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A Study of the Formation and Self-Lubrication Mechanisms of Boric Acid Films on Boric Oxide Coatings

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A STUDY OF THE FORMATION AND SELF-LUBRICATION MECHANISMS OF BORIC ACID FILMS ON BORIC OXIDE COATINGS

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ABSTRACT

An investigation was made of the formation and self-lubrication mechanisms of boric acid films on boric oxide coatings prepared by vacuum evaporation. Measured friction coefficients of a steel ball sliding on a boric-oxide-coated-steel disk and a sapphire ball sliding on a boric-oxide-coated-alumina disk were 0.025 to 0.05 at steady state, depending on load and substrate material. This low friction was correlated with the formation of a lubricious boric acid film on boric oxide coatings exposed to open air. For the mechanism of self-lubrication, the layered-triclinic-crystal structure of boric acid was proposed. The atoms constituting each boric acid molecule are arrayed in closely packed and strongly bonded layers that are 0.318 nm apart and held together by weak forces, such as van der Waals. It is hypothesized that during sliding, these layers can align themselves parallel to the direction of relative motion, and once so aligned, can slide over one another with relative ease to provide low friction. Structural and chemical findings were included to substantiate the proposed solid lubrication mechanism.

INTRODUCTION

Solid lubricants continue as prominent choices for triboapplications involving high vacuum and temperatures where liquid counterparts can not operate efficiently. Molybdenum disulfide (MoS_2), because of its ultralow friction coefficient in vacuum and inert gas environments, has been of particular importance for spacecraft mechanisms [1-3]. With the use of advanced sputtering and ion-beam technologies, great strides have been made in both the application and use of this lubricant where precision control of mechanical motion is of utmost concern [3,4]. Recent experimental studies indicate that sputtered and/or ion-beam-deposited MoS_2 coatings can achieve friction coefficients as low as 0.01 and functional lifetimes of hundreds of thousands of cycles [1,4,5]. A major drawback of MoS_2 is its inability to provide low friction where moisture is present [6,7].

This paper describes a new solid lubricant that can result from chemical reaction between moisture in open air and boric oxide (B_2O_3) coatings on steel and ceramic substrates. The lubricious film is boric acid (H_3BO_3). Based on thermodynamic data and crystal-chemical knowledge, the self-formation and -lubrication mechanisms of boric acid films are elucidated.

Both boric oxide and its hydrated form, boric acid, attracted some attention in past years mainly for lubrication at high temperatures. Peterson et al. observed that at temperatures above the glass-transition point of vitreous boric oxide (e.g., about 450°C), viscosity decreases sharply [8], and dramatic reductions in friction coefficients occur in tribosystems lubricated with boric oxide [8,9]. For example, Johnson and Sliney measured a friction coefficient of 0.14 at 732°C for a sliding interface using a boric oxide coating [9]. Despite these high-temperature studies, it appears that neither the lubricity nor the lubrication mechanism of boric oxide and/or boric acid have been reported in the literature. This study provides tribological data that illustrate the unusual lubrication capacity of boric oxide coatings in normal air environments and proposes a crystal-chemical model that describes the lubrication mechanism of this solid. Effects of load and substrate material on friction are also explored.

EXPERIMENTAL DETAILS

Substrate Materials

Two types of materials were chosen as the substrates for boric oxide coatings; hardened AISI-M50 tool steel and polycrystalline α-alumina. These disk-shaped substrates were 50 mm in diameter and 6 mm thick, and both had surface finishes of approximately 0.05 μm center-line-average (CLA). Base Vickers hardness values were approximately 7.8 for the M50 and 16 GPa for the alumina. Before deposition of boric oxide, the substrates were cleaned ultrasonically in acetone and methanol for 300 s each and then oven-dried at 110°C for 10 min.

Deposition of Boric Oxide

Boric oxide was deposited on the steel and alumina disks in a high-vacuum system equipped with an electron-beam-heated evaporator. The disks were attached to a sample holder above the evaporation source. They were sputter cleaned before deposition of B_2O_3 with a flux of Ar ions emitted from a Kaufman-type ion gun operated at 300 V. Deposition was carried out at room temperature and at a chamber pressure of 5×10^{-4} Pa. A quartz-crystal rate monitor was used to control and estimate the evaporation rate. Coatings evaluated in this study were approximately 2 μm thick.

