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SELF-LUBRICATING BORIC ACID FILMS FOR TRIBOLOGICAL APPLICATIONS*

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Because of its layered crystal structure, boric acid, has been found to be lubricious. Its self-lubricating mechanism is related to the easy shear of atomic layers over one another. Moreover, laser-Raman spectroscopy and electron microscopy analyses have confirmed that thin boric acid films can form on surfaces containing boron and boric oxides. To study the lubricity and self lubricating mechanism of boric acid, pin-on-disk tests were performed on pairs of boric acid compacts and steel disks, boric oxide films and steel pins, boron films and steel pins, and boron-implanted steel disks and steel pins. The mean steady-state friction coefficients of these tribosystems ranged from 0.04 to 0.12.

INTRODUCTION

Because of their easy-shear capabilities, certain inorganic solids are used as lubricants in a wide range of tribological applications where liquid lubricants are inefficient [1-4]. Lubricity in these solids is related primarily to their layered-crystal structures and unique bond characteristics. The atoms of each layer are closely packed and strongly bonded to one another, while the layers themselves are widely spaced and held together by relatively weak bonds such as van der Waals' forces [3-6]. When interposed between sliding interfaces, the layers align themselves parallel to the direction of relative motion. Once so aligned, they slide over one another with relative ease, thus affording low friction. Well-known examples are molybdenum disulfide (MoS_2), graphite, and hexagonal-boron nitride (HBN) [1,4]. Due to its relatively high lubrication capability, MoS_2 has attracted particular attention [2,7,8], but its broad utilization has been hindered by its incompatibility with humid and/or oxidizing environments [9,10].

The primary goal of this study is to describe the lubricity and solid lubrication mechanism of an inorganic compound that appears to have attracted very little attention in the past; that compound is boric acid (H_3BO_3). Johnson and Sliney reported a friction coefficient of 0.23 for boric-acid-containing tribosystems at temperatures to 93°C [11]. They noted sharp increase in friction beyond 93°C and attributed this to the decomposition of boric acid into boric oxide and water. Boric acid is available in bulk form, but can also develop naturally on surfaces containing boron and boric oxides. These surfaces can be prepared by using vapor-phase deposition and/or ion-beam-processing techniques, as demonstrated in this study.

EXPERIMENTAL PROCEDURES

Tribological experiments were conducted with four different test pairs: (1) boric acid compacts and steel disks, (2) boric oxide films and steel pins, (3) boron films and steel pins, and (4) boron-implanted steel disks and steel pins. The specific test conditions for each test pair are given in Table 1.

In the first series of tests, pairs of boric acid pins and AISI-52100 steel disks were evaluated. The pins (1.27 cm in diameter) were compacted from boric acid powders (99.8 wt.% pure, particle size = 10-20 μm) by cold-pressing under a pressure

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Table 1. Friction test conditions for test pairs.

Parameters	H_3BO_3 Pin/ 52100 Disk	M50 Pin/ B_2O_3-coated M50 Disk	M50 Pin/ B-coated M50 Disk	M50 Pin/ B^+impl. M50 Disk
Load (N)	5.0	5.0	1.0	1.0
Sliding velocity (m/s)	0.1	0.1	0.1	0.05
Relative humidity (%)	50±10	50±10	50±10	50±10
Number of revolutions	750	750	750	250
Wear track diameter (mm)	40	40	40	8
Ambient temperature (°C)	23±1	23±1	23±1	23±1
Number of tests	3	5	3	5
Tip radius of pins (mm)	50	4.8	4.8	4.8

of 35 MPa. To establish a point contact, one end of each pin was finished with a hemispherical cap of 5 cm-radius. These were subsequently installed in a pin-on-disk machine and rubbed against 5-cm-diameter steel disks whose Vickers hardness and surface roughness values were about 7.8 GPa and 0.1 µm center-line-average (CLA), respectively.

The second and third series of tests used pairs of AISI-M50 steel pins and boric oxide- and boron-coated AISI-M50 steel disks. The steel pins had a tip radius of 4.8 mm and the steel disks were 5 cm in diameter. Vickers hardness and surface roughness values of the pins were about 7.3 GPa and 0.05 µm (CLA), respectively. For comparison, several pairs were tested without the boric oxide and boron coatings.

