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TRIBOLOGICAL PROPERTIES OF BORIC ACID AND BORIC-ACID-FORMING SURFACES: PART II: FORMATION AND SELF-LUBRICATION MECHANISMS OF BORIC ACID FILMS ON BORON- AND BORIC-OXIDE-CONTAINING SURFACES

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TRIBOLOGICAL PROPERTIES OF BORIC ACID AND BORIC-ACID-FORMING SURFACES. PART II: FORMATION AND SELF-LUBRICATION MECHANISMS OF BORIC ACID FILMS ON BORON- AND BORIC-OXIDE-CONTAINING SURFACES*

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ABSTRACT

This paper describes the formation and self-lubricating mechanisms of boric acid films on boron- and boric oxide-containing surfaces. As reported in part I, boric acid, owing to a layered triclinic crystal structure and weak interlayer bonds, enjoys an unusual lubrication capability. RF-magnetron sputtering and vacuum evaporation techniques were used to produce thin coatings of boron and boric oxides on steel substrates. The results of tribological experiments indicate that the room temperature friction coefficient of tribosystems that include boron and/or boric oxide coatings ranges from 0.05 to 0.07, depending on the coating type. Laser-Raman spectroscopy of these surfaces revealed that this low friction is associated with a thin boric acid film that forms on the surfaces of these coatings. The fabrication and potential importance of boric acid and boric acid-forming surfaces for practical applications are enumerated. Surface engineering of tribomaterials, such as these demonstrated in this paper, is suggested as a new lubrication concept for use in present and future tribological industries.

INTRODUCTION

Solid lubricants are extensively used in critical applications where liquid lubricants can no longer operate because of the instabilities associated with environmental and mechanical constraints. Two classical examples are solid graphite and MoS_2 lubricants which have been ordinarily applied to the tribological interfaces by means of burnishing, rubbing, spraying, etc. The overall aim of these practices is to create a surface film that minimizes the wear damage and the frictional losses during relative motion (1-4). In general, these solid films have performed very well, except for one drawback: their poor adhesion to the tribological surfaces often limited their functional lifetimes (4-6).

Sputter deposition has later emerged as a more efficient means of producing solid-lubricant films on tribological surfaces (7). In general, it was observed that the sputtered films adhered to tribological surfaces much better than those prepared by the conventional methods (7,8). Furthermore, with the sputtering process, the control of coating morphology and thickness was much easier. As a consequence, the tribological performance of these solid lubricant films was found to be superior to that produced by the other methods (8),(9). Sputter deposition has been and is still used to produce high-performance solid lubricant coatings on critical surfaces of aerospace tribosystems.

With the advent of ion-beam technology, another approach, based on the use of directed ion beams, has recently been introduced into the field of solid lubrication. The general aim is to (1) further improve the adhesion of solid films to the underlying substrates and (2) better control the film microstructure, because in the past, both the adhesion and the microstructural characteristics of solid lubricant films were found to influence their endurance and effectiveness. Tribological data available in the literature suggest that ion-beam-processed solid lubricant films exhibit significantly better friction and wear properties than those produced by other means, including sputtering (10-13).

Apart from the incremental advances that have been achieved in the fabrication of solid lubricant films, very little progress has so far been reported on the development of new solid lubricants. The lubrication needs of both the present and future tribosystems surpass the capabilities of most solid lubricants when used in extreme environments. Therefore, there exists a continuing need for new solid lubricants and new lubrication concepts that can contribute to the present state of the art in solid lubrication. A particularly promising route is solid lubrication by naturally forming reaction films in an open air environment.

This paper introduces a solid lubricant film that can spontaneously form on surfaces including a boron or boric oxide (B_2O_3) coating. The naturally occurring reaction film is boric acid, H_3BO_3, whose crystal chemistry, lubricity, and self-lubrication mechanism were presented in part I. This paper, part II, will focus on the formation and self-lubrication mechanisms of boric acid as a thin film on boron and boric oxide coatings produced on steel substrates. Furthermore, novel lubrication concepts, based on the synthesis of lubricious boric acid films on tribological surfaces, will be suggested.