Friction Tests

Friction tests were performed with pairs of M50 ball/B_2O_3-coated M50 disk and sapphire ball/B_2O_3-coated alumina disk in a pin-on-disk tribometer. For comparison, a few pairs were tested without the B_2O_3 coatings under a load of 5 N. The M50 balls were 9.5 mm in diameter and had a surface finish of approximately 0.03 μm CLA. The sapphire balls were 6.3 mm in diameter and had a surface finish of about 0.005 CLA. These balls were firmly secured to a stationary holder for the ball-on-disk configuration. Disks were attached to a horizontal chuck driven by a variable-speed electric motor. Frictional force was monitored by a linear-voltage displacement transducer attached to the ball holder and was recorded continuously. All tests were performed at room temperature (about 23°C) in open air of 60 ± 5% relative humidity. Dead weights of 1, 5, and 10 N were used during tribotests. Tests were conducted at a constant rotational speed of 10 rev. min^{-1}. Depending on wear track diameter, sliding velocity ranged from 0.05 to 0.15 m.s^{-1}.

Scanning electron microscopy (SEM) and laser-Raman spectroscopy were used for morphological and structural characterization of films and of the sliding surfaces. To overcome charging of insulating coating and substrate materials, a

5-nm-thick gold/palladium film was sputter-deposited onto the surface to be examined by SEM.

RESULTS

The boric oxide coatings deposited on the steel and alumina disks were colorless and transparent immediately after deposition. With time, however, the coatings became dull and took on a color similar to that of mother-of-pearl.

Friction Measurements

M50/M50 Pairs. Figure 1 shows friction coefficients of M50 test pairs, with and without boric oxide coatings, as a function of sliding cycles. The friction coefficient of the M50/M50 pair without boric oxide coating is initially about 0.4, but increases with distance and stabilizes at a value of 0.77. In contrast, the initial friction coefficients of pairs with a boric oxide film are in the range of 0.08 to 0.11, depending on load (Fig. 1). With further sliding, these values decrease sharply and stabilize at 0.04 to 0.06. The lowest steady-state friction coefficient, 0.04, was measured on pairs tested at 5 N. For the 1-N load, the initial and steady-state friction coefficients were 0.11 and 0.5, respectively. With a 10-N load, the friction coefficient was initially low, e.g., 0.08. However, during sliding it decreased to about 0.036 and then began to increase sharply with further sliding (e.g., beyond 100 revolutions). Visual inspection of the wear track revealed that the boric oxide coating was removed from the surface and that wear had occurred on steel.

Sapphire/Alumina Pairs. Figure 2 shows friction coefficients of sapphire/alumina test pairs with and without boric oxide coatings. The friction coefficient of the sapphire/alumina pair is initially about 0.25, increases during successive revolutions and stabilizes at about 0.4. The friction coefficients of pairs with a boric oxide coating vary widely with applied load. For a load of 1 N, the initial friction coefficient is about 0.08. At steady state, the friction coefficient becomes 0.045. For a 5-N load, the friction coefficient is initially about 0.055, but decreases rapidly to about 0.027 and then remains relatively unchanged. With a load of 10 N, the initial friction coefficient is approximately 0.05, but decreases to about 0.025 at steady state.

Under the test conditions explored in this study, it was noted that regardless of test loads and substrate material, the records of frictional force (as recorded on chart paper) were smooth (i.e., fluctuations from the mean were in the ±1% range).

Structural and Chemical Analyses

Electron microscopy inspection of the disk surfaces revealed that shallow wear tracks had formed during sliding of balls against the boric-oxide-coated disks and that some coating material had transferred onto the rubbing surfaces of the balls. Wear of balls that were slid against the boric oxide coatings was practically unmeasurable except for those in the 10-N test. A circular wear scar was seen on balls slid against uncoated disks.

Electron microscopy of wear tracks formed on the boric-oxide-coated-steel and alumina disks revealed some plate-like crystallites exhibiting a preferred alignment parallel to the sliding direction (see Figure 3). Noticeable in this micrograph are microfeatures suggesting the occurrence of intercrystalline slip possibly due to frictional traction. Plate-like crystallites were also seen in areas away from the rubbing surfaces (see Figure 4), but these crystallites appeared to have random orientations.

