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TRIBOLOGICAL PROPERTIES OF BORIC ACID AND BORIC-ACID-FORMING SURFACES: PART I: CRYSTAL CHEMISTRY AND SELF-LUBRICATING MECHANISM OF BORIC ACID

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TRIBOLOGICAL PROPERTIES OF BORIC ACID AND BORIC ACID FORMING SURFACES. PART I: CRYSTAL CHEMISTRY AND SELF-LUBRICATING MECHANISM OF BORIC ACID

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ABSTRACT

An in-depth understanding of the atomic-scale structure and chemistry of self-lubricating solids and how they relate to the efficiency and endurance of large-scale tribosystems is critically important. Of particular interest is the utilization of this understanding for the development of mechanistic models that can increase our ability to assess and predict the capabilities of self-lubricating solids. Accordingly, a comprehensive investigation was made of the crystal chemistry and self-lubrication mechanisms of boric acid and boric acid-forming surfaces. In this paper, the fundamentals of the crystal chemistry and the proposed lubrication mechanism of boric acid are described. Pin-on-disk tests performed on cold-pressed boric-acid pins and AISI 52100 steel disks, showed that the friction coefficient of this tribosystem is approximately 0.1. The results of this investigation indicate that boric acid, owing to its unique crystal structure and bond characteristics, is a promising solid lubricant for a wide range of tribological applications.

INTRODUCTION

Certain inorganic solids, owing to a layered crystal structure and weak interlayer bonds, enjoy unusual lubrication capabilities (1-3). Well-known examples are MoS_2, graphite and hexagonal BN. The crystal structures of these solids are such that while the atoms lying on the same layer are closely packed and strongly bonded to each other, the layers themselves are relatively far apart and are bonded only by weak forces, such as van der Waals (1,4,5). When present between sliding interfaces, these layers can align themselves parallel to the direction of relative motion and slide over one another with relative ease, thus providing low friction. In addition, strong interatomic bonding and packing in each layer is thought to help in reducing the wear damage (2).

Many studies indicate that the ambient surroundings can profoundly affect the lubricity of most inorganic solids. For example, graphite was found to lubricate better in a humid environment than in a dry environment (6), whereas, MoS_2 was found to lubricate better in dry and vacuum environments (5),(7). This type of contrasting behavior of self-lubricating solids has been and still is the subject of numerous studies. So far, it has been suggested that the enhanced lubricity of graphite in a humid environment may be related to the weakening effect that water molecules have on the residual π-bonds that exist between the layers of graphite crystal (4,6). As for the poor lubricity of MoS_2, it was suggested that water molecules either directly or indirectly react with MoS_2, thus altering the interatomic array and bonding which in turn increase the friction (4,5).

The lubrication needs of both the present tribosystems and those being designed for future uses are steadily increasing. Therefore, new solid lubricants and lubrication concepts are needed. In accordance with these needs, this paper introduces boric acid (H_3BO_3) as a new solid lubricant and describes the fundamentals of the crystal chemistry and a proposed lubrication mechanism for boric acid. Although a few studies have existed in the previous literature, its lubricity, self-lubrication mechanism and potential importance for tribological applications appear to be relatively unexplored. A paper by Johnson and Sliney was concerned with the effect of ambient temperature on frictional behavior of a boric acid-containing tribosystem (8). They reported a friction coefficient of 0.23 for this system at a temperature range from room to 93°C. A sharp increase was noted by these investigators beyond 93°C and was attributed to the decomposition of boric acid into boric oxide and water molecules. A few other studies were focused on the frictional behavior of vitreous boric oxide at temperatures beyond its softening point of 450°C (9,10). The principal goal of all these studies was to establish model relationships between the rheological and frictional behavior of boric acid and/or oxide as a function of temperature.

