



# Communication **Tribological Property of Al<sub>3</sub>BC<sub>3</sub> Ceramic: A Lightweight Material**

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Abstract: Lightweight materials with a density less than  $3 \text{ g/cm}^3$  as potential tribo-materials for tribological applications (e.g., space tribology) are always desired. Al<sub>3</sub>BC<sub>3</sub> ceramic, a kind of ternary material, is one of the lightweight materials. In this study, dense Al<sub>3</sub>BC<sub>3</sub> ceramic is prepared via a reactive hot-pressing process in a vacuum furnace. Its tribological properties are investigated in two unlubricated conditions (one is at elevated temperature up to 700 °C in air, and another is in a vacuum chamber of back pressures from  $10^5$  Pa to  $10^{-2}$  Pa at room temperature) and lubricated conditions (i.e., water and ethanol as low-viscosity fluids). At 400 °C and lower temperatures in air, as well as in vacuum, the tribological property of  $Al_3BC_3$  ceramic is poor due to the fracture of grains and formation of a mechanically mixed layer. The beneficial influence of adsorbed gas species on reducing friction is very limited. Due to the formation of lubricious tribo-oxide at 600  $^{\circ}$ C and 700  $^{\circ}$ C, the friction coefficient is reduced from ca. 0.9 at room temperature and 400 °C to ca. 0.4. In the presence of low-viscosity fluids, a high friction coefficient and wear but a polished surface are observed in water, while a low friction coefficient and wear occur in ethanol. A lubricious carbide-derived carbon (CDC) coating on top of Al<sub>3</sub>BC<sub>3</sub> ceramic through high-temperature chlorination can be fabricated and the wear resistance of CDC can be improved by adjusting the chlorination parameters. The above results suggest that Al<sub>3</sub>BC<sub>3</sub> ceramic is a potential lubricating material for some tribological applications.

Keywords: Al<sub>3</sub>BC<sub>3</sub> ceramic; lightweight; wear and tribology; liquid lubrication; self-lubrication

## 1. Introduction

There is ongoing demand for light-weight lubricating materials for many tribological applications (e.g., gyro for space tribology). Because of its low density (2.66 g/cm<sup>3</sup>) and high elastic modulus (137 GPa), Al<sub>3</sub>BC<sub>3</sub> ceramic is an attractive material for lightweight structural components [1–3]. From the viewpoint of tribology, lamellar Al<sub>3</sub>BC<sub>3</sub> ceramic is also considered as an attractive candidate for tribological components under both unlubricated and lubricated conditions. For example, based on the ratio of hardness to Young's modulus (Hv/E = 0.068), Al<sub>3</sub>BC<sub>3</sub> ceramic is predicted to have excellent wear resistance at room temperature [1]. In addition, the stiffness of Al<sub>3</sub>BC<sub>3</sub> ceramic at 1600 °C is 79%, as high as that at room temperature, which is much higher than that of Ti<sub>3</sub>SiC<sub>2</sub> [1]. This suggests that Al<sub>3</sub>BC<sub>3</sub> ceramic is a candidate for the production of high-temperature wear-resistant materials [1–4].

Up until now, there have been no published reports on the fundamental tribological property of Al<sub>3</sub>BC<sub>3</sub> ceramic under both unlubricated conditions (e.g., air bearings for gyro)



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). and lubricated conditions (e.g., bearings and surface finishing). As a result, the application of Al<sub>3</sub>BC<sub>3</sub> ceramic is greatly hindered due to the lack of basic data of the tribological property. Currently, a tentative exploration of the tribological properties of Al<sub>3</sub>BC<sub>3</sub> seems to be the first step.

The importance of the tribological properties in air at elevated temperatures and in vacuum is highly valued due to the physical, chemical, and mechanical properties of  $Al_3BC_3$  ceramic. In addition, technical solutions to obtain low friction of the  $Al_3BC_3$ ceramic by liquid lubrication or solid lubrication are no doubt necessary in some cases. It is well known that water and ethanol are environmentally friendly and efficient as a lubricant and a polishing agent as well. A carbide-derived carbon coating on top of  $Al_3BC_3$ ceramic is also expected to be an effective method of self-lubrication. In this connection, the fundamental tribological property, as well as the liquid lubrication and self-lubrication of  $Al_3BC_3$  ceramic are presented in this study.

#### 2. Materials and Methods

## 2.1. Preparation of Al<sub>3</sub>BC<sub>3</sub> Ceramic and Carbide-Derived Carbon Coating

Lamellar Al<sub>3</sub>BC<sub>3</sub> ceramic is prepared by reactive hot-pressing at 1800 °C and 15 MPa starting from powders of Al, B<sub>4</sub>C, and graphite in a vacuum furnace. The powders of Al, B<sub>4</sub>C, and graphite (-200 mesh) with a mole proportion of 3.2:0.25:2.30 are used to prepare Al<sub>3</sub>BC<sub>3</sub> ceramic with low impurities. Al<sub>3</sub>BC<sub>3</sub> has a lamellar structure (see Figure 1). The Al<sub>3</sub>BC<sub>3</sub> ceramic for the tribological tests is dense with a porosity less than 2%. Some of the physical and mechanical properties of Al<sub>3</sub>BC<sub>3</sub> ceramic include a density of 2.56 g/cm<sup>3</sup>, three-point bending strength of 175 MPa, microhardness (10 gf) of 12.1 GPa, and indentation fracture toughness of 2.1 MPa·m<sup>1/2</sup>.