EXPERIMENTAL DETAILS

Substrate Material

Substrates used in this study were cut from a 5 cm-diameter AISI-M50 steel rod into 6 mm-thick disks. These disks were then subjected to a hardening heat treatment which resulted in a nominal Vickers hardness of about 7.8 GPa. Subsequently, they were surface-finished by means of mechanical grinding and metallographic polishing. The surface roughness of the finished disks was about 0.05 μm center-line-average (CLA). Prior to the deposition of boron and/or boric oxide, they were ultrasonically cleaned sequentially for 10-minute periods in trichloroethylene, acetone, and methanol and dried in an oven at 100°C for 20 minutes.

Deposition of Boric Oxide

Deposition of boric oxide was achieved in a high-vacuum system equipped with an electron-beam-heated evaporator. The steel disks were attached to a holder that was above the evaporation source. Deposition was carried out at room temperature. Typical base pressures in the turbopumped vacuum system were in the low 10^{-5} Pa. The evaporation rate was measured and controlled during deposition with the aid of a quartz-crystal rate monitor. The estimated thickness of the oxide film was 2 μm.

Deposition of Boron

Deposition of boron on the substrate disks was performed in an rf-magnetron sputtering system. The sputter-cleaning and deposition conditions are shown in Table 1. This system incorporates a turn-table which facilitates the manipulation of substrates both prior to and during sputtering. Initially, the boron target was sputter-cleaned in an argon plasma to remove the contaminants that generally build on the surface of a boron target upon venting to atmospheric pressure. To avoid the contamination of substrate disk while sputter-cleaning the boron target, the turn table was rotated by 180°, thus moving the substrates away from the boron target. Subsequently, the deposition condition shown in Table 1 was established and the specimens were brought back underneath the boron target. The sputter deposition of boron on these substrates then started and continued until a 70 nm-thick boron film was obtained. The thickness of the sputtered films was estimated from the calibrated deposition rate of boron (0.075 nm/s.kW).

Friction Tests

Friction tests were performed on a pin-on-disk machine. AISI-M50 steel balls with a diameter of 9.5 mm and a surface finish of 0.03 μm CLA were firmly mounted on a special holder to serve as the stationary pins. The Vickers hardness of these balls was approximately 7.8 GPa. The disks, coated with either boron or boric oxide, were fitted into a chuck driven by a variable-speed motor. The friction force, which was monitored by a linear-voltage displacement transducer, was recorded continuously throughout the tests which were performed at room temperature (about 23°C) and in open air of 50 percent relative humidity. A dead weight of 1 N was chosen for the friction tests and was applied onto the pins during unidirectional sliding. The sliding velocity was 0.1 m/s.

To ascertain the morphological and chemical characteristics of the surface films and the wear tracks, a scanning electron microscope and a laser-Raman spectroscope were utilized. To minimize electronic charging of the insulating coatings during electron microscopic studies, a 10-nm thick carbon film was sputtered onto the surfaces.

RESULTS AND DISCUSSION

Boric Oxide Coatings

The friction coefficient of a steel pin sliding on a steel disk coated with boric oxide is shown in Figure 1. The initial value of the friction coefficient of this pair is about 0.065, which decreases monotonically with distance and reaches a steady-state value of 0.05. For this low friction coefficient, we propose the following mechanistic interpretation derived from the electron microscopic observations and the Raman spectroscopic data.
Electron microscopic inspection of the wear tracks of the disks revealed that there exist large colonies of plate-like crystallites aligned parallel to the contact surface (see Figure 2). We believe that the low friction coefficient of this tribosystem was a direct consequence of the formation, and the structural and rheological characteristics of these crystallites. The principal questions are then: (1) what are these crystallites ?, (2) how do they form ?, and (3) how do they provide low friction ?.

To answer the first question, we employed a laser-Raman spectroscope to determine the chemical nature of near-surface regionns of the crystallites. The surface reaction film was too thin to be analyzed by standard X-ray diffraction. We obtained a Raman spectrum of the near-surface region of a boric-oxide-coated steel disk and compared it with that of a boric acid standard. These spectra are shown in Figures 3a and b. It is clear from these

Figures that except for a possible minor peak with a wavenumber of 450, the near-surface chemistry of the boric oxide coating is identical to that of the boric acid standard.

In answer to the second question, owing to a negative standard heat of reaction, (see Figure 4), boric oxide reacts spontaneously with the water molecules available in an open environment at room temperature. As illustrated in Figure 4, the reaction product is a thin boric acid film on a boric oxide coating.