Micro-laser-Raman spectroscopy of boric oxide coatings showed very strong Raman lines at approximately 482 and 862 cm^{-1}. Using the same instrument, another spectrum was obtained from a boric acid standard. Except for a minor peak at 450 cm^{-1}, the near-surface structure of the boric oxide coating was found to be identical to that of the boric acid standard within the range surveyed in this study (i.e. 250 to 1000 cm^{-1}). The values reported here are somewhat lower than those (e.g., 500 and 881 cm^{-1}) reported for bulk boric acid (H_3BO_3) in Ref. 10. The discrepancy (e.g., about 20 cm^{-1}) between measurements may have been due to calibration errors in the instrument used in our study.

DISCUSSION

The results demonstrate that (1) in general, low friction can be achieved on surfaces coated with boric-oxide and (2) friction coefficient can vary with substrate type, applied load, and sliding distance. For the low-friction behavior of boric oxide coatings, we propose the following interpretation: Because of a negative standard heat of reaction, boric oxide reacts spontaneously with moisture in open air and becomes boric acid (H_3BO_3). This reaction was given in Ref. 11 as

$$1/2\ B_2O_3 + 3/2\ H_2O \longrightarrow H_3BO_3$$

$$\Delta H_{298} = -45.1\ \mathrm{kJ.mol^{-1}}.$$

We believe that the rapid change in the appearance of boric oxide coatings after exposure to open air was a consequence of the chemical reaction given above. The reaction film, boric acid, was largely responsible for the change from a transparent to semitransparent nature in this coating. Structural data obtained through micro-laser-Raman spectroscopy confirmed the formation of boric acid on boric oxide coatings by revealing Raman lines that are similar to those of bulk boric acid.

What is the mechanism of the low-friction character of boric acid film formed on boric oxide coatings?. It is known that boric acid crystallizes in a triclinic crystal structure made up of atomic layers parallel to the basal plane [12,13]. The atoms lying on each layer (e.g., boron, oxygen, and hydrogen) are closely packed and strongly bonded to each other. The bonds between the boron and oxygen atoms are described as mostly covalent with some ionic character, and hydrogen serves to connect the planar boron-oxygen groups to each other. The atomic layers are widely spaced and held together by weak forces e.g., van der Waals [13]. A depiction of the unit cell of boric acid is shown in Figure 5, based on data given in Refs. 12 and 13. With its layered-crystal structure, boric acid resembles those other solids known for their good lubrication capabilities (e.g., MoS_2, graphite, and hexagonal-boron-nitride). Therefore, we believe that the low friction measured on the boric-oxide-coated steel and alumina disks was a direct consequence of the formation of lubricious boric acid films.

Mechanistically, we propose that under shear stresses, plate-like crystallites (Figure 3) (possibly consisting of several thousand atomic layers) can align themselves parallel to the direction of relative motion; once so aligned, they can slide over one another with relative ease and thus impart low friction. The relatively high friction coefficients observed at the start of the friction tests are attributed to the initially random orientation of crystalline layers (see Figure 4). It is thought that randomly oriented crystallites shear with greater difficulty and thus give a relatively high friction coefficient. Figure 3 presents some physical evidence that plate-like crystallites were present at the sliding interfaces and that some intercrystallite slip had occurred.

As shown in Figures 1 and 2, the measured friction coefficient varies with substrate and applied load. This variation between materials can be attributed to the fact that frictional force was lower for sapphire/alumina than for M50/M50. Frictional force (F) is essentially a product of the shear strength (s) of a solid lubricant film multiplied by the real contact area (A) due to elastic and plastic deformation, i.e., $F = s \times A$ [14]. In our friction tests, we used sapphire balls of 3.1-mm radius against the boric-oxide-coated alumina disks, but M50 balls of 4.7-mm radius against the boric-oxide-coated M50 disks. It is obvious that because of the smaller ball radius and greater hardness and elastic modulus, the real contact area between the sapphire ball and the boric-oxide-coated-alumina disk will be smaller than that between the M50 ball and the boric-oxide-coated-M50 disk. According to the expression given above, in the presence of a solid lubricant film, a smaller contact area results in a lower frictional force and/or lower friction. For a more thorough understanding of the phenomenon briefly described above, readers should refer to the original concept developed by Bowden and Tabor [14] and to a paper by Roberts [4].

