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PREPARATION OF ULTRALOW FRICTION SURFACE FILMS ON VANADIUM DIBORIDE*

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ABSTRACT

In this paper, we present a simple annealing procedure (which we refer to as "flash-annealing" because of short duration) that results in the formation of an ultralow friction surface film on vanadium diboride (VB_2) surfaces. This annealing is done in a box furnace at 800°C for a period of 5 min. During annealing, the exposed surface of the VB_2 undergoes oxidation and forms a layer of boron oxide (B_2O_3). In open air, the B_2O_3 layer reacts spontaneously with moisture and forms a boric acid (H_3BO_3) film. The friction coefficient of a 440C steel pin against this H_3BO_3 film is $\approx$0.05, compared to 0.8 against the as-received VB_2. Based on Raman spectroscopy and electron microscopy studies, we elucidate the ultralow friction mechanism of the flash-annealed VB_2 surfaces.

INTRODUCTION

Many transition metal diborides, i.e., TiB_2, ZrB_2, VB_2, etc. possess exceptional hardness, high elastic modulus, and excellent thermal and electrical conductivity [1,2]. Chemically, most of them are very inert and provide excellent protection against oxidation at elevated temperatures. Some borides (e.g., TiB_2 and ZrB_2) are metallic conductors [2]. Owing to a high elastic modulus and good chemical stability at elevated temperatures, TiB_2 fibers and particulates are used extensively in the production of reinforced ceramic composites [3]. In short, because of their unique thermal, mechanical, electrical, and chemical properties, borides are expected to find increased usage in a variety of industrial applications.

In past years, coatings of transition metal diborides (e.g., TiB_2, ZrB_2 etc.) have been produced by reactive sputtering and chemical vapor deposition on a variety of metalforming dies and machine parts to combat wear [4,5]. Despite their excellent chemical stability and high wear resistance over a wide range of temperatures, most borides cannot afford low friction to dry sliding surfaces. In this paper, we introduce a very simple annealing procedure that results in the formation of a low friction film on the surface of vanadium debarred (VB_2). In a series of studies, Bindal and Erdemir [6], and Erdemir et al. [7] used a similar annealing procedure to achieve ultralow friction surface films on borided steels and boron carbide. The annealing procedure of this study results in the formation of a lubricious surface film providing friction coefficients as low as 0.05. The goal of this paper is to elucidate the formation and ultralow friction mechanisms of this surface film on VB_2 surfaces.

EXPERIMENTAL DETAILS

The VB_2 material used in our experiments was in the form of a 200 µm thick coating attached to a copper plate by means of explosion bonding. In order to achieve strong adhesion between VB_2 and copper plate, a layer (50 µm thick) of pure vanadium was first applied onto copper plate again by explosion bonding. The test pieces for tribotesting were in the shape of squares with nominal dimensions of 40 X 40 mm and 6 mm. The surface finish of the test pieces was in the range of 0.2 to 0.3 µm center-line-average (CLA). The annealing of the test pieces was performed in a box furnace at 800°C for 5 min. Specifically, the VB_2 test pieces were placed on a ceramic plate and inserted into the box furnace at 800°C. After 5 min exposure time, they were taken out of the furnace and cooled to room temperature in open air.

Friction and wear tests were performed in a tribometer with ball-on-disk type contact geometry under a load of 5 N and at room temperature (about 23°C). The relative humidity of the test chamber varied between 38 and 84%. Rotational velocity was 6 to 8 rev. min^{-1} which translated into a sliding velocity of 5.3 $mm.s^{-1}$. The counterface materials were made of 440C steel pins (9.5 mm in diameter). One end of each pin was rounded to a radius of curvature of 127 mm and used as the contact surface. It was polished to a surface finish of 0.01 µm CLA roughness. The sliding distance was 275 m (or 5000 cycles). Before each sliding test and annealing heat - treatment, the ceramic pins and flats were cleaned ultrasonically in acetone and methanol for 300 s each and then oven-dried at 110°C for 10 min. Laser-Raman spectroscopy was used to characterize the structure and chemical nature of the sliding surfaces. The Raman spectroscope used an HeNe laser at 632.8

nm with an output power of 25 mW focused to a spot size of 2 to 3 μm. Duplicate tests were run with flash-annealed VB_2 surfaces to check the reproducibility of test results.