CRYSTAL CHEMISTRY OF BORIC ACID

A survey of the crystallography literature has revealed that boric acid exists in two major crystalline forms: metaboric acid, $H_2O.B_2O_3$ or HBO_2, and orthoboric acid, $3H_2O.B_2O_3$ or H_3BO_3 (11-13). Furthermore, metaboric acid has been reported to crystallize in three different forms. These are: orthorhombic or α-metaboric acid (11), monoclinic or ß-metaboric acid (11), and cubic or Γ-metaboric acid (12). Among these, orthorhombic metaboric acid exhibits a layered crystal structure (11). It is hence possible that this substance may possess some self-lubrication capabilities, but this paper will primarily focus on the most common form of boric acid; orthoboric acid. It exists as a natural deposit known as sassolite in mineralogy books (13). For the sake of simplicity and less confusion, the name "boric acid" will be adopted and used in this paper to embody those less-known names e.g., orthoboric acid and sassolite.

Early studies dealing with the crystal structure of boric acid are due to Zachariasen (14), Cowley (15), and Craven et al. (16) who used x-ray, electron, and neutron diffraction methods respectively. Recently, Gajhede et al. used a low-temperature x-ray diffraction technique to reexamine the crystal structure and to study the electronic charge distribution in boric acid (17). Except for minor variations in measured atomic positions, they all concur that the unit cell of boric acid is triclinic and made up of boron, oxygen and hydrogen which are arrayed in layers parallel to the basal plane of the triclinic crystal. The cell parameters of the triclinic crystal structure of boric acid are depicted in Table 1 (13).

Table 1. Cell parameters of the triclinic crystal structure of boric acid.

$a=0.7039$ nm $\alpha=92.58^\circ$
$b=0.7053$ nm $\beta=101.17^\circ$
$c=0.6578$ nm $\Gamma=119.83^\circ$

The volume of the unit cell is 0.263 nm^3 which accommodates 4 boric acid molecules. Figure 1 illustrates the layered-crystal structure of boric acid. Figure 2 shows the planar configuration of boron, oxygen and hydrogen in one of the layers of the unit cell. The types of bonds holding these species together are also indicated. It is interesting to note that each boron cation is surrounded by three oxygen anions to form triangular BO_3 groups. Owing to electronegativity values of 2 for boron and 3.5 for oxygen, the bonding between them has been described as mostly covalent with some ionic character (18). The distance between boron cations and oxygen anions is 0.136 nm and the oxygen anions are 0.236 nm apart from each other. These planar BO_3 groups are linked to each other by hydrogen bonds. The distance between the oxygen anions of neighboring BO_3 groups is 0.272 nm. It is interesting to note from Figure 2 that hydrogen protons that bridge two oxygen anions are not centered. Each position shown is one of a pair of positions between which the proton resonates.

Due to the triclinic crystal structure, the c axis is inclined to the basal plane at an angle of 101° (see Figure 1). This inclination causes shifting of alternate layers along the c axis. The layers are 0.318 nm apart and are held together by weak van der Waals forces.

LUBRICITY AND PROPOSED LUBRICATION MECHANISM OF BORIC ACID

As described above, boric acid possesses a layered crystal structure and unique bond characteristics similar to those of graphite and MoS_2. Therefore, it is hypothesized that boric acid should also possess self-lubrication capabilities. To demonstrate the validity of this hypothesis, a series of friction tests were performed with solid compacts of boric acid on a pin-on-disk machine. Cylindrical rods with a nominal diameter of 1.27 cm were compacted from boric acid powders (99.8 weight percent H_3BO_3) by means of cold-pressing under a pressure of about 35 MPa. The rod-shaped compacts had a hemispherical cap of 5 cm radius at one of the ends, so that a point contact could be established during friction tests. Subsequently, the boric acid pin was attached to the pin holder of a pin-on-disk machine and rubbed against a 50 cm-diameter AISI 52100 steel disk. The friction test parameters are shown in Table 2. The Vickers hardness of the steel disk was about 7.8 GPa and it had a surface finish of approximately 0.1 μm center-line-average (CLA).

Table 2. Friction test parameters

Load = 5 N
Sliding velocity = 0.1 m/s
Relative humidity = 50 percent
Sliding distance = 100 m
Ambient temperature = 23°C

The friction coefficient of the pin/disk pair described above was measured as a function of sliding distance, and is presented in Figure 3. Under the test conditions given in Table I, the initial value of the friction coefficient of this tribosystem is approximately 0.2, and then decreases steadily with distance and eventually reaches a steady-state value of 0.1 after sliding for about 20 m. This simple test demonstrates that boric acid indeed has some self-lubrication capabilities.

