A Comparison

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Introduction

Optimizing the functioning of lubricant additives and formulations would be greatly assisted by characterizing the reaction films that form in worn contacts. A large body of fundamental and applied work has been performed to that end [1]. However, the reaction films have been challenging to characterize, particularly because of their tendency to be altered when the bulk oil is removed by solvents [2]. The techniques used to analyze the films can be broadly grouped into chemical, optical, surface-science, and mechanical approaches. In some of these approaches, it has been easier to use characterization methods on samples that were prepared thermally (i.e., by the immersion of metal into heated oil) than on those prepared tribologically. Although it has been found that thermal and mechanical films have similar film chemistries under some circumstances [3], the two types of films have not been compared in detail because the characterization methods that are appropriate for one type of sample are often not useful for the other. The objective of the present work is to show that one cannot assume that thermally formed additive reaction films are equivalent to those formed mechanically.

Methods and Materials

Flats of polished AISI H-13 steel (UNS# T20813) were austenitized and quenched to a hardness of Rockwell C 56 and polished to a roughness R_a of 1-2 nm. Reaction films were formed on the flats from lubricants consisting of polyalphaolefin (PAO) oil mixed with Lubrizol 1095, a zinc dialkyl dithiophosphate (ZDDP) additive. Lubricants with ZDDP in PAO at concentrations of 50, 25, 12.5, and 6.25 wt% were made.

Thermal films were formed by immersing the flats in oil and heating them to 150°C for 24 hours under an atmosphere of slowly flowing dry N_2 . Temperature was measured with a thermocouple suspended in the oil next to the sample. Mechanically formed films were produced in a high-frequency reciprocating rig (HFRR) wear tester. A 9.5-mm-diameter (3/8-in.-diameter) Al_2O_3 ball counterface and a load of 668 N (150 lb) were used with a reciprocating track length of 0.021 m. The environment was laboratory air, and the tests were conducted at room temperature. The frequency of reciprocation was increased from 60 to 510 rpm in steps of 30 rpm each 60 seconds during the test. Friction

coefficients of 0.07 to 0.12, typical of the boundary lubrication regime, were measured.

The collection of x-ray fluorescence data has been described elsewhere [4]. Experiments were performed at beamline 12-BM at the APS. An incident beam energy of 20 keV was chosen (wavelength $\lambda = 0.06201$ nm). The beam illuminating the sample was approximately 0.7 mm square, comparable to the width of the mechanically formed reaction films. Slits allowed fluorescence detection only from an area approximately 6 mm long in the center of the wear scar or thermally treated area. The reaction films were prepared for x-ray examination by resting the samples on their sides and allowing excess oil to drain. The residual oil was not rinsed away with solvents.

Results

Fluorescent intensities from Zn and Fe atoms as a function of incident angle are shown in Fig. 1. The sample examined was produced by wear in oil containing 6.25-wt% ZDDP; the results in Fig. 1 were typical. Fluorescent spectra were recorded at each setting of the incident angle θ , and the number of counts in the $ZnK\alpha$ and $FeK\alpha$ peaks were noted. Each data point represented a detection of 800 or more photons (10^4 - 10^5 photons at high incident angles). These values

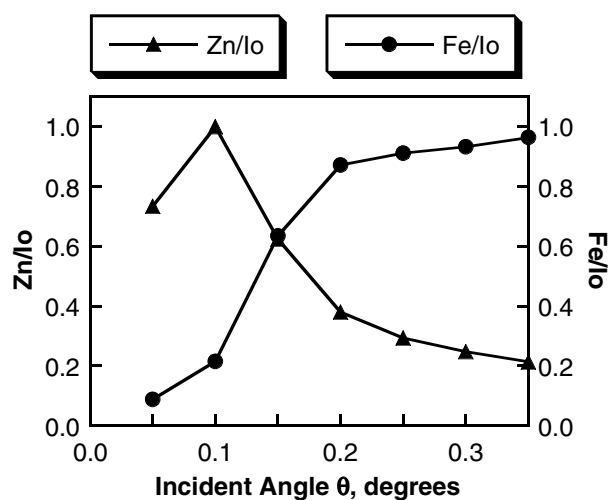


FIG. 1. Fluorescent intensities from Zn and Fe atoms versus incident angle. Intensities corrected for strength of incident beam and normalized to maximum values.