Boric oxide was deposited on the disks in a high-vacuum system equipped with an electron-beam-heated evaporator, under conditions shown in Table 2. The boron coatings were sputtered onto the disks in an RF-magnetron sputtering system (see Table 2).

The final series of tests used pairs of boron-ion-implanted disks of AISI-M50 steel (approximately 10 mm in diameter) and AISI-M50 pins (tip radius = 4.8 mm). Base hardness and surface roughness values of these steels were comparable to those used in the tests of the boron and boric oxide coatings. The disks were implanted with boron in a dose of 2×10^{17} ions/cm^2 at an acceleration voltage of 40 keV. Using these conditions, the mean projected range (R_p) and the maximum concentration at projected range (N_{max}) were estimated from the LSS theory to be 46.5 nm and 29 at.%, respectively. The samples were friction-tested in a pin-on-disk machine under the conditions given in Table 1.

Scanning electron microscopy (SEM) and laser-Raman and X-ray photo-electron spectroscopy (LRS and XPS) were used to characterize the structural and chemical nature of the friction- and wear-tested surfaces.

Table 2. Conditions for deposition of boric oxide and boron on steel disks.

Systems Parameters	Magnetron Sputtering	Vacuum Evaporation
RF-bias voltage(V)	1700	-
Chamber pressure(Pa)	0.195	10^{-4}
Argon flow rate(cm^3/s)	0.4	-
Deposition rate(nm/s.W)	0.0755	-
Film thickness(nm)	70	2000

RESULTS

Table 3 presents the mean friction coefficients of the test pairs. All of the pairs with boric acid, boric oxide, and boron attained relatively low friction coefficients during the sliding tests. The pairs with boron and boric oxide coatings appeared to attain relatively lower friction coefficients than the other test pairs. The lowest steady-state friction coefficient (0.04), is seen in the pairs with a boric oxide film at the sliding interface. Pairs using boron at the sliding interface exhibited a somewhat higher friction coefficient of 0.065. The compacted boric acid pins exhibited a steady-state friction coefficient of about

Table 3. Mean coefficients of friction of test pairs.

Test Pairs	Friction Coefficient Initial[a]	 Steady-State[b]
M50/M50	0.3±0.1	0.7±0.05
H_3BO_3/52100	0.2±0.01	0.1±0.005
M50/B_2O_3-coated M50	0.06±0.005	0.04±0.001
M50/B-coated M50	0.07±0.01	0.065±0.005
M50/B^+implanted-M50[c]	0.1±0.05	0.12±0.02

a: First 5 to 10 revolutions
b: 100 to 500 revolutions
c: Friction coefficient began to increase after ~70 revolutions.

0.1 against the steel disk. Note that the steady-state friction coefficient of M50/M50 test pairs is about 0.7.

Electron microscopy inspection of the wear scars and tracks revealed (1) a circular wear scar that formed on the tips of boric acid pins and (2) no evidence of measurable wear on the disk side during sliding. Instead, some boric acid appeared to have been transferred onto the rubbing surfaces of the disks. At higher magnifications, sheet-like crystallites aligned parallel to the sliding interface were visible on the rubbing surfaces (see Fig. 1).

High-magnification electron microscopy of a wear track formed on the surface of a steel disk coated with boric oxide showed large colonies of sheet-like crystallites with preferred alignments parallel to the sliding surfaces (Fig. 2). Electron microscopy of the wear tracks of disks coated and/or implanted with boron failed to reveal sheet-like crystallites similar to those shown in Figs. 1 and 2.

Figure 3 compares the LRS spectrum of a boric acid pin with that of a boric-oxide-coated steel surface. Except for a minor peak at 450 cm^{-1}, the near-surface structure of the boric oxide coating appears to be the same as that of the boric acid pin.

Table 4. The boron 1s and oxygen 1s binding energies for boron and oxygen in various states.