The third question can be satisfied by referring to the fundamental knowledge provided in part I of this study. Boric acid possesses a layered triclinic crystal structure. The atoms lying on planar layers are bound to each other by strong covalent/ionic and hydrogen bonds, whereas, the layers themselves are 0.318 nm apart and held together only by weak van der Waals forces. Under shear stresses, these layers apparently can align themselves parallel to the direction of relative motion and, and once so aligned, can slide over one another with relative ease, thus providing low friction as seen in Figure 1. In support of this mechanistic interpretation, the electron micrographs in Figure 2 show some evidence that some crystallites were indeed aligned parallel to the sliding surface.

Boron Coatings

The friction coefficient of a steel pin sliding against a boron-coated steel disk is shown in Figure 5. The steady-state friction coefficient is about 0.07. This value is somewhat higher than that reported for the boric oxide coating. However, it is fairly low and the mechanistic interpretation of this low friction is given below.

It is hypothesized that, upon exposure to an open environment at room temperature, boron reacts with oxygen, thus forming a thin boric oxide film on the exposed surface. Boric oxide concomitantly reacts with the water molecules within the same surrounding, thus partially transforming into a boric acid film. The model system and the sequence of chemical reactions are depicted in Figure 6. As described in part I and again in the foregoing, the boric acid film, owing to a layered crystal structure and unique bond characteristics, is lubricious and the tribosystems that incorporate boric acid either as a bulk (see part I) or as a thin surface film (see Figures 1 and 5) will enjoy low friction.

Electron microscopic efforts failed to produce micrographs showing the details of the plate-like crystallites. It is presumed that the average size of these crystallites forming on a boron film that is only 70 nm thick, was perhaps very small. Hence, they were hard to resolve with the electron microscope employed in our study.

New Lubrication Concepts

We believe that lubricious boric acid films can also be successfully synthesized on surfaces that have been (1) implanted with boron, (2) ion-beam mixed with layers of boron and/or boric oxides, and (3) coated with boron sub-oxides. Surface engineering of tribomaterials such as those exemplified in this study, as well as those cited above, suggests novel concepts for use in present and future tribosystems. The following are conceptual ideas for synthesizing lubricious boric acid films.

(1) Ion-beam processing of tribological surfaces by ion-implantation is a well-established practice. We hypothesize that solid-lubricant boric acid can be synthesized on tribological surfaces that have been implanted with boron, with the result that low friction is attained while sliding. A survey of the literature on the subject revealed a number of studies which reported low friction and low-wear for a variety of alloy-steels implanted with boron (14,15). However, a mechanism based on the formation of a lubricious boric acid film has been lacking in these studies.

(2) Ion-beam mixing of boron and/or boric oxide layers with other ceramic and metal surfaces can achieve an intermixed region near the surface. This intermixed layer can gradually transform into boric oxide and/or boric acid, thus providing these surfaces with low friction.

(3) Some sub-oxides of boron have been reported to possess hardness values that are comparable to that of natural diamond (16). We believe that lubricious boric acid films can be synthesized on top of these super-hard oxides. Owing to a very hard underlying film

and an easily sheared surface film, the resultant composite system can afford an ultra-low friction coefficient and an ultra-low wear rate during sliding contact.

CONCLUDING REMARKS

Thin films of boric oxide and boron were vacuum-evaporated and sputter-deposited respectively on steel surfaces. Electron microscopic and laser-Raman spectroscopic studies were performed to ascertain the structural and chemical nature of the surface films that formed in open air at room temperature. It was found that boric acid forms on boric oxide coatings and possibly on boron coatings too, provided that these coatings are exposed to a natural environment. Friction tests on these boric acid-forming surfaces demonstrated that these surfaces can attain quite low friction coefficients in sliding contacts. Because of the distinctive nature of both the self-formation and lubrication mechanisms of boric acid on surfaces containing boron and/or boric oxide, a series of new lubrication concepts were suggested for tribological applications.

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Table 1. Sputter-deposition conditions for boron on steel disks.

A) Sputter Cleaning of Boron Target

rf-Bias voltage = 1600 V

Sputtering time = 900 s

Chamber pressure = 0.58 Pa

Argon flow rate = 1.16 cm^3/s

B) Sputter Deposition of Boron

rf-Bias voltage on the target = 1700 V

Bias voltage on the substrates = 0

Chamber pressure = 0.195 Pa

Argon flow rate = 0.4 cm$_3$/s

Sputtering rate of boron = 0.0755 nm/s.kW

FIGURE CAPTIONS:

Fig.1. The friction coefficient of a steel pin/boric oxide-coated steel disk test pair as a function of sliding distance.