were divided by $\sin(\theta)$ to correct for the intensity of illumination by the incident beam. This correction was based on the observation that the distribution of intensity in the beam was approximately uniform throughout its area and on the fact that the sample surface would intercept an increasing fraction of the beam with an increasing incident angle in this range of angles. After this correction, the sets of values for Zn and Fe fluorescence were each normalized to their maximum for ease in plotting. Separate Y axes were provided for the two elements because the normalization was different for each. The Zn fluorescent intensity was observed to rise to a peak at an incident angle of 0.1° and then fall, while the intensity from Fe was low at low incident angles, rose steeply between 0.1° and 0.2° , and then rose slowly.

We used data like those shown in Fig. 1 to calculate the total amount of Zn in each reaction film as follows. In Fig. 1, data collected at incident angles above approximately 0.2° represented the travel of the incident beam through the reaction film and into the steel flat, because the critical angle for the total external reflection of 20-keV x-rays from steel was 0.159° . Knowing the absorption of the incident beam photons in steel, we calculated the depth of penetration of the beam into the steel. This provided the number of Fe atoms per unit area illuminated by the incident beam. Knowing the relative efficiencies of production of $\text{FeK}\alpha$ and $\text{ZnK}\alpha$ photons (the fluorescence cross section, proportional to the absorption of the incident beam by the element), we calculated the number of Zn atoms per unit area required to produce the observed number of $\text{ZnK}\alpha$ photons. This process was iterated because of the need to correct the intensity of the incident beam reaching the steel for the absorption of the beam within the Zn-bearing layer. Absorption of fluorescent photons within the steel and the Zn-bearing layer, and refraction of the beam by the reaction layer and by the steel, were also taken into account. In correcting for absorption, it was assumed that the only absorbing species were Fe and Zn. Absorption by C and other elements likely to be present in significant amounts would have been negligible. To correct for refraction, which was dependent on the electron density of the refracting medium, it was assumed that the electron density of the Zn-bearing layer was equal to that of the oil plus the electrons present in the Zn; alteration of this value did not greatly affect calculation of the number of Zn atoms present in the film. In the manner described above, the number of $\text{ZnK}\alpha$ and $\text{FeK}\alpha$ photons collected at the incident angle of 0.35° was used to calculate the areal density of Zn atoms in each reaction film. This data reduction technique was not sensitive to film thickness, so the number of Zn atoms per unit volume could not be determined.

Figure 2 shows the calculated number of Zn atoms per square centimeter for the thermally and

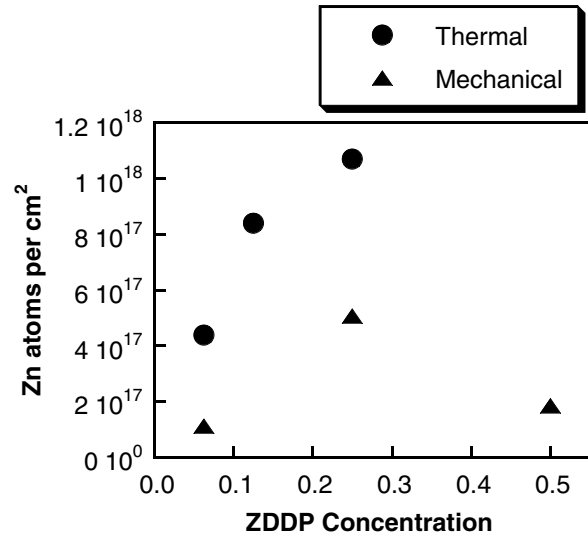


FIG. 2. Areal density of Zn atoms in reaction films formed thermally and mechanically, shown as a function of ZDDP concentration in oil.

mechanically formed reaction films as a function of the concentration of ZDDP in the lubricant. Values from the sample worn in oil containing 12.5-wt% ZDDP and from the sample heated in 50-wt% ZDDP were not available because debris or other solids were present on the reaction films. Nonplanar foreign material on the surfaces of these samples caused their Zn and Fe fluorescent intensities to be insensitive to the incident angle [5] (see discussion of Fig. 1 below). For comparison, a $0.15\text{-}\mu\text{m}$ -thick layer of metallic Zn contains 1×10^{18} Zn atoms/cm². In the thermally formed films, the Zn content increased with increasing ZDDP concentration, while in the mechanically formed films, the Zn content increased with ZDDP concentrations from 6.25 to 25 wt% but decreased at a ZDDP concentration of 50 wt%. At ZDDP concentrations of 6.25 and 25 wt%, where data from both thermal and mechanical films were available, the Zn content was greater in the thermal films.