Chemical State	Binding Energy (eV)
B 1s as-implanted	187.1 191.0 193.1
B 1s elemental [12]	187.0
B 1s oxidized (B_2O_3) [12]	193.0
O 1s as-implanted	531.2
O 1s as-implanted	530.5

The XPS data obtained from the boron-implanted steel surface are summarized in Table 4. To minimize a possible interference from surface contaminants, the implanted surface was Ar-ion-sputtered to a depth of about 5. The XPS spectra were then taken to determine the boron 1s and oxygen 1*s* binding energies. The boron 1*s* binding energies for boron in elemental and oxidized (B_2O_3) states were taken from Ref. 12 and included in Table 4 for comparison. According to the XPS data, implanted boron appears to exist in three different forms: elemental, represented by a boron 1*s* binding energy of 187.1 eV; oxidized (possibly boric oxide, B_2O_3), represented by a boron 1*s* binding energy of 193.1 eV; and another form, represented by a boron 1*s* binding energy of 191.0 eV. The peak at 191.0 eV was relatively taller than the other peaks which appeared as shoulders. The unaccounted form may have been due to an iron boride. Binding energies for boron 1*s* core electrons in the elemental and oxidized (B_2O_3) states are reported to be 187.0 and 193.0 eV, respectively (12,13). The oxygen 1*s* binding energies were 530.5 and 531.2 eV in the implanted surface. Although we do not know the binding energy of oxygen 1*s* core electrons in boric oxide (B_2O_3), one of these binding energies may have been representing oxygen in boric oxide.

Figure 1. Scanning electron micrograph showing sheet-like nature of boric acid crystals on the wear scar of a boric acid pin.

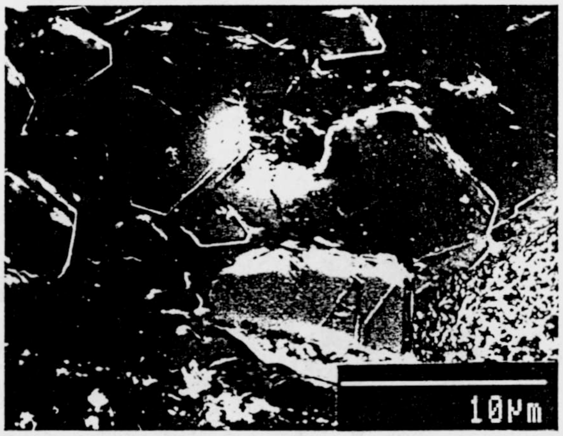

Figure 2. Scanning electron micrograph revealing the presence of sheet-like crystallites on the wear track of a boric-oxide-coated M50 disk.

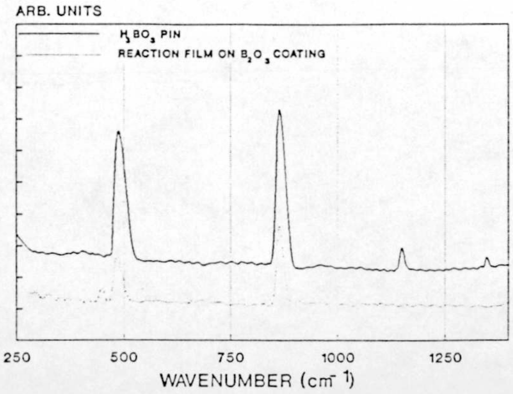

Figure 3. Laser-Raman spectra of surfaces of a boric acid pin and a boric oxide coating on a steel substrate.

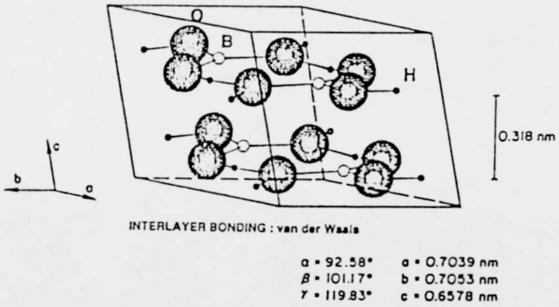

Figure 4. Unit cell and cell parameters of boric acid (H_3BO_3).