RESULTS AND DISCUSSION

Figure 1 shows the variation of friction coefficients of 440C steel pins during sliding against an as-received and flash-annealed VB_2 sample. The friction coefficient of steel pin is initially 0.15 against VB_2, but increases rapidly as sliding continues and reaches a value of 0.8 toward the end of the test. The initially low friction coefficient may have been due to the presence of some surface adsorbates and/or a thin chemical film. As the adsorbed film is removed or worn through, the friction coefficient increases and the frictional trace becomes very unsteady, possibly because of increased metal-to-VB_2 contact and greater stick-slip. In short, the test result confirms that VB_2 is not a low friction material and cannot provide lubrication under dry sliding conditions. The wear rate of steel pin used against the as-received VB_2 was 1.7×10^{-4} $mm^3.N^{-1}.m^{-1}$.

The initial friction coefficient of a 440C steel pin sliding against the flash-annealed VB_2 surface is 0.1, but decreases to 0.05 after about 8000 s and remains constant for the rest of the test. This result confirms that the simple annealing procedure used in our study produces a slippery film on the sliding contact surface of VB_2. Also, the frictional behavior of this test pair is very steady and does not show much fluctuation. The wear rate of 440C pin used against the flash-annealed VB_2 is 3.5×10^{-6} $mm^3.N^{-1}.m^{-1}$. This is nearly 50 times lower than that of the pin slid against the as-received VB_2.

In an attempt to elucidate the structural chemistry as well as the fundamental mechanisms of the low friction films on annealed VB_2 surfaces, we used a Raman spectroscope equipped with an HeNe laser operating at 632.8 nm with an output power of 25 mW focused to a spot size of 2 to 3 μm. The Raman spectrum of the flash-annealed VB_2 surface revealed two strong Raman bands centered at approximately 498 and 880 cm^{-1} (see Fig. 2a). We found that these values were very close to those (i.e., 500 and 881 cm^{-1}) of the bulk boric acid (H_3BO_3) reported in Refs. 8 and 9. Furthermore, in previous studies, we have verified that films forming on B_2O_3 has a similar H_3BO_3 structure [5,6].

In order to better make sure and further verify that the surface reaction film was indeed H_3BO_3, we obtained Raman spectrum of a piece of standard boric acid and have included its spectrum in Fig. 2b for comparison. As is clear, the principal Raman bands of this spectrum match perfectly with those from on the surface of the annealed VB_2. Note that the Raman spectrum of as-received VB_2 is very different from those of the boric acid standard and annealed VB_2 sample. In short, the low friction behavior of annealed VB_2 surface (see Fig. 1) must have been closely related to the formation of a thin boric acid film on the exposed surface.

Based on some thermodynamics and kinetics considerations, we can provide some explanation for the formation of lubricious H_3BO_3 film on VB_2 surface. We believe that during exposure to 800°C, the boron atoms within VB_2 structure gain high mobility and activation energies for diffusion. Those boron atoms reaching the surface can readily react with oxygen in open air to form B_2O_3 (e.g., layer 1 in Fig. 3). The standard heat of reaction for B_2O_3 formation at 800°C is -290.6

kcal/mol [10], hence the formation of B_2O_3 is thermodynamically favorable at 800°C. As indicated in Ref. 10, V can also readily oxidizes at 800°C, and the range of vanadium oxides includes V_2O_3 and V_2O_5. The standard heats of reaction for V_2O_3 formation is -291.5 kcal/mol and for V_2O_5 formation is -362.3 kcal/mol [10]. During our annealing experiments, we noticed that if we held the VB_2 sample in the furnace for more than 5 min, we would see the formation of some liquidlike islands on the surface. We believe that these islands were primarily composed of vanadium oxides. V_2O_5 melts at 670°C [10].