In an effort to better understand the self-lubrication mechanism of boric acid, electron microscopic studies were performed on both the free-standing particles and the friction-tested compacts of boric acid. An electron micrograph of a free-standing boric acid particle in Figure 4 shows the plate-like nature of boric acid. It is interesting to note that these crystallites are stacked-up parallel to each other. This observation is in keeping with the layered crystal structure of boric acid. The micrographs in Figure 5 were taken from the sliding surface of a boric acid compact. They further reveal that the region near the contacting surface is made-up of plate-like crystallites with a preferred alignment parallel to the sliding surface.

Based on the results of the friction tests, and the electron microscopic evidence, it can be concluded that boric acid, owing to its layered crystal structure and unique bond characteristics, is a self-lubricating solid. As for the mechanism, it has been proposed that under shear stresses, plate-like crystallites consisting of several thousands of atomic layers (see Figure 4) align themselves parallel to the direction of relative motion (see Figure 5), slide over one another with relative ease and give a low steady-state friction coefficient (see Figure 3). The initially high friction coefficient of the tribosystem in Figure 3 can be attributed to the random orientation of crystalline layers as observed during electron microscopic inspection. It is thought that randomly oriented crystallites would be more difficult to shear, thus generating relatively high frictional forces at the outset of the sliding test.

SUMMARY

The crystal chemistry and a proposed self-lubrication mechanism of boric acid were described. It was shown that the crystal structure of this solid is triclinic. Boron, oxygen and hydrogen are arrayed to form extensive layers parallel to the basal plane of triclinic crystal. While the bonding between the species lying on the same plane is covalent/ionic and hydrogen-bond type, the layers are 0.318 nm apart and held together only by weak van der Waals forces. Owing to unique combination of bonds and a layered crystal structure it was hypothesized that boric acid is a self-lubricating solid. It was experimentally demonstrated that a tribosytem made up of a boric acid pin and a steel disk could attain a steady-state friction coefficient of 0.1 during unidirectional sliding. Electron micrographs revealed that an undisturbed boric acid particle was made up of plate-like crystallites. After friction test, an electron microscopic inspection of the sliding pin-surfaces further revealed the layered nature of boric acid. Both the tribological data and the electron microscopic evidence were supportive of the hypothesis. It was concluded that boric acid, owing to an easily sheared, layered crystal structure, is a lubricious solid.

ACKNOWLEDGEMENT

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REFERENCES

1. Clauss, F. J. Solid Lubricants and Self-lubricating Solids, Academic Press, New York (1972), pp 15-41.

2. Kanakia, M. D. and Petterson, M. B., Literature Review of the Solid Lubrication Mechanisms, Southwest Research Institute, Interim Report, BFLRF # 213, San Antonio, TX, (1987), pp 6-18.

3. Farr, L. P. G., "Molybdenum Disulphite in Lubrication. A Review," Wear, 35, pp 1-22 (1975).

4. Jamison, W. E., "Structure and Bonding Effects on the Lubrication Properties of Crystalline Solids," ASLE Trans., 15, pp 296-305 (1972).

5. Winer, W. O., "Molybdenum Disulfide as a Lubricant: A Review of the Fundamental Knowledge," Wear, 10, pp 422-452 (1967).

6. Rowe, G. W., "Some Observations on the Frictional Behavior of Boron Nitride and of Graphite," Wear, 3, pp 274-285 (1960).

7. Pritchard, F., and Midgley, J. W., "The Effect of Humidity on the Friction and Life of Unbounded Molybdenum Disulfide Films," Wear, 13, pp 39-50 (1969).

8. Johnson, R. L. and Sliney, H. E., "Ceramic Surface Films for Lubrication at Temperatures to 2000°F," Ceramic Bull., 41, pp 504-408 (1962).

9. Peterson, M. B., Murray, S. L, and Florek, J. J., "Consideration of Lubricants for Temperatures Above 1000°F," ASLE Trans., 2, pp 225-234 (1960).