Figure 1. SEM micrograph of the edge of Al<sub>3</sub>BC<sub>3</sub> grains.

Carbide-derived carbon (CDC) coating on top of  $Al_3BC_3$  ceramic is prepared via a high-temperature chlorination process [5]. By varying the concentration of  $Cl_2$  in a  $Cl_2 + Ar$  mixture and the duration of chlorination, two CDC coatings are prepared. Schedule A is prepared in 6.67%  $Cl_2 + Ar$  at 800 °C for 2 h and schedule B is a two-step process of 6.67%  $Cl_2 + Ar$  at 800 °C for 20 min and 3.33%  $Cl_2 + Ar$  at 800 °C for 1 hr. Dechlorination is not conducted and residual adsorbed  $Cl_2$  is not removed. The thickness of the CDC coating is 20 to 30 µm. The advantage of CDC coating is its low internal stress [6]. The microstructure of the CDC coating on top of the  $Al_3BC_3$  ceramic is different from that of the CDC coating on SiC and  $Ti_3SiC_2$  (see Figure 2). A possible chemical reaction for high-temperature chlorination is as follows:

$$Al_3BC_3(s) + Cl_2(g) \rightarrow AlCl_3(g) + BCl_4(g) + C(s), \tag{1}$$



**Figure 2.** (a) Microstructure of CDC coating under low magnification; (b) the white particles are AlCl<sub>3</sub> (EDS spectrum in (b)).

## 2.2. Tribological Tests

Two kinds of tribo-meters are employed to conduct tribological tests. A CSM THT tribo-meter with a ball-on-disk configuration is used for the evaluation of tribological properties (1) at high temperature, (2) in liquid lubrication, and (3) in the presence of a CDC coating. A home-made vacuum friction tester with a ball-on-disk configuration is used for tribological tests in vacuum. A G3 grade  $Si_3N_4$  ball with a diameter of 3.175 mm is used for both tribo-meters. Fluctuation of the friction coefficient data of a given tribo-couple is frequently observed in this study, and it depends on the materials and assembly of the tribo-couple and sensitivity of the sensor to detect a friction force.

#### 2.2.1. CSM THT Tribo-Meter with a Ball-on-Disk Configuration

A silicon nitride ball (3.175 mm in diameter) sliding on a bare  $Al_3BC_3$  ceramic disk or CDC on  $Al_3BC_3$  ceramic disk (25 mm in diameter and 3 mm in thickness) is used. For liquid lubrication, the disk is immersed in either flooded distilled water or flooded ethanol. Test conditions are 0.1 m/s for sliding speed, 5 N for normal load, temperature from 25 °C (for liquid lubrication and CDC coating) to 400 °C, 600 °C, and 700 °C. The wear volume is determined by a surface stylus profiler.

## 2.2.2. A Home-Made Tribo-Meter with a Ball-on-Disk Configuration

A silicon nitride ball (3.175 mm in diameter) sliding on a bare  $Al_3BC_3$  ceramic disk is used. The test begins at a back pressure of  $10^5$  Pa for 10 min. After evacuation to a back pressure of  $10^4$  Pa, the test starts by using the same  $Si_3N_4$  ball on the same wear track. The same process is repeated for back pressures of  $10^3$  Pa,  $10^2$  Pa,  $10^1$  Pa, 100 Pa,  $10^{-1}$  Pa, and  $10^{-2}$  Pa. The test conditions are 10 rpm rotation speed at a diameter of 12 mm, 2 N for normal load, and room temperature. The wear volume is determined by a surface stylus profiler.

## 3. Results

#### 3.1. Tribological Property at Elevated Temperatures and in Vacuum

At room temperature, a stage of low friction coefficient (SLFC, ca. 0.2 in vacuum test, Figure 3a and ca. 0.4 in tests of high-temperature series, Figure 3b) before a stage of high friction coefficient (SHFC) is observed. In Figure 3a, such a SLFC occurs at back pressures of 10<sup>5</sup> Pa and 10<sup>4</sup> Pa, while no such SHFC occurs at back pressures of 10<sup>3</sup> Pa and lower. This implies that the SLFC is associated with an adsorption and desorption mechanism of gas species on the worn surface. In the vacuum test, a tribological test is begun at a

back pressure of  $10^5$  Pa. After a ten-minute sliding test, the chamber is evacuated to a back pressure of  $10^4$  Pa and the re-adsorption of gas species on the sliding surface occurs. This enables a SLFC stage at  $10^4$  Pa. At back pressures of  $10^3$  Pa and lower, the time for the re-adsorption of gas species might be too long to fulfill multi-layer adsorption. Therefore, SHFC occurs at the very beginning of the sliding at back pressures of  $10^3$  Pa and lower.