Figure 2. Electron micrographs taken from the wear tracks of a steel disk coated with boric oxide showing the size, morphology, shape and orientation of plate-like boric acid crystallites.

Figure 3. Laser-Raman spectrum of (a) a boric acid standard and (b) a boric oxide coating. This shows that the surface of boric oxide was covered with a boric acid film.

Figure 4. A schematic representation of the formation of boric acid on top of the boric oxide coating.

Figure 5. The friction coefficient of a steel pin/boron-coated steel disk test pair as a function of sliding distance.

Figure 6. A schematic representation of the formation of boric oxide and boric acid on the sputtered-boron coating.

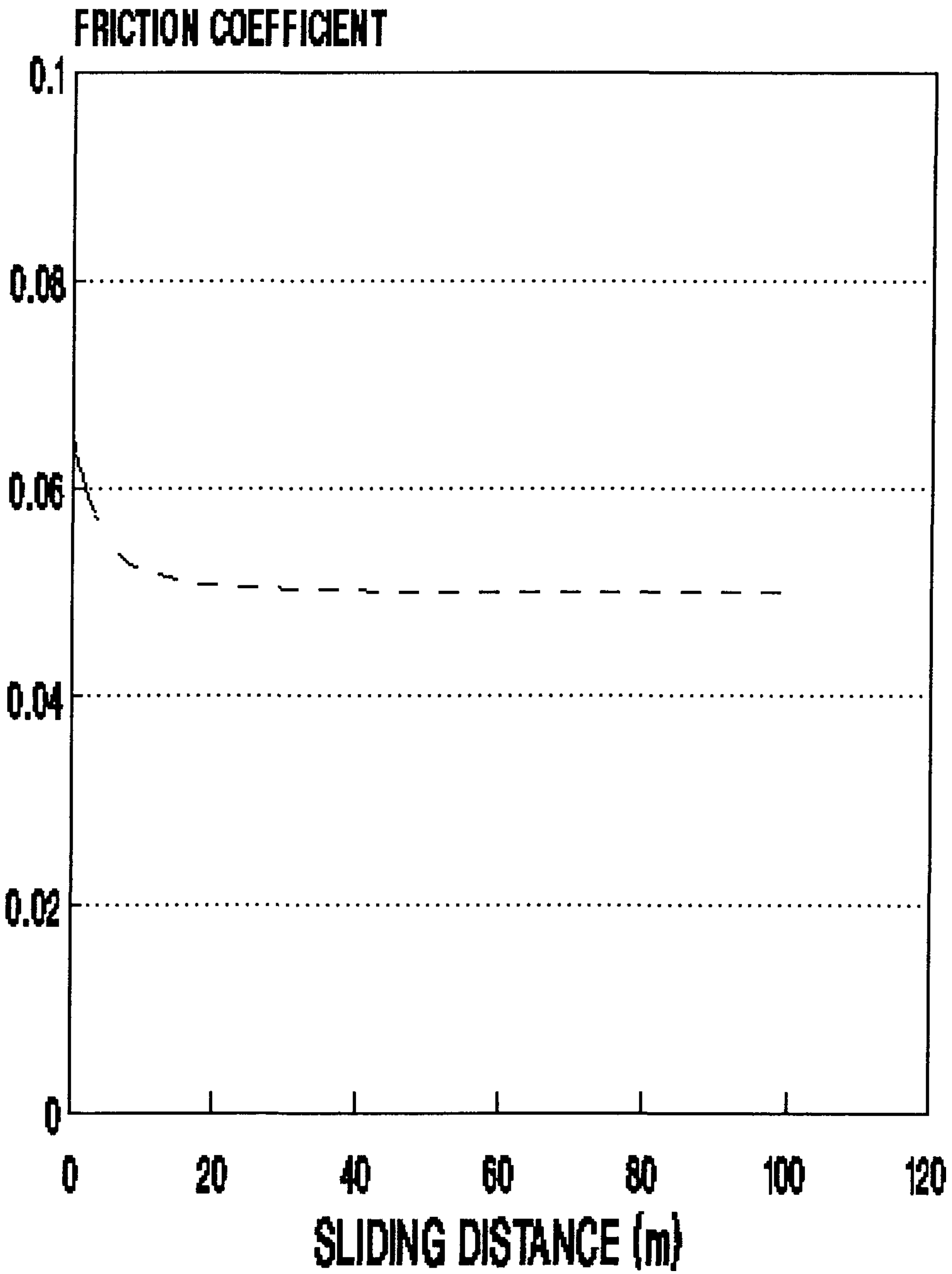

FRICTION COEFFICIENT
0.1
0.08
0.06
0.04
0.02
0
0
20
40
60
80
100
120
SLIDING DISTANCE (m)