10. Rabinowicz, E. and Imai, M., "Boric Oxides as a High Temperature Lubricant," ASME Paper No. 61-LUBS-17

11. Zachariasen, W. H., "The Crystal Structure of Monoclinic Metaboric Acid," Acta Cryst., 16, pp 385-389 (1961).

12. Zachariasen, W. H., "The Crystal Structure of Cubic Metaboric Acid," Acta Cryst., 16, pp 380-384 (1963).

13. Palache, C., Berman, H., and Frondel, C., The System of Mineralogy, John Wiley and Sons, Inc., New York (1958), pp 662-663.

14. Zachariasen, W. H., "The Precise Structure of Orthoboric Acid," Acta Cryst., 7, pp 305-310 (1954).

15. Cowley, J. M., "Structure Analysis of Single Crystals by Electron Diffraction. II: Disordered Boric Acid Structure," Acta

Cryst., 6, pp 522-529 (1953).

16. Carven, B. M., and Sabine, T. M., "A Neutron Diffraction Study of Orthoboric Acid $D_3{}^{11}BO_3$," Acta Cryst., 20, pp 214-219 (1966).

17. Gajhede, M., Larsen, S., and Rettrup, S., "Electron Density of Orthoboric Acid Determined by X-ray Diffraction at 105 K and ab-initio Calculations," Acta Cryst., B42, pp 545-552 (1986).

18. Cooper, W. F., Larsen, F. K., Coppens, P., and Giese, R. F., "Electron Population Analyses of Accurate Diffraction Data. V. Structure and One-center Charge Refinement of the Light Atom Mineral, Kernite," Am. Mineral., 58, pp 21-31 (1973).

FIGURE CAPTIONS:

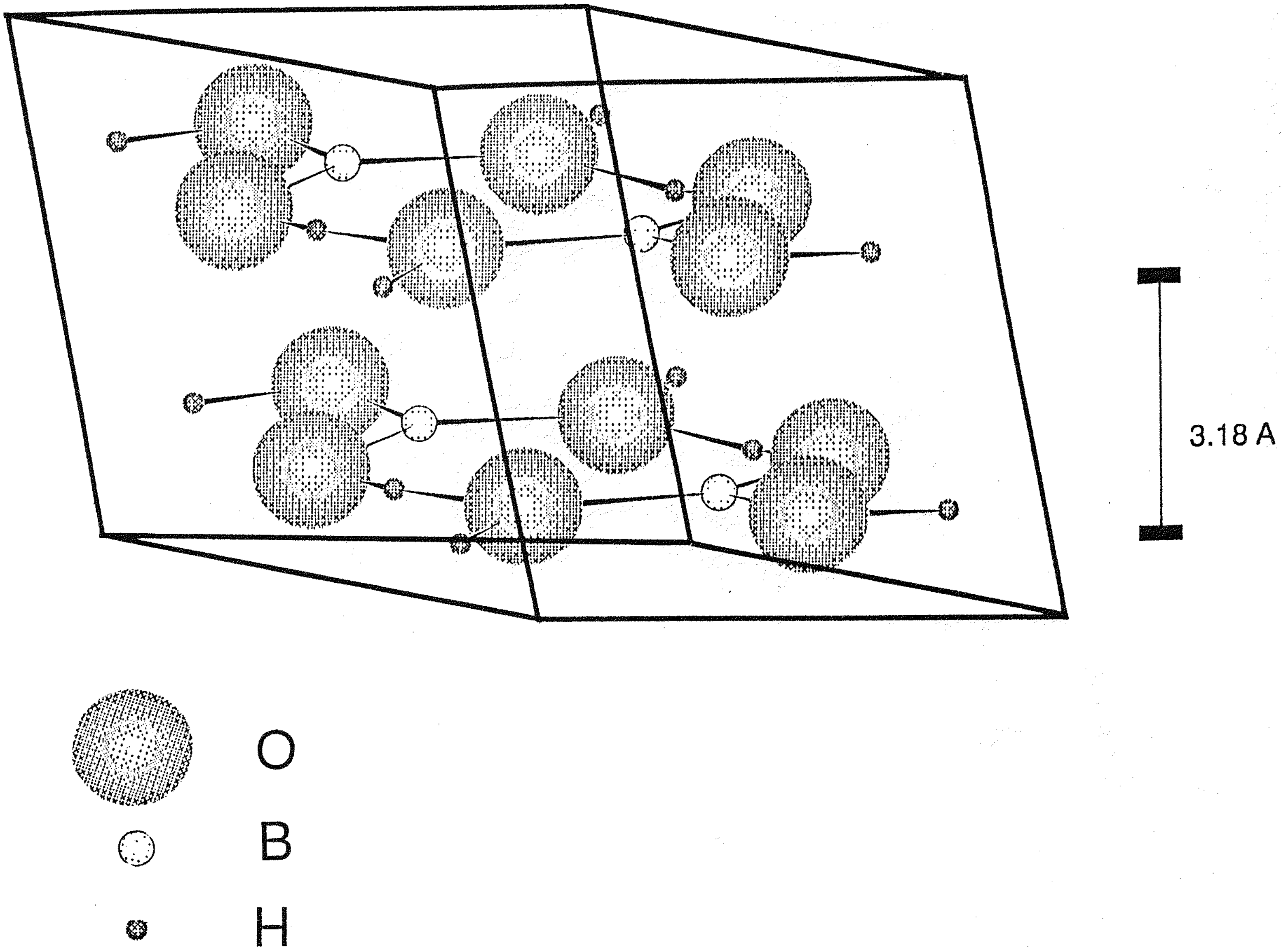
Fig. 1. A schematic representation of the layered-triclinic crystal structure of boric acid.

