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Atom-probe tomography of tribological boundary films resulting from boron-based oil additives

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ABSTRACT

Correlative characterization using atom-probe tomography (APT) and transmission electron microscopy (TEM) was performed on a tribofilm formed during sliding frictional testing with a fully formulated engine oil, which also contains a boron-based additive. The tribofilm formed is ~15 nm thick and consists of oxides of iron and compounds of B, Ca, P, and S, which are present in the additive. This study provides strong evidence for boron being embedded in the tribofilm, which effectively reduces friction and wear losses.

Solid and liquid lubricants are used extensively by industry to reduce friction, wear, and heat-related degradation of machine parts that move relative to one another [1,2]. By volume, liquid lubricants account for the bulk of the commercial lubricants market and they contain several additives (that is, including anti-wear, friction modifier, viscosity modifier, antioxidant, detergent, dispersant, etc.), which enable them to achieve multi-functionality over the very broad operating conditions of moving mechanical systems for long times. One of the most effective anti-wear additives is zinc dialkyl-dithiophosphate (ZDDP), which is able to decompose and form wear-protective tribofilms at sliding contact interfaces [3]. Environmental regulations have, however, been pushing, for a long time, for the development and use of ash-less oil additives containing little or no ZDDP [4]. Therefore, in recent years, the research community in the lubrication field has been exploring new additives that can substitute for ZDDP without creating harmful by-products or ash [5].

In addition to liquid anti-friction and wear additives, many researchers have also explored the potentials of nano-sized particulate additives in lubricating oils and have shown that these can indeed play an important role in reducing wear and friction [6–8]. The improved performance is closely dependent on both the physical and chemical characteristics (that is, chemical nature, size, morphology, and concentration) of the nanoparticles being evaluated. The fundamental mechanisms responsible for friction and wear reduction by nanoparticles in lubricants have been speculated as being a colloidal effect, rolling effect, hard and protective film formation, and third body or tribofilm formation effects [6].

Among many nanosize additives, boron-based layered lattice compounds have been extensively studied as an oil-soluble additive in both liquid and solid forms. In particular, boric acid and boron oxide have been reported to reduce the coefficient of friction (COF) of sliding contact interfaces rather dramatically to values as small as 0.01 [9–11]. Several studies indicate that liquid borate esters and solid potassium triborate [12], calcium borate [13], and other types of organic compounds can also be utilized [14–17] as additives, mainly because of their unusual anti-friction and -wear properties as well as their abilities to act as anti-oxidants, provide low toxicity and good biodegradability. Many fundamental questions remain unknown, however, such as the structural features and the exact mechanisms by which B interacts with sliding surfaces as well as the other ingredients of the oil additives embedded in the tribofilms (employing various characterizing techniques) [3,5,18–23].

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In an effort to better ascertain the chemical nature of the highly wear protective boundary film with respect to a boron additive in a lubricant, we employed a cylinder-on-flat type, high-frequency reciprocating test rig followed by correlative transmission electron microscopy (TEM) and atom-probe tomographic (APT) chemical analyses. Commercial SAE 5W30 grade automotive engine oil (kinematic viscosity of 61.7 mm^2 s^{-1} at 40 °C and 11 mm^2 s^{-1} at 100 °C) was used as a specific oil lubricant in our tribological tests. This oil was further blended with a boron-based additive (at about 0.5 wt.%) to examine the role of such additives on the chemical nature of a tribofilm, which ultimately determines friction and wear performance. In our experiment, the cylindrical pins, fabricated from AISI 52100 steel, were slid against a flat specimen (also fabricated from 52100 steel and was 10 × 10 × 3 mm) in an oscillatory motion at a frequency of 5 Hz and a stroke length of 6 mm for 3600 s. The contact load applied on the steel pin was 350 N. The surfaces of the sliding test pair were initially mirror-like polished to avoid scratching and any abrasive wear effects that may arise from sharp asperities.

Along with a TEM's crystallographic information on site-specific regions of interest, APT characterization produces a three dimensional (3-D) reconstruction of the direct lattice on an atom-by-atom basis, which permits one to obtain accurate chemical concentrations of all the elements in the periodic table with essentially the same detection efficiency. The 3-D atomic scale reconstruction of a sample is obtained by combining the times-of-flights (TOFs), which yield the mass-to-charge state ratio, m/n, of each evaporated atom, and the x-, y-, and z-positional data of all the evaporated atoms in an analyzed volume with sub-nanoscale spatial resolution. Additionally, TOF mass spectra, based on m/n ratios, are utilized to obtain quantitative chemical analyses of the 3-D reconstructed sample [24,25].