Fig.1

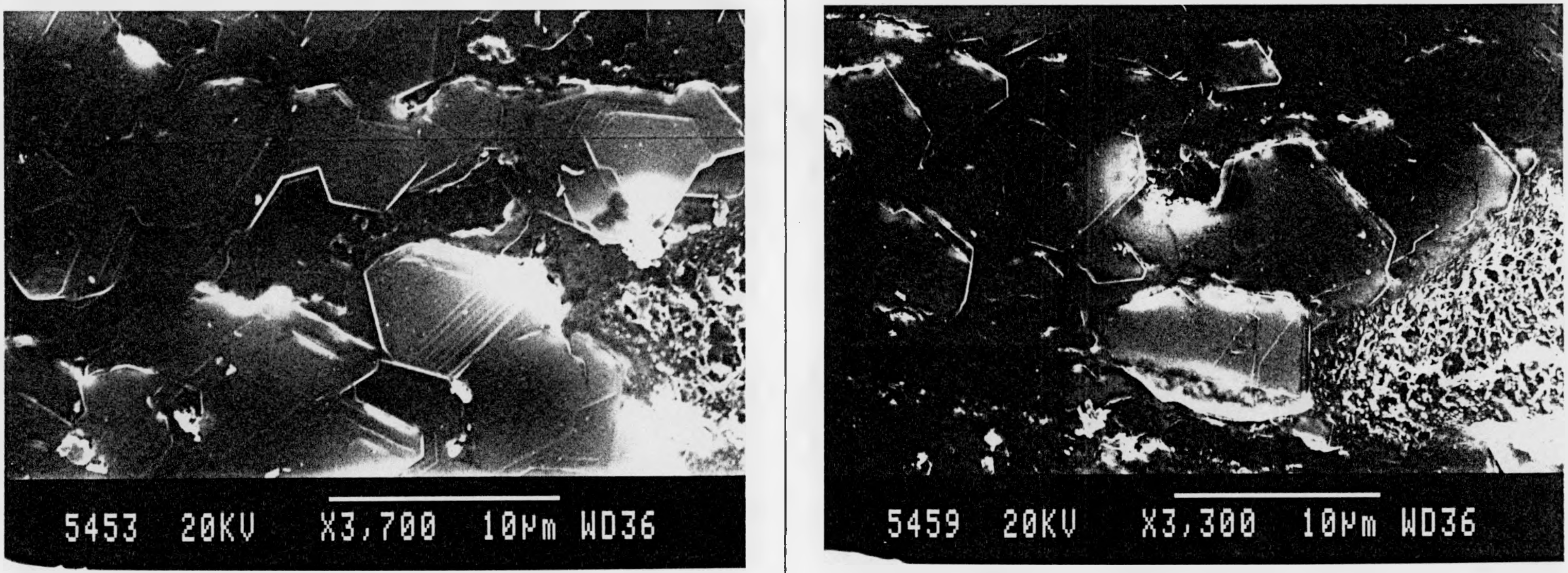


Fig. 2

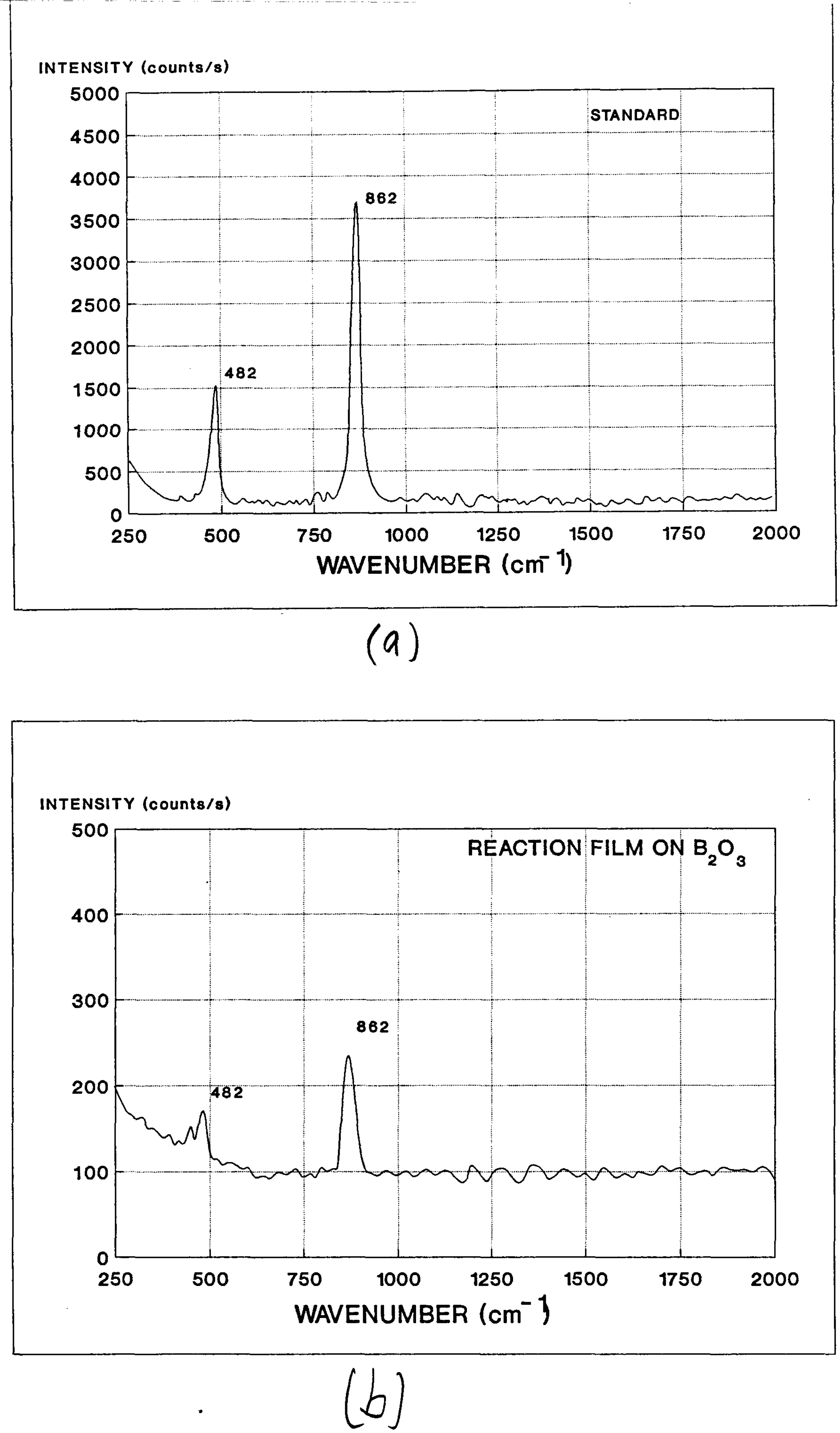