Fig.2. A schematic representation of interatomic array and bonding in a layer consisting of two boric acid molecules.

Fig. 3. Variation of the friction coefficient of a boric acid pin/steel disk test pair as a function of sliding distance.

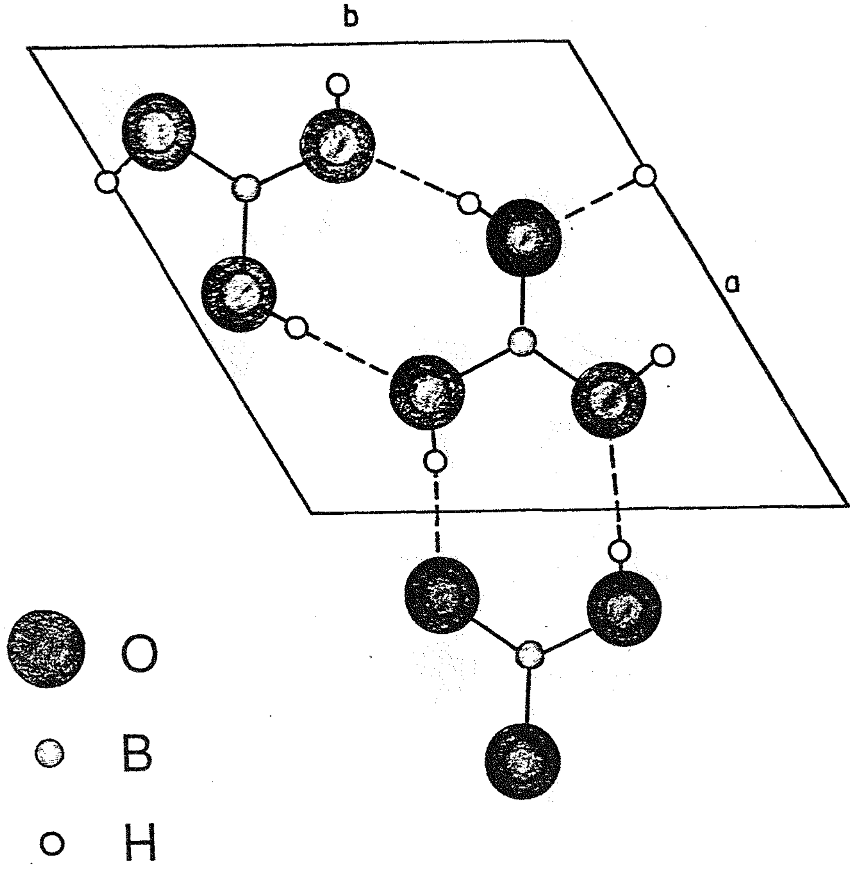
Fig. 4. An electron micrograph of a free-standing boric acid particle showing the plate-like crystallites aligned parallel to each other.