It is our opinion that B_2O_3 layer forming at 800°C during short duration results from the oxidation of interstitially accommodated boron atoms within the VB_2 structure. The oxidation of VB_2 is also possible at high temperatures (especially when exposure time and/or temperature is higher than 5 min or 800°C) but as a very stable compound, it will be rather difficult to extract free boron atoms from the highly stable VB_2. Obviously, the thermodynamics and kinetics of the physical/chemical events taking place at 800°C are rather complex and require more in-depth studies, but in general the short-duration annealing procedure adopted in our study seems to result in B_2O_3 formation.

As illustrated in Fig. 3 and described in detail in Refs. 9 and 11, boron oxide undergoes a secondary reaction with moisture in surrounding air (because of a negative standard heat of reaction). The end product is a thin boric acid film on the upper surface as verified by Raman spectroscopy in Fig. 2.

The ultralow friction mechanism of boric acid film forming on the surface can be explained as follows. Boric acid has a layered triclinic crystal structure as described in Ref. 12. The atomic layers in its crystal structure are parallel to the basal plane and they are made up of boron, oxygen, and hydrogen atoms. These atoms are closely packed and strongly bonded to each other by covalent, ionic, and hydrogen bonds, whereas the atomic layers are widely spaced (i.e., 0.318 nm) and held together by weak forces, e.g., van der Waals (Fig. 4). In a sense, the layered-crystal structure of boric acid resembles those of MoS_2, graphite, and hexagonal boron nitride which are well established as lamellar solid lubricants. Therefore, we believe that the ultralow friction behavior of the flash-annealed VB_2 surfaces is associated with the formation of a thin boric acid film that has a layered crystal structure. Mechanistically, we propose that under shear forces, atomic layers of boric acid crystal align themselves parallel to the direction of relative motion; once so aligned, they can slide over one another with relative ease to provide the low friction coefficient shown in Fig. 1.

SUMMARY

In this study, we demonstrated that ultralow friction coefficients can be achieved on VB_2 surfaces after short-duration annealing. We believe that the sequential formation of first a boric oxide layer during annealing at 800°C and then a boric acid film during cooling on VB_2 surface are the main reason for low friction properties. The boric acid film formed on the surface has a layered crystal structure. Boron, oxygen, and hydrogen atoms making up the layers are closely packed and strongly bonded to each other, while the layers themselves are relatively apart and bonded together with weak van der Waals forces. When present at a sliding surface, the layers can shear easily, thus providing low friction. The findings of this study suggest that other transition metal diborides, such as TiB_2 and ZrB_2 can also be made slippery by performing a similar annealing procedure at elevated temperatures.