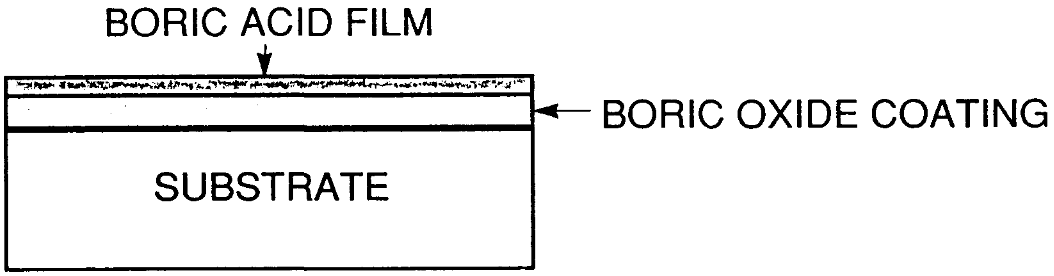
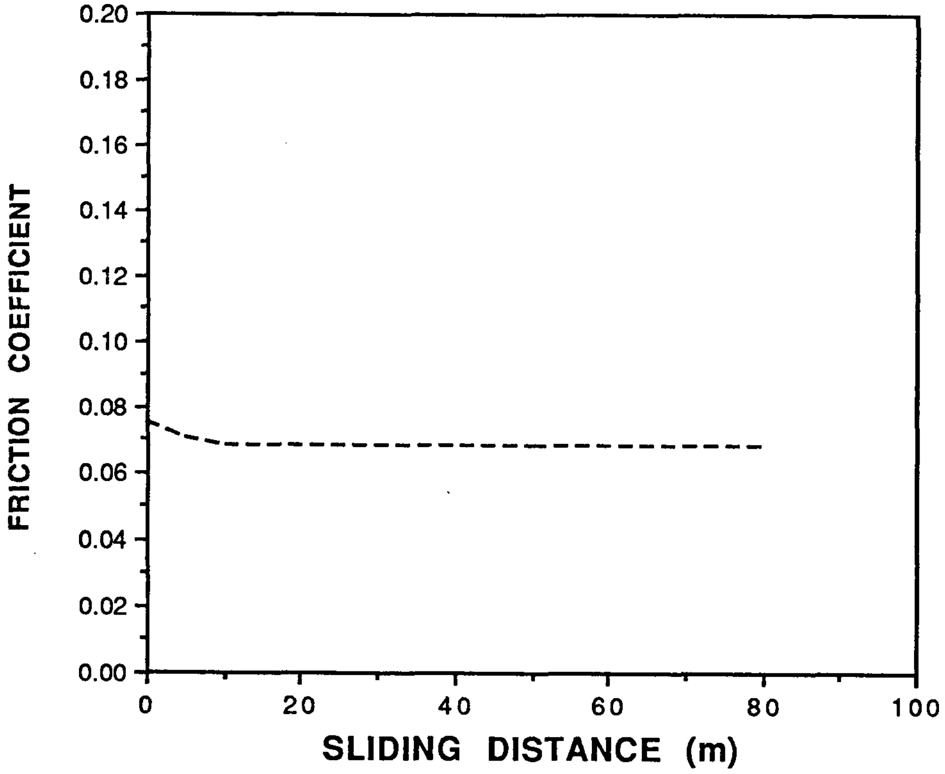