DISCUSSION OF RESULTS

Tribological data presented in Table 3 demonstrate that sliding interfaces containing boric acid, boron, and boric oxide are generally capable of attaining low friction. Variations in measured friction coefficients between pairs may be attributed to the fact that friction is primarily the property of a system rather than a material. As shown in Tables 1 and 2, different parameters and elements were used in each tribosystem examined in this study. However, in each case, the measured friction coefficients of systems using boron, boric oxide, and boric acid were significantly lower than those of the uncoated steel surfaces (i.e., 0.04 to 0.12 vs 0.7). To elucidate the mechanism of low-friction behavior of these tribosystems, we present the crystal structure of boric acid in Fig. 4. This is drawn with graphics software and based on the crystallographic data provided in Refs. 14-17. Boric acid has a triclinic crystal structure with sheets of atoms stacked parallel to the basal plane. The atoms lying on each sheet are closely packed. According to Ref. 18, the bonds between the boron and oxygen atoms are mostly covalent but have some ionic character as well. Hydrogen, the third element, links the planar BO_3 groups to each other. As for the atomic sheets themselves, they are widely spaced and held together by weak bonding e.g., by van der

Walls' forces [14,15]. A more detailed description of the crystal chemistry of boric acid and how it relates to the solid lubrication mechanism proposed above is found in Ref.19.

From the foregoing, one can deduce that with its layered crystal structure and highly anisotropic bonds, boric acid is in the same category as those other solids known for their unique lubrication capabilities (e.g., MoS_2, graphite, and HBN). Therefore, we propose that the low friction mechanism of boric-acid-containing and/or -forming surfaces is related primarily to the layered-crystal structure of boric acid. Because of the strong interatomic, but weak interlayer, bonds, the layers shown in Fig. 4 slide over one another with relative ease, thereby reducing friction. In support of this mechanistic interpretation, the micrographs in Figs. 1 and 2 present some physical evidence. Specifically, they reveal that sheet-like crystallites were present at the sliding interfaces of boric acid/52100 and M50/boric-oxide-coated-M50 test pairs. These crystallites may consist of several thousand layers of atoms.

Although other pairs, e.g., M50/boron-coated M50 and M50/boron-implanted M50, lacked evidence of the formation of sheet-like crystallites when inspected by SEM at magnifications up to 50,000X, the XPS spectrum of the boron-implanted surface revealed evidence that some boric oxide had formed on this surface. Therefore, a mechanism based on the formation of lubricious boric acid cannot be ruled out for the low-friction behavior of these surfaces. The proposed chemical reactions leading to the formation of boric acid on surfaces coated with boric oxide and boron, and on those implanted with boron, are:

$1/2B_2O_3$ (coating) + $3/2H_2O$ (moisture) = H_3BO_3 (boric acid) $\Delta H_{298} = -9.1$ kcal/mol.

2B (coated or implanted) + $3/2\ O_2$ (air) = B_2O_3 $\Delta H_{298} = -303$ kcal/mol.
$1/2B_2O_3 + 3/2H_2O$ (moisture) = H_3BO_3 $\Delta H_{298} = -9.1$ kcal/mol.

The XPS data in Table 4 suggest that on surfaces implanted with boron, both the elemental and oxidized (B_2O_3) forms of boron are present. According to the chemical reactions given above, both of these forms can react with oxygen and water molecules in the surrounding environment to form boric acid. Although other mechanisms may have also been involved, we believe that the low friction coefficients measured on the boron-implanted steel surfaces are due largely to the formation of lubricious boric acid at the sliding interfaces. However, more studies are needed for further insight into the mechanism of the low-friction behavior of boron implanted surfaces. A review of the literature indicates that low-friction surfaces have been reported on several steels implanted with boron [20-22]; however, a mechanism based on the formation of lubricious boric acid is not mentioned in those studies.

CONCLUSIONS

(1) Under the test conditions explored in this study, low friction can be attained with sliding interfaces that use boric acid, boric oxide, and boron.

(2) The mechanism of the low-friction behavior of these interfaces has been related to the presence and/or formation of boric acid, which has a layered crystal structure and anisotropic bond characteristics. Under shear stresses at sliding interfaces, the layers appear to align themselves parallel to the direction of sliding motion; once so aligned, they can shear easily, thus lowering friction.

(3) In support of the proposed mechanism, electron microscopy studies revealed large colonies of sheet-like crystallites with alignments parallel to the sliding interfaces between boric acid pins and steel disks and between steel pins and boric-oxide-coated steel disks.

(4) X-ray photoelectron spectroscopy of boron-implanted surfaces suggests that boric acid may also form on these surfaces, with the result that low friction is attained.

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