For the explanation of lower friction coefficients under heavier loads, we refer to a plastic flow model introduced by Kanakia and Peterson [15]. According to this model, under low pressures the real contact area (A) is controlled largely by film properties, whereas under high pressures it is controlled largely by mechanical properties of the substrate. Under a 1-N load, we believe that contact area was largely determined by the flow properties of boric acid/boric oxide composite layer. Hence, measured friction coefficients were dominated by film properties. Under a low load of 1 N, the steady-state friction coefficients of the steel/steel and ceramic/ceramic test pairs using boric acid films are 0.05 and 0.045, respectively which suggests that perhaps the plastic flow model is in effect. However, under heavier loads, of 5 and 10 N, the measured friction coefficients decrease regardless of substrate material. This trend can be ascribed to the greater effect of substrate properties on the extent of contact areas established between balls and coated disks. The somewhat lower friction coefficients measured on ceramic/ceramic pairs may have been due in part to the smaller radius of the sapphire balls used in these tests. However, contributions due to the higher hardness and elastic modulus of the ceramic/ceramic test pairs are also thought to have substantial effects on the friction levels measured for these pairs. Using a dual fast atom beam technique, Kuwano and Nagai recently produced thin MoS_2 coatings on surfaces with different hardness values [5]. They noted that friction coefficients measured on hard surfaces were significantly lower than those measured on softer ones.

As for the short lifetime of boric oxide coatings on M50 but long lifetime on alumina substrates during sliding under a 10-N load, we believe that chemical compatibility was the dominant factor. Low adhesion is generally observed on coatings deposited by vacuum evaporation processes. However, such an argument cannot be made for this study, because we prepared all the boric oxide coatings under the same conditions. Both substrates were sputter-cleaned prior to the deposition of B_2O_3. We believe that another influence -- the chemical compatibility -- was more prevalent in our study. Boric oxide, which is an oxide ceramic, may have had poor chemical compatibility with the metallic M50 steel but good compatibility with the alumina, which is also an oxide ceramic.

CONCLUSIONS

Under the test conditions of this study, low friction can be achieved on metallic and ceramic surfaces through the use of boric oxide coatings. Low friction is a direct consequence of the spontaneous formation of a boric acid film on boric oxide coatings exposed to open air.

Friction coefficient decreases with increasing load and distance, and varies with substrate type.

Mechanistically, it is proposed that the low friction of boric acid is due to its layered-triclinic-crystal structure and unique bond characteristics. Under shear stresses, the layers can align themselves parallel to the direction of sliding motion; once so aligned, they can slide one over another, thus providing low friction.

Electron microscopy studies revealed plate-like crystallites with alignment parallel to the sliding surface; some microfeatures suggest that intercrystallite slip had occurred between the plate-like crystallites while sliding.

Unlike MoS_2, which provides low friction in nonhumid environments, boric acid is formed in a humid environment and, as demonstrated in this study, can provide low friction in such environments.

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FIGURE CAPTIONS

Figure 1. Friction coefficients of M50/M50 pairs with and without boric oxide coatings under loads of 1, 5, and 10 N as a function of sliding cycles.

Figure 2. Friction coefficients of sapphire/alumina test pairs with and without boric oxide coatings under loads of 1, 5, and 10 N as a function of sliding cycles.

Figure 3. SEM micrograph of the plate-like crystallites found on a wear track of boric-oxide-coated steel disk.

Figure 4. SEM micrograph of the plate-like crystallites found in areas away from wear tracks.

Figure 5. Depiction of unit cell and cell parameters of bulk boric acid.