INTENSITY (counts/s)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
STANDARD
862
482
250
500
750
1000
1250
1500
1750
2000
WAVENUMBER (cm^{-1})
(a)
INTENSITY (counts/s)
500
400
300
200
100
0
REACTION FILM ON B_2O_3
862
482
250
500
750
1000
1250
1500
1750
2000
WAVENUMBER (cm^{-1})
(b)

Fig. 2



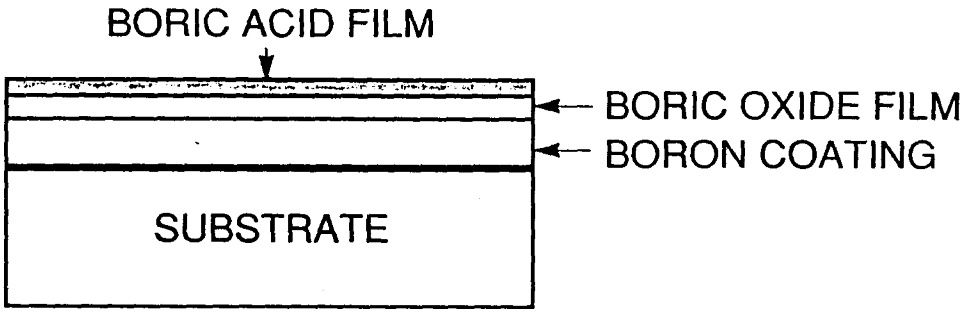
$$1/2\ B_2O_3 + 3/2\ H_2O \longrightarrow H_3BO_3 \qquad \Delta H_{298} = -9.1\ \text{kcal/mol.}$$

Fig. 4



FRICTION COEFFICIENT
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
20
40
60
80
100
SLIDING DISTANCE (m)

Fig. 5



$$2\,B + 3/2\,O_2 \longrightarrow B_2O_3 \qquad \Delta H_{298} = -303\ \text{kcal/mol.}$$

$$1/2\,B_2O_3 + 3/2\,H_2O \longrightarrow H_3BO_3 \qquad \Delta H_{298} = -9.1\ \text{kcal/mol.}$$

Fig. 6