Fig. 5. Electron micrographs taken from the wear scars of boric acid pins showing some evidence of inter-crystalline slip that may have occurred during sliding contact.



INTERLAYER BONDING : van der Waals

Fig. 1



BONDING

B-O: COVALENT/IONIC
O-O: HYDROGEN

Fig. 2

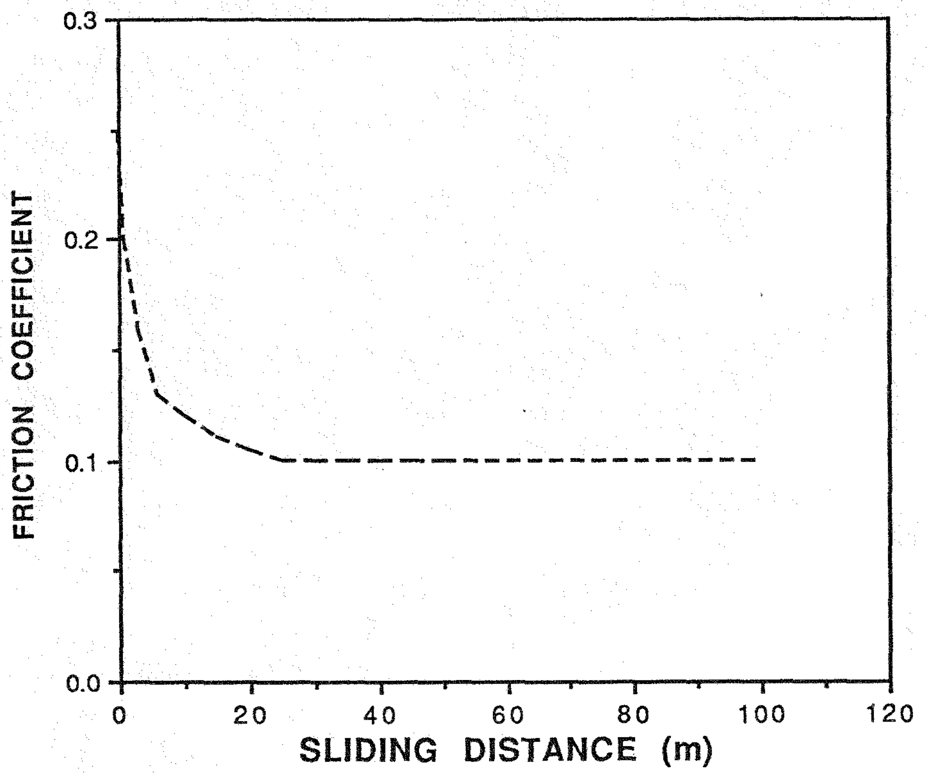
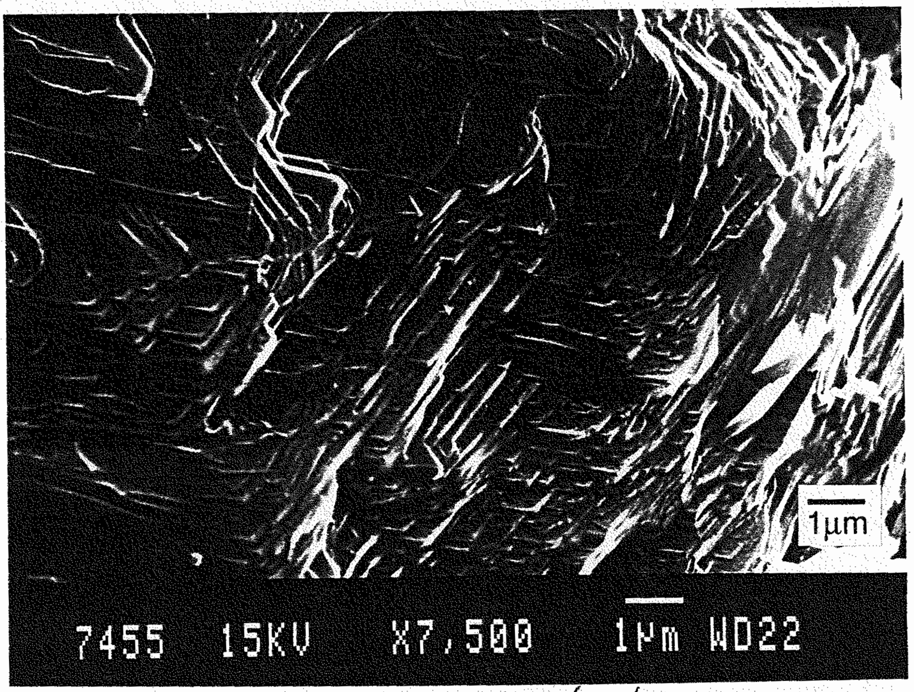