ACKNOWLEDGMENTS

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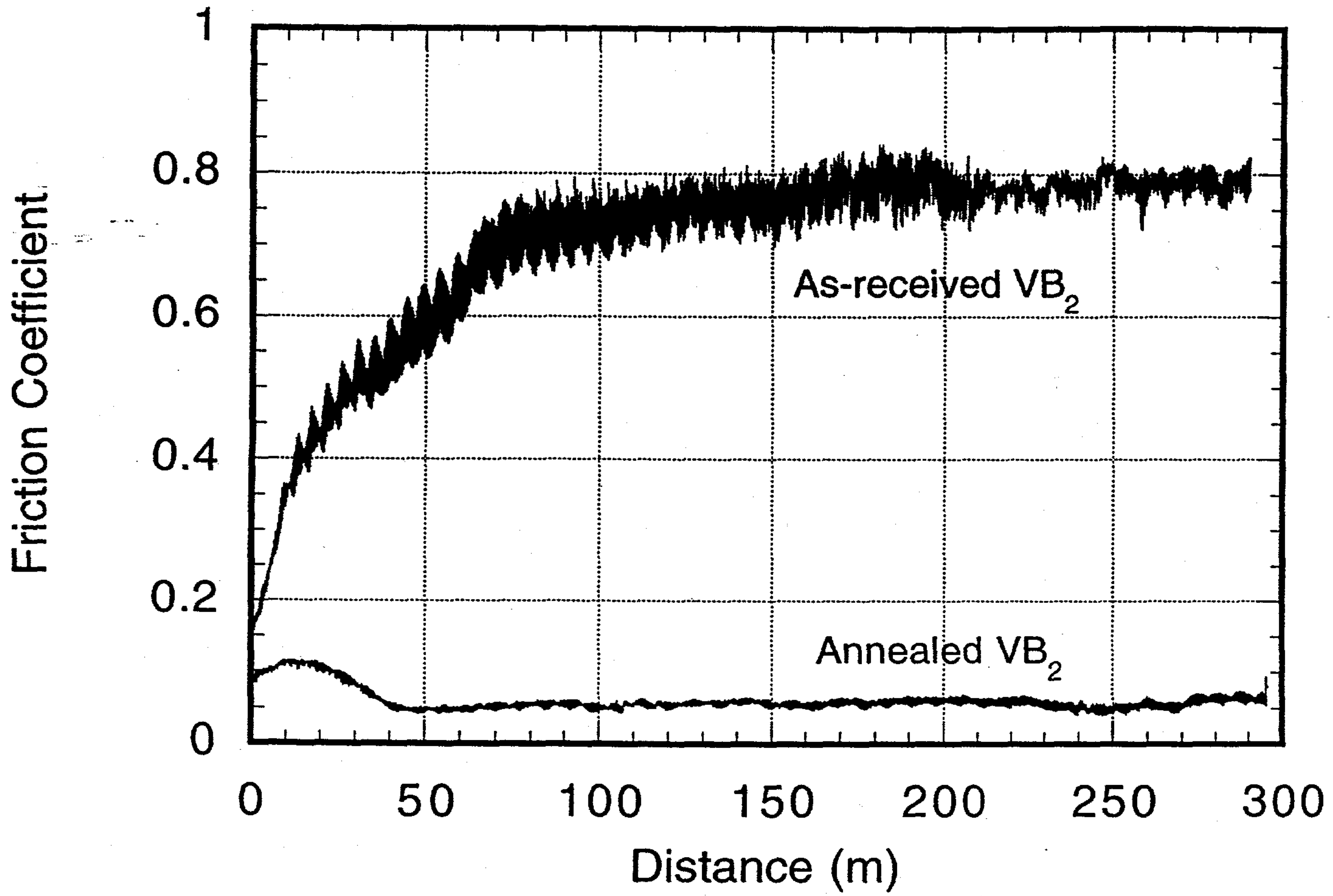
FIGURE CAPTIONS:

Fig. 1. Variation of friction coefficients of 440C steel pins during sliding against as-received and flash-annealed VB_2.

Fig. 2. Raman spectra of (a) as-received and flash-annealed VB_2 and (b) standard H_3BO_3 samples.

Fig. 3. Schematic illustration of formation of B_2O_3 and H_3BO_3 films on VB2 surfaces.

Fig. 4. Layered triclinic crystal structure of H_3BO_3.