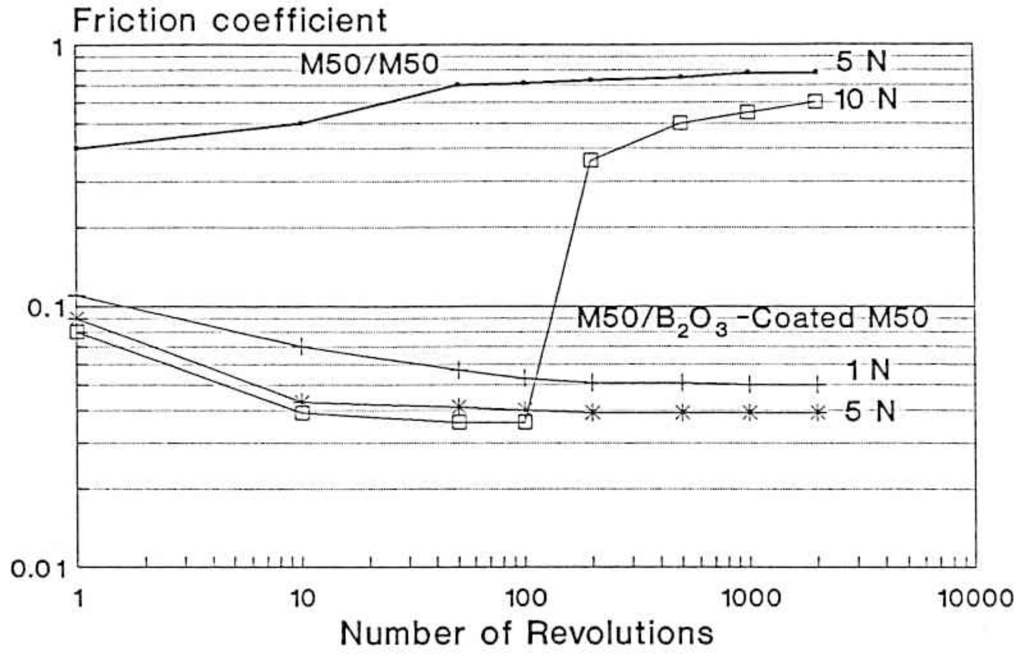

Friction coefficient
1
0.1
0.01
M50/M50
5 N
10 N
M50/B_2O_3-Coated M50
1 N
5 N
1
10
100
1000
10000
Number of Revolutions

Fig. 1

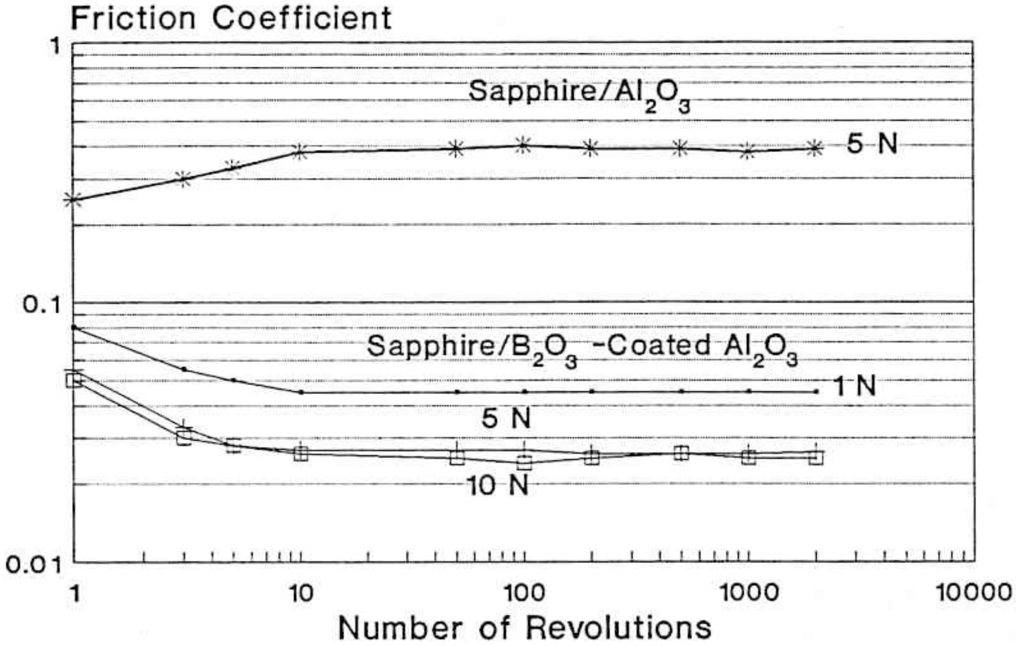

Friction Coefficient
1
0.1
0.01
Sapphire/Al_2O_3
5 N
Sapphire/B_2O_3 -Coated Al_2O_3
1 N
5 N
10 N
1
10
100
1000
10000
Number of Revolutions