0.3
0.2
0.1
0.0
FRICTION COEFFICIENT
0
20
40
60
80
100
120
SLIDING DISTANCE (m)

Fig. 3



H_3BO_3 Standard

Fig. 4

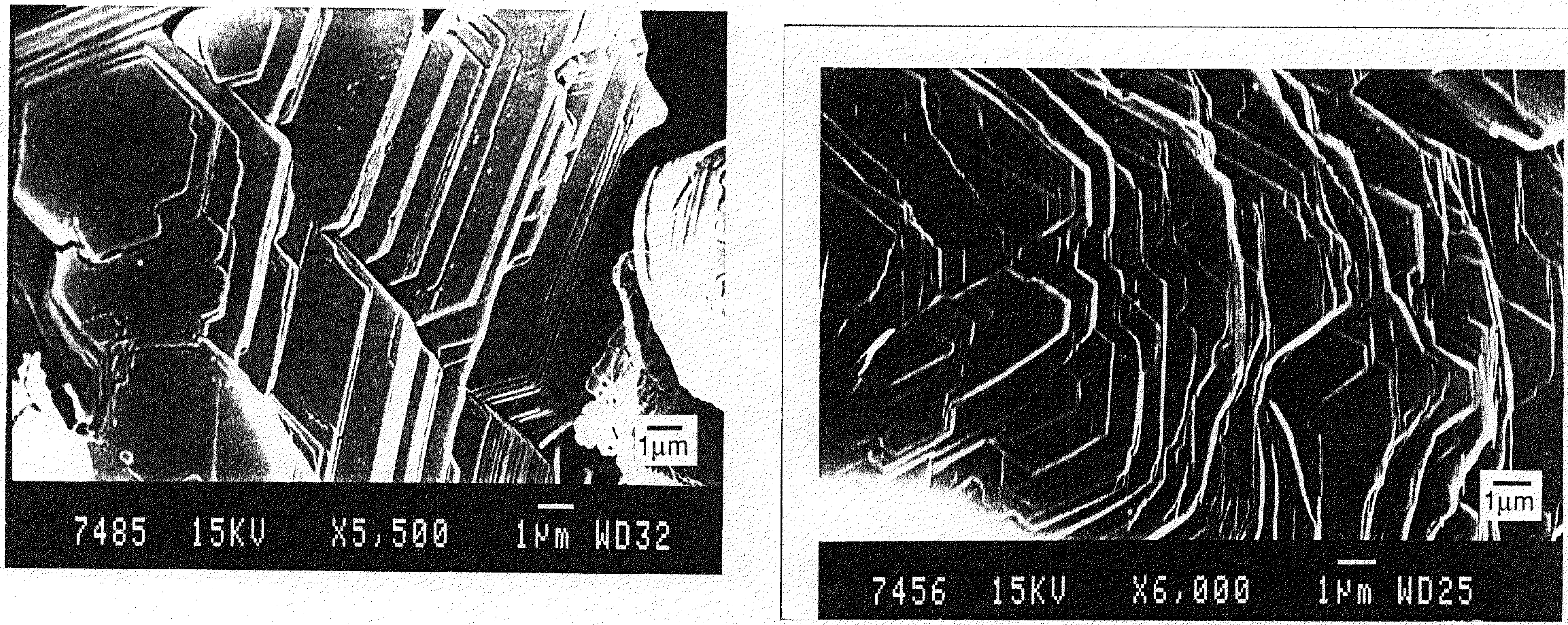


Fig. 5