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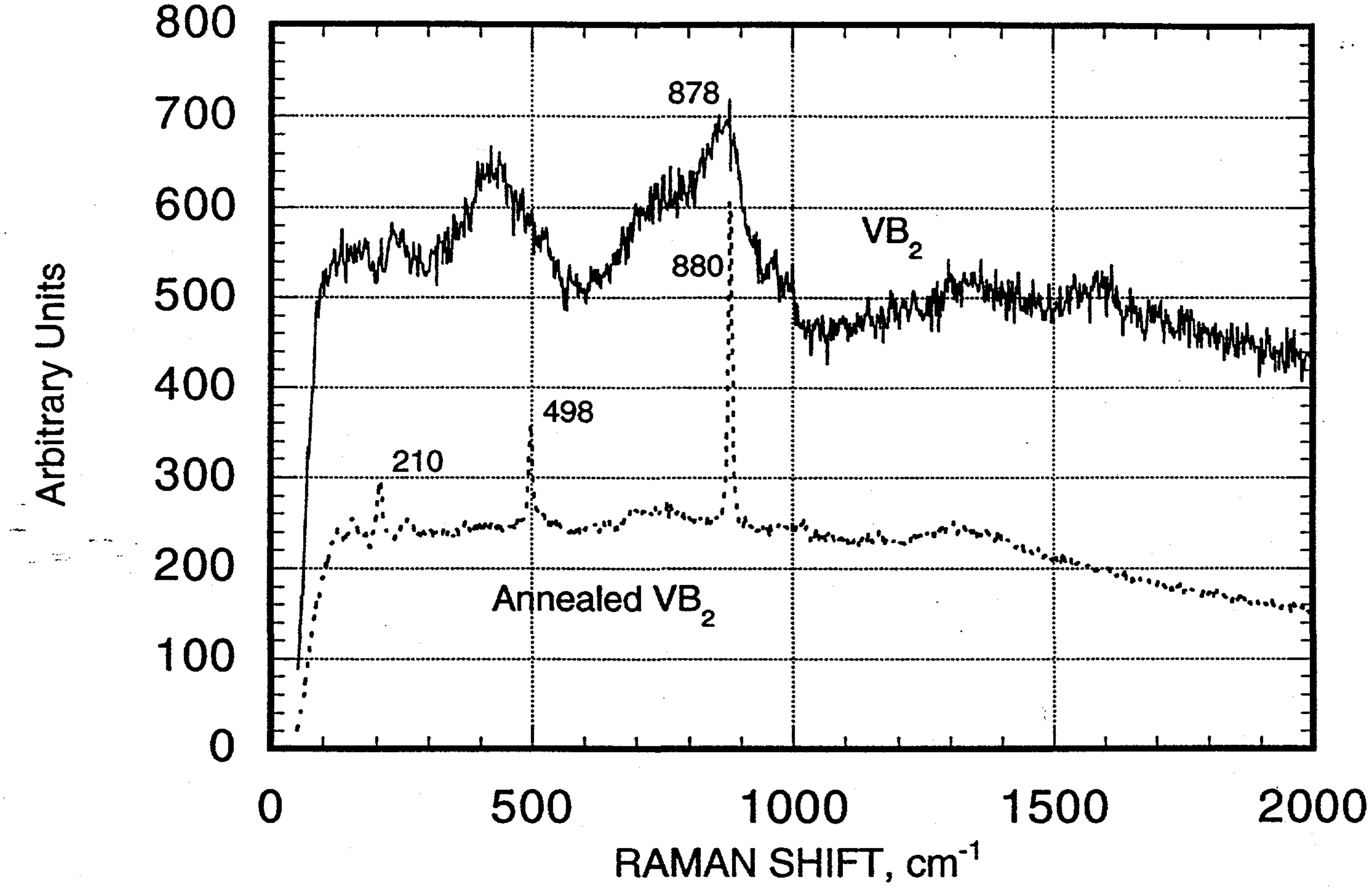
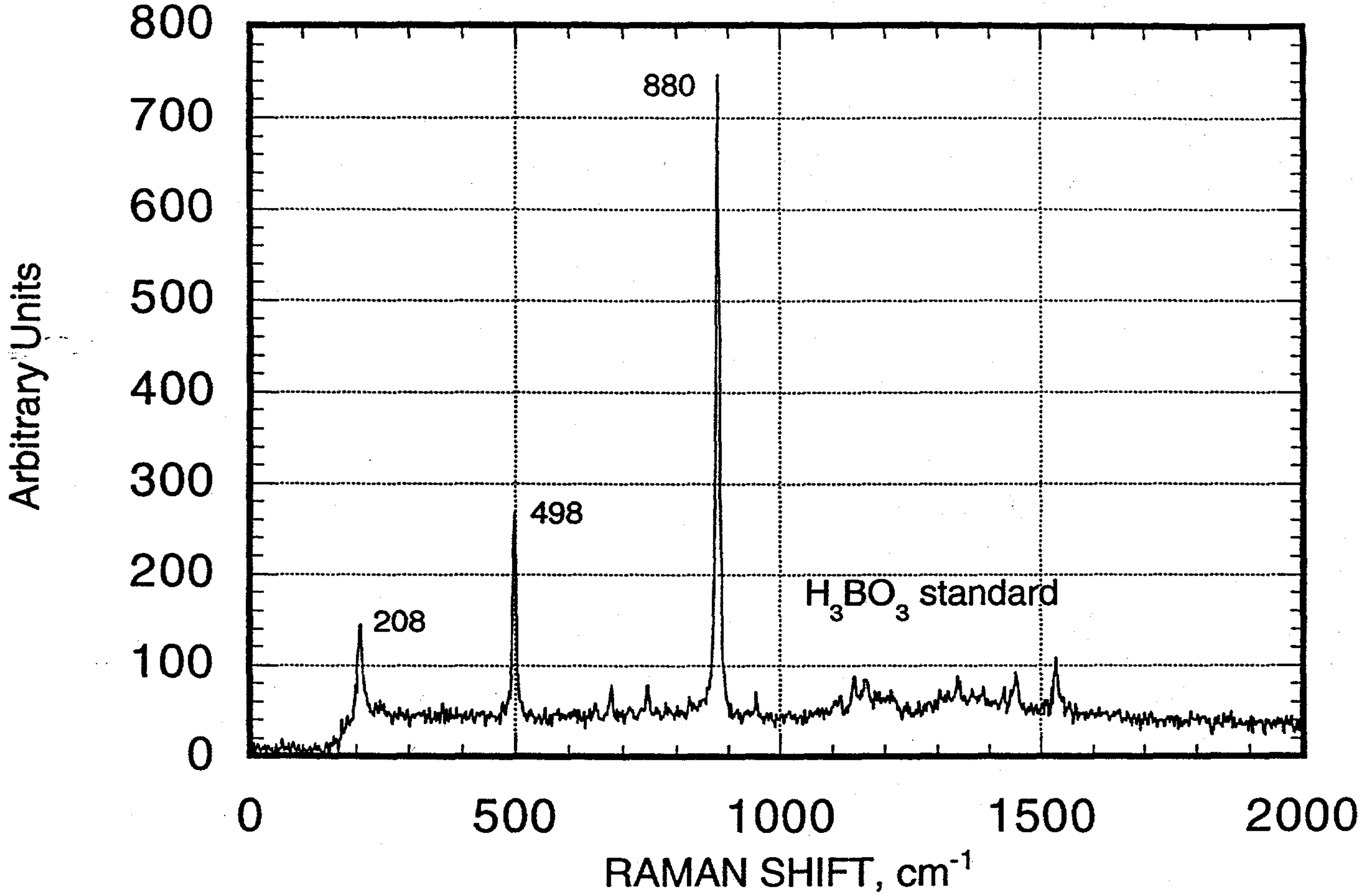