**Figure 3.** (a) Frictional trace of Al<sub>3</sub>BC<sub>3</sub> ceramic in vacuum at room temperature; (b) average friction coefficient and wear rate at elevated temperatures in air. The black dash line is the average friction coefficient of PM304.

The SLFC is not observed due to the desorption of gas species at 400 °C together with a lack of lubricious tribo-oxide, Figures 3b and 4. The low friction coefficients at 600 °C and 700 °C are mainly attributed to tribo-oxides ( $B_2O_3$ ). On one hand, the ionic potential of  $B_2O_3$  is as high as 12, suggesting that  $B_2O_3$  is a good high-temperature solid lubricant [7]. On the other hand,  $B_2O_3$  is a glaze substance at 600 °C and 700 °C.



Figure 4. Frictional traces of Al<sub>3</sub>BC<sub>3</sub> ceramic disk in sliding against a Si<sub>3</sub>N<sub>4</sub> ball at elevated temperatures.

In summary, the tribological property of  $Al_3BC_3$  ceramic in sliding against a  $Si_3N_4$  ball is not plausible in vacuum at room temperature or in air at temperatures of 400 °C and lower. At temperatures of 600 °C and 700 °C, the tribological property of  $Al_3BC_3$  ceramic is much better. Notably, the friction coefficients of  $Al_3BC_3$  ceramic at 600 °C and 700 °C are comparable to that of a high temperature self-lubricating composite PM304 at 630 °C (Figure 3b, data from the authors' laboratory). The frictional traces at elevated temperatures in air can be found in Figure 4.

### 3.2. Lubrication in Water and Ethanol

It is clear that the high friction (Figure 5a) and severe wear (Figure 5b) of  $Al_3BC_3$  ceramic and its counterpart material under an unlubricated condition can be reduced by using either flooded water or flooded ethanol as a lubricant. Specifically, Figure 5a suggests that under unlubricated conditions, a SLFC stage occurs (the same reason as

the above-mentioned) and the friction coefficient increases gradually to a high friction coefficient of 0.6. It is obvious that the fracture of grains and formation of a discontinuous mechanically mixed layer (Figure 5c) are the two main characteristics of the worn surface of Al<sub>3</sub>BC<sub>3</sub> ceramic under unlubricated sliding. The fracture of grains and formation of such a tribo-layer on Al<sub>3</sub>BC<sub>3</sub> ceramic are commonly found in ceramics, including MAX phase materials [8,9].



**Figure 5.** (a) Frictional traces of  $Al_3BC_3$  ceramic under unlubricated and lubricated conditions; (b) wear rates of  $Al_3BC_3$  ceramic and  $Si_3N_4$  ceramic under unlubricated and lubricated conditions; (c) SEM micrograph of the worn surfaces of  $Al_3BC_3$  ceramic under unlubricated conditions; (d) SEM micrograph of the worn surfaces of  $Al_3BC_3$  ceramic in water.

Although no such SLFC and friction coefficient are stably as high as ca. 0.5 in distilled water, the worn surface is smooth as a result of a polishing effect. Water, at the least, can be a good polishing agent for the planarization of  $Al_3BC_3$  ceramic. Additionally, it is reasonable that a well-polished surface enables the application of self-lubricating film (e.g., diamond-like carbon film and graphene film) in good quality.

Ethanol, as a good lubricant, significantly reduces the friction coefficient, which is observed for many ceramics [9]. Some reports emphasize the role of tribo-chemical products, while some focus on the role of the physical adsorption of ethanol on the sliding surface in the lubricating behavior of ethanol. It is an interesting but also challenging topic.

It is well known that water and ethanol have almost identical viscosities at room temperature. Therefore, the role of viscosity for the different tribological properties in water and in ethanol is insignificant. The water dissolution of friction-induced fresh asperities might be a good reason for the polished worn surface. A low and stable friction coefficient suggests that the robust physical adsorption of ethanol on the sliding surface rather than tribochemistry is the main reason. In case of friction dominated by tribochemistry, the friction coefficient will decrease with sliding duration.

#### 3.3. Self-Lubrication by CDC Coating

As seen in Figure 6a, CDC coatings significantly reduce the friction coefficient to 0.3 or even lower. The problem of the CDC coating is its relatively high wear rate (see Figure 6a). Similar results are found for CDC coating on top of  $Ti_3SiC_2$ . The wear resistance of CDC can be improved by adjusting the chlorination parameters (see Figure 6a). As seen in Figure 6b, the two CDC coatings are composed of poly-crystalline graphite, similar to  $Ti_3SiC_2$  [5]. In addition, schedule A produces a 'thicker' CDC coating while schedule B produces a 'thinner' CDC coating. That might be the reason for the better wear resistance by schedule B.



**Figure 6.** (a) Friction coefficient and wear rate of CDC coatings prepared using different chlorination schedules; (b) XRD patterns of  $Al_3