ATOM-PROBE TOMOGRAPHY OF TRIBOLOGICAL BOUNDARY FILMS RESULTING FROM BORON-BASED OIL ADDITIVES

Yoon-Jun Kim¹, Sung-Il Baik^{2,3}, Leonardo Bertolucci-Coelho⁴, Luca Mazzaferro⁴, Giovanni
Ramirez⁵, Ali Erdermir⁵, David N. Seidman^{2,3,*}

¹ Department of Materials Science and Engineering, Inha University, 100 Inharo, Nam-Gu, Incheon 22212, Korea

² Department of Materials Science and Engineering, Northwestern University, 2220 Campus Dr., Evanston, IL 60208, U.S.A.

³ Northwestern University Center for Atom-Probe Tomography (NUCAPT), 2220 Campus Dr., Evanston, IL 60208, U.S.A.

⁴ Materials Science and Engineering Graduate Program, Federal University of Santa Catarina, P.O. Box 476, 88040-900 Florianópolis, SC, Brazil.

⁵ Energy Systems Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60349, U.S.A.

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.

Keywords: Atom probe tomography; Transmission electron microscopy, Tribofilm; Boron oxide; Lubricant;

* Corresponding author: Prof. David N. Seidman
Tel: +1 847 491 4391, Fax: +1 847 491 7820, E-mail: d-seidman@northwestern.edu

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 ashless 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].

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 $61.7 \text{ mm}^2 \text{ s}^{-1}$ at $40 \text{ }^\circ\text{C}$ and $11 \text{ mm}^2 \text{ s}^{-1}$ at $100 \text{ }^\circ\text{C}$) 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 $10 \times 10 \times 3 \text{ mm}^3$) 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 subnanoscale 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, ~50 nm in thickness, using an ion-beam sputter (IBS) system (South Bay Technology, model IBSe), and then another Pt protective layer, ~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 (FEI Helios Nanolab) [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 to 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).

Figure 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.

Figures 1b and 1c show the conditions of wear scars formed on the rubbing cylindrical surfaces of the steel pins after test in 5W30 engine oil without and with 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 Figs. 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.

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. Figure 2 displays a 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 IBS/e and dual-beam FIB microscopy. The thin film below the protective layers is the specific tribofilm, which exhibits brighter contrast and is ~10 to 40 nm in thickness. The thickness of the tribofilm is nonuniform throughout the sandwiched area between the Fe (b.c.c.)-matrix and the Pt protective-layers. Figure 2b displays the thinnest region, ~10 nm in thickness, is seen above a globular-shaped carbide precipitate. A selected area diffraction (SAD) pattern taken on a $\bar{1}10$ zone axis (see inset in Fig. 2b) and EDS analyses (Table 1) prove that the precipitate is cementite (Fe_3C with

an orthorhombic structure) within the severely deformed ferrite (b.c.c.) matrix (the rings in the SAD pattern). Since the tribofilm is generated by mechanical contacts, and since soft material produces a wider contact area, hard cementite precipitates usually prevent the formation of very thick tribofilms just above them.

Table 1 also lists the compositions of the tribofilm, cementite precipitate, and matrix as determined by EDS. Unlike the matrix (which consists of 98.4 Fe plus 1.5 Cr at.%), the tribofilm has a totally different chemical composition: 34.4 P, 24.3 S, 28.0 Ca, 11.8 Fe, and 1.5 Zn at.%. The chemical species P, S, Ca, and Zn are all present in the additive package and are generated by complex tribochemical reactions between sliding steel surfaces and lubricant subjected to reciprocating sliding conditions. Detection of boron in the tribofilm was, however, unsuccessful due to the detection limit of EDS analysis for this light element (mass = 10.811 amu).

The APT analysis produces more precise 3-D chemical maps, including light elements such as B ($Z = 5$) and O ($Z = 8$). Figure 3 displays a 3-D reconstruction of a portion of a tribofilm in a nanotip sample containing 25 molecular species of total 238,649 atoms. Among which predominant species are Fe, Ca, P, S, Cr, O, B, C, ZnO, CrO, FeO, B₂O₃, BO, Fe₂O, FeS plus Pt and Ga from FIB milling process. Although sensitive chemical analyses were possible using APT, the B species may not be fully detected in Figs. 3 and 4 due to the difficulty of decoupling overlapped boron compound peaks with some other peaks, such as BO⁺ ($m/n=26-29$) with Cr²⁺ ($m/n=25-27$) and Fe²⁺ ($m/n=27-29$), and B₂O₃⁺ ($m/n=68-72$) with CrO⁺ ($m/n=66-71$) and FeO⁺ ($m/n=70-74$). The tribofilm observed between the Pt protective layer and the steel substrate has an approximate average thickness of 15 nm. Chemical species detected in a time-of-flight (TOF) mass spectrum and typical chemical constituents are displayed in Fig. 3: Fe, Pt, Ca in Fig. 3a, B in Fig. 3b, FeO in Fig. 3c, and CrO in Fig. 3d. Figure 4 exhibits line scans of chemical concentrations measured in at.% from the Pt protective layer and the bulk steel