Discussion

The angular dependence of fluorescent intensity from Zn and Fe in Fig. 1 was the result of refraction and absorption of the incident beam within the sample [6]. Refraction causes total external reflection of x-rays from interfaces. At incident angles of 0.1° and smaller, the beam reflected from the steel but did not reflect from the film. The electron density of the film was lower than that of the steel, giving the film a lower angle for total external reflection, and the film's surface may have been sufficiently rough or diffuse to prevent total reflection. Absorption of the incident beam within the reaction film produced fluorescence from the

absorbing species (Zn) and reduced the incident intensity available to produce fluorescence from the Fe below the film. The decrease of Zn fluorescence above 0.1° was caused by the geometrical decrease in total distance traveled by the beam through the Zn-bearing layer as the incident angle was increased. The slight increase of Fe fluorescence above 0.2° was caused by decreased absorption of the beam by Zn. Observation of the angular dependencies described above indicated that the steel and reaction film were planar and that the detected fluorescence did not arise from the bulk oil or from debris. Data were also collected from unworn but oily areas of the flats upon which the mechanically formed films were made. In all cases, the amount of Zn detected was much lower than the amount detected in the worn area, eliminating the possibility that the bulk oil was the source of Zn fluorescence.

The higher Zn concentration that was found in thermally formed films than in mechanically formed films from the same lubricant might have been caused by several things. The first was temperature. The conversion of ZDDP to Zn-bearing reaction film material occurs through a highly complex set of breakdown and synthesis reactions [7], the rates of which depend on temperature. While immersion temperatures of 150°C have been found to produce reaction films [3], tribological contacts have been known to greatly exceed that temperature locally for short periods, even if the bulk oil remained at ambient temperature. The relative rates of the various breakdown pathways and film-formation reactions should thus have been expected to differ between thermally and mechanically formed films.

A second difference between the thermal and mechanical means of film formation was that the thickness of the mechanically formed films was due to simultaneous film formation and loss, while the thermal films suffered no material loss. The mechanical action also had the effect of selecting reaction film material with mechanical properties that would allow the material to remain in the contact rather than being pushed away. The absence of such a selection mechanism in thermal film formation allowed material of indiscriminate mechanical properties to build the film.

A third difference between the two methods of film formation in this study was the atmosphere. It was dry N_2 in the case of the thermally formed films and laboratory air in the case of the wear tests. The presence of O_2 and water vapor could have significantly affected the reactions within the lubricant. The additive ZDDP has antioxidant properties, so some additive could have been affected by the reaction with O_2 in the wear tests.

The mechanical properties of the films might also provide an explanation for the decrease in Zn detected in the film formed mechanically from 50-wt% ZDDP lubricant when compared with that formed

mechanically from 25-wt% ZDDP lubricant. In the absence of other mechanisms, films formed from lubricants containing more additive should have contained more reaction products of that additive, and this trend was observed in all the thermal and mechanical films, with the exception noted above. It was likely that during formation, the film material incorporated molecules of PAO oil, either physically or by chemical reaction. The decrease in PAO availability accompanying the increase of ZDDP concentration to 50 wt% might have prevented inclusion of sufficient PAO in the film to provide the mechanical properties necessary to prevent removal of the film material after its formation.

An improved understanding of the nature of these films will require more comprehensive characterization of the films. In future work, we plan to collect fluorescent intensities and x-ray reflectivity data simultaneously, comparing the two data sets to the output of a model that will take into account the thickness, composition, and roughness of several layers within the film and substrate [4]. Knowledge of the thicknesses and Zn contents of various parts of the films, which have been shown to be inhomogeneous [2], will begin to answer some of the questions raised by this work.

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