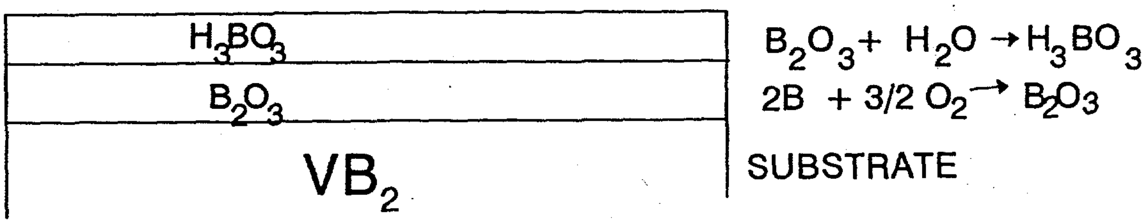
800
700
600
500
400
300
200
100
0
Arbitrary Units
0
500
1000
1500
2000
RAMAN SHIFT, cm^{-1}
878
880
498
210
VB_2
Annealed VB_2

(a)



(b)

Fig. 2. Raman spectra of (a) as-received and flash-annealed VB_2 and (b) standard H_3BO_3 samples.



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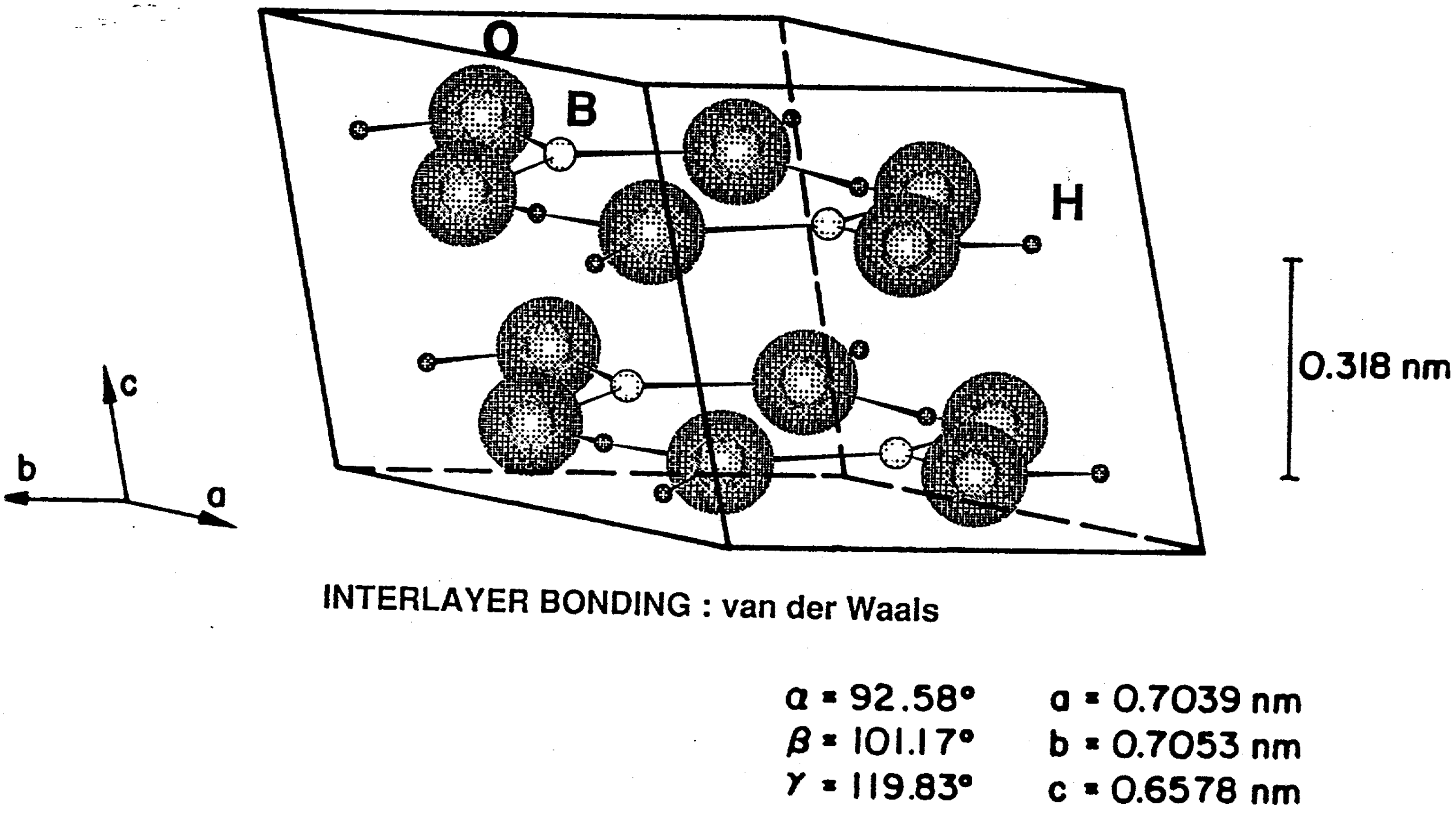

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