substrate. The distance from 2 to 10 nm can be considered to be a tribofilm because of the following evidence: (1) The Pt protective layer disappears at ~2 nm; and (2) the concentration of Fe increased to ~ 98 at.% and stabilized at a distance of 10 nm. The concentration profiles of the tribofilm, Fig. 4, consist of Ca, O, S, B, and Cr, which are especially enriched plus ~40 at.% Fe. As stated above based on correlative TEM and EDS analyses, chemical species inside the tribofilm are products due to repeated friction and wear of sliding contacts. Among the chemical species obtained from the tribofilm Ca, S, and B are typically the major ingredients of lubricating oil and those are also comparable to the TEM/EDS results given in Table 1. The surface oxides of AISI 52100 steel, such as Fe- and Cr-oxides, were decomposed and reacted chemically with the ingredients of the lubricating oil to form a tribofilm.

The existence of B in the tribofilm and its interaction with the steel's surface oxides are important factors reducing the COF displayed in Fig. 1. A mechanism has been reported in several studies suggesting that boron is relevant to self-lubrication due to the formation of boron oxide (B_2O_3) and boric acid (H_3BO_3) thin films on the surface of boron oxide substrates. Such a lubricating effect is attributed to their layered crystal structures [9-11] or the formation of a glass-like boron oxide layer with very low COF, as small as 0.05 [11]. Addition of the boron-based additive, as a frictional modifier, exhibits a friction and wear performance that is superior to the conventional anti-friction and -wear additives alone. The B anions in a boron-based additive react with iron oxide to form a tribofilm made of a borate glass network that digests the abrasive iron oxide in a manner similar to ZDDP [30]. This finding is the key mechanism as to how wear protection can be provided [31].

In summary, we present evidence of boron embedded in a tribofilm as a result of repeated sliding friction. APT in combination with TEM is demonstrated to be a powerful approach for analyzing the chemical nature of wear protective tribofilms resulting from additives in lubricating oils. The boron in a tribofilm is a product of a tribochemical reaction

during sliding friction of AISI 52100 steels in the presence of a commercial 5W-30 grade automotive engine oil containing boron additives. The correlative atom-probe tomographic and transmission electron microscopy characterization of the wear track of the friction tested steel surface revealing approximately 15 nm in thickness of the tribofilm. The major chemical components of this film are Ca, O, S, B, Cr and ~ 40 at.% Fe, which reflects the fact that a tribochemical reaction occurred between the steel's surface oxide and the lubricant oil. Interaction of boron with Fe- or Cr-oxide exerts an enhanced lubricating effect on the metal surfaces, presumably due to its layered crystal structure, which results in a significant reduction in the coefficient of friction.

Atom-probe tomography measurements were performed at the Northwestern University Center for Atom-Probe Tomography (NUCAPT) and the LEAP tomograph was purchased and upgraded with funding from the NSF-MRI (DMR 0420532) and ONR-DURIP (N00014-0400798, N00014-0610539, N00014-0910781) programs. NUCAPT is a Shared Facility of the Materials Research Center of Northwestern University, supported by the National Science Foundation's MRSEC program (DMR-1121262). We are grateful to the Initiative for Sustainability and Energy at Northwestern for grants to upgrade NUCAPT's capabilities. This work was also supported by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Vehicle Technologies Program, under contract DE-AC02-06CH11357

REFERENCES

- [1] R.G. Budynas, J.K. Nisbett, Shigley's mechanical engineering design, 9th ed., McGraw-Hill, New York, 2011.
- [2] J.A. Williams, Engineering tribology, Cambridge University Press, New York, 2005.
- [3] J.F. Graham, C. McCague, P.R. Norton, Tribol Lett, 6 (1999) 149-157.
- [4] S. Equey, S. Roos, U. Mueller, R. Hauert, N.D. Spencer, R. Crockett, Tribol Int, 41 (2008)

1090-1096.