To preserve the tribofilm formed at the surface area of the steel sample during TEM/APT sample preparation, the sample was firstly coated with Pt, $\sim$50 nm in thickness, using an ion-beam sputtering and etching system (South Bay Technology, model IBSe), and then another Pt protective layer, $\sim$1 µm in thickness, was deposited using a dual-beam focused-ion beam (FIB) microscope (FEI Helios Nanolab). TEM/APT samples were prepared using a standard lift-out technique employing a dual-beam FIB microscope [24–27]. Tribofilms were firstly characterized using TEM (JEOL JEM-2100F) to measure their thicknesses and chemical compositions using energy dispersive spectroscopy (EDS). Once TEM analyses were finished, a thin foil-type TEM sample was then fabricated into needle-shaped specimens with a nanotip diameter of <20 nm for APT analyses. Nanotip samples were then delivered immediately to the APT's ultrahigh vacuum chamber to minimize its exposure to air. An ultraviolet (wavelength = 355 nm) picosecond laser-assisted local-electrode atom-probe tomograph (Cameca LEAP 4000XSi) was employed utilizing the following analytical parameters: (a) an evaporation rate of 0.005–0.02 ions per pulse; (b) a pulse repetition rate of 250 kHz; (c) a pulsed laser energy of 50 pJ per pulse; and (d) a specimen temperature of 25 K. The 3-D image reconstruction and chemical analyses were performed using a software (IVAS 3.6.6).

Fig. 1a displays typical COF of commercial SAE 5W30 lubricating engine oil and the same oil with a 0.5 wt.% B-based additive. When the B additive is present in the oil, the COF decreases approximately 50% with respect to the B-free commercial SAE 5W30 oil. This reduction can be attributed to the formation of a B-rich tribofilm on the sliding steel surface. Fig. 1b and c shows the conditions of wear scars formed on the rubbing cylindrical surfaces of the steel pins after testing in 5W30 engine oil without and with a boron additive. In both cases, the amount of wear is very small and limited to the further polishing of the rubbing surface. The wear scar widths are essentially the same and hence the tribofilms formed on rubbing surfaces in both cases were highly protective against wear. Much of the wear scar width in both Fig. 1b and c is due largely to elastic Hertzian contact and perhaps to mild or polishing wear of the cylinders, thus suggesting unmeasurable wear, which confirms the excellent antiwear properties of the fully formulated SAE 5W30 engine oil.

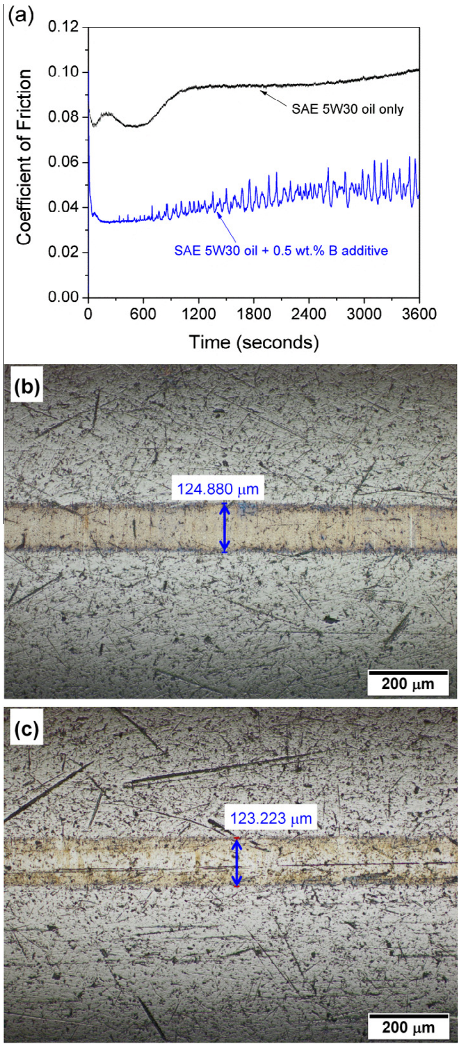

Fig. 1. (a) Friction behavior of SAE 5W30 engine oil with and without a 0.5% boron additive. Wear tracks formed utilizing (b) SAE 5W30 and (c) SAE 5W30 + B additive.

The correlative APT/TEM analyses elucidate improved friction and wear characteristics with respect to the structural and chemical details of the tribofilm, which is a result of using a B-containing commercial SAE 5W30 grade oil. The chemical and structural characteristics of the fully formulated SAE 5W30 grade engine oils have been well-documented in the archival literature [28,29] and hence our surface and structural and analytical studies are more focused on the tribofilm lubricated using B added SAE 5W30 oil. Fig. 2 displays TEM bright-field images of the contact area, which exhibits a layered surface region of the friction tested sample utilizing both commercial SAE 5W30 (Fig. 2a) and the B-containing 5W30 lubricating oils (Fig. 2b); the topmost layer is a Pt protective layer deposited to preserve the tribofilm from the effects of the IBSe and dual-beam FIB microscopy. The thin film below the protective layers is the specific tribofilm, which exhibits brighter contrast and is $\sim$10–40 nm in thickness. The thickness of the tribofilm is nonuniform throughout the sandwiched area between the Fe (bcc)-matrix and the Pt protective-layers. Fig. 2b