Fig. 2

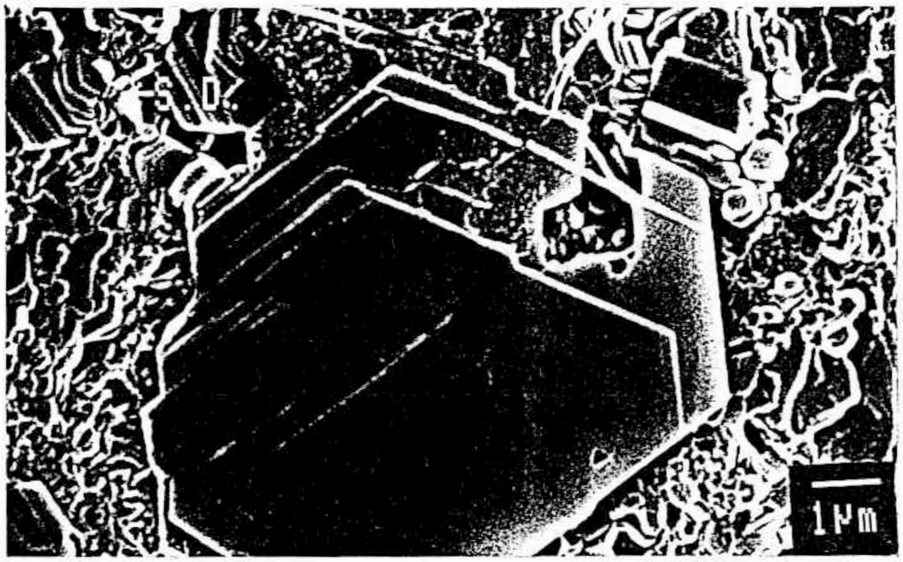


Fig. 3

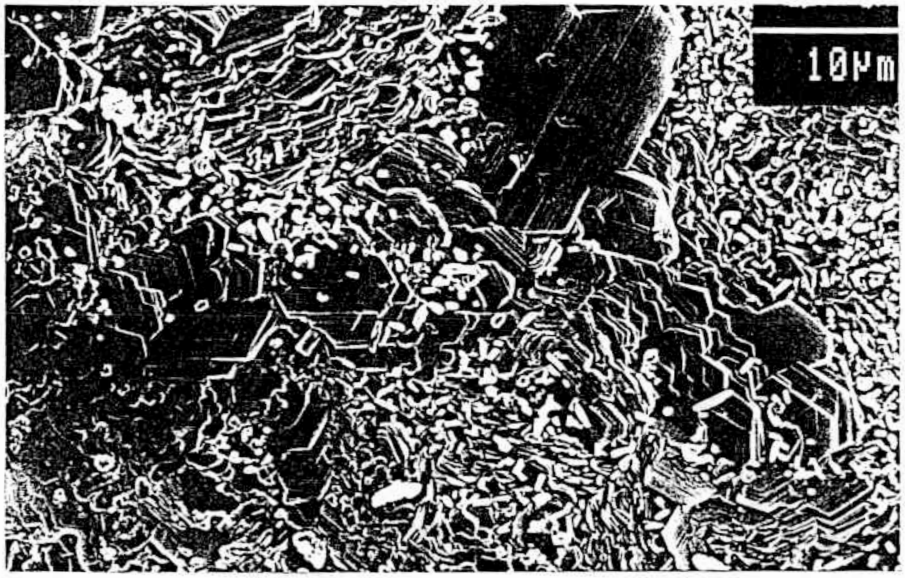
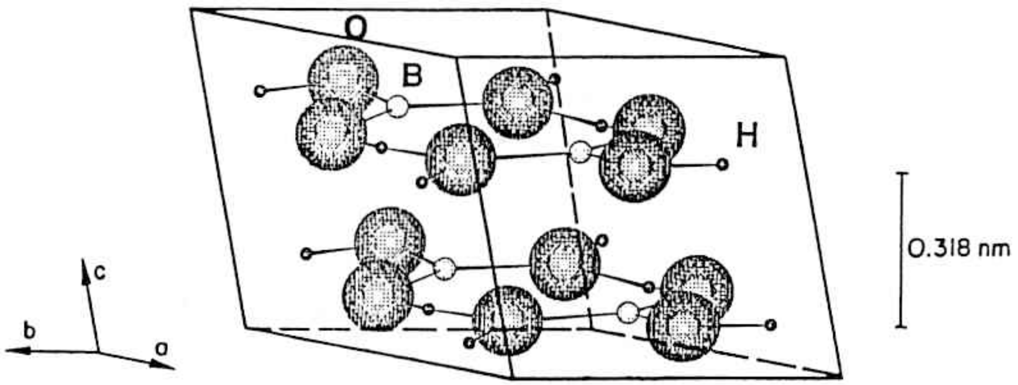


Fig.4



INTERLAYER BONDING : van der Waals

$\alpha = 92.58°$ $a = 0.7039$ nm
$\beta = 101.17°$ $b = 0.7053$ nm
$\gamma = 119.83°$ $c = 0.6578$ nm

Fig. 5