- [5] M.I. de Barros'Bouchet, J.M. Martin, T. Le-Mogne, B. Vacher, *Tribol Int*, 38 (2005) 257-264.
- [6] Y.Y. Wu, W.C. Tsui, T.C. Liu, *Wear*, 262 (2007) 819-825.
- [7] W.Y. Zhang, D. Demydov, M.P. Jahan, K. Mistry, A. Erdemir, A.P. Malshe, *Wear*, 288 (2012) 9-16.
- [8] B. Li, X. Wang, W. Liu, Q. Xue, *Tribol Lett*, 22 (2006) 79-84.
- [9] C. Bindal, A. Erdemir, *Appl Phys Lett*, 68 (1996) 923-925.
- [10] A. Erdemir, C. Bindal, G.R. Fenske, *Appl Phys Lett*, 68 (1996) 1637-1639.
- [11] A. Erdemir, C. Bindal, C. Zuiker, E. Savrun, *Surface and Coatings Technology*, 86-87, Part 2 (1996) 507-510.
- [12] K. Masenelli-Varlot, M. Kasrai, G.M. Bancroft, G. De Stasio, B. Gilbert, E.S. Yamaguchi, P.R. Ryason, *Tribol Lett*, 14 (2003) 157-166.
- [13] J.M. Martin, C. Grossiord, K. Varlot, B. Vacher, J. Igarashi, *Tribol Lett*, 8 (2000) 193-201.
- [14] K.G. Stanulov, H.N. Harhara, G.S. Cholakov, *Tribol Int*, 31 (1998) 257-263.
- [15] J.Y. Zhang, W.M. Liu, Q.J. Xue, *Wear*, 224 (1999) 68-72.
- [16] Y. Sun, L. Hu, Q. Xue, *Wear*, 266 (2009) 917-924.
- [17] F.U. Shah, S. Glavatskih, E. Höglund, M. Lindberg, O.N. Antzutkin, *Acs Appl Mater Inter*, 3 (2011) 956-968.
- [18] J. Qu, H. Luo, M. Chi, C. Ma, P.J. Blau, S. Dai, M.B. Viola, *Tribol Int*, 71 (2014) 88-97.
- [19] K. Ito, J.-M. Martin, C. Minfray, K. Kato, *Tribol Int*, 39 (2006) 1538-1544.
- [20] M. Aktary, M. McDermott, G. McAlpine, *Tribol Lett*, 12 (2002) 155-162.
- [21] M. Dienwiebel, K. Pöhlmann, *Tribol Lett*, 27 (2007) 255-260.
- [22] R. Mourhatch, P.B. Aswath, *Tribol Int*, 44 (2011) 187-200.
- [23] S.K. Dey, T.A. Perry, A.T. Alpas, *Wear*, 267 (2009) 515-524.
- [24] D.N. Seidman, *Annu Rev Mater Res*, 37 (2007) 127-158.
- [25] D.N. Seidman, K. Stiller, *Mrs Bull*, 34 (2009) 717-724.
- [26] M.K. Miller, K.F. Russell, K. Thompson, R. Alvis, D.J. Larson, *Microsc Microanal*, 13 (2007) 428-436.
- [27] D.N. Seidman, *Rev Sci Instrum*, 78 (2007) 030901.
- [28] Z. Tang, S. Li, *Current Opinion in Solid State and Materials Science*, 18 (2014) 119-139.
- [29] B. Kim, J.C. Jiang, P.B. Aswath, *Wear*, 270 (2011) 181-194.
- [30] M.R. Lovell, M.A. Kabir, P.L. Menezes, C.F. Higgs, *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 368 (2010) 4851-4868.
- [31] J. Qu, D.G. Bansal, B. Yu, J.Y. Howe, H. Luo, S. Dai, H. Li, P.J. Blau, B.G. Bunting, G. Mordukhovich, D.J. Smolenski, *Acs Appl Mater Inter*, 4 (2012) 997-1002.

List of figure captions

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.

Fig. 2. TEM cross-sectional micrograph of friction tested AISI 52100 steel surface lubricated using (a) SAE 5W30 and (b) SAE 5W30 + B additive. Inset of (b): SAD pattern of cementite on a 110 zone axis.

Fig. 3. Chemical mapping of an atom-probe tomographic reconstruction of the tribofilm: (a) Fe and Ca; (b) B; (c) FeO; and (d) CrO.

Fig. 4. Chemical composition profiles of the Pt protective layer to the bulk steel. Inset: An enlarged concentration profile of the tribofilm from 2 to 10 nm in depth.

Fig. 1.

Fig.2.

Fig. 3.

Fig. 4.

Table 1. TEM/EDS chemical analysis results from tribofilm, cementite, and steel matrix. (unit: at. %)

	P	S	Ca	Cr	Fe	Zn
Tribofilm	34.4	24.3	28.0	0.0	11.8	1.5
Cementite	0.0	7.14	0.0	10.1	82.7	0.0
Steel matrix	0.0	0.0	0.0	1.5	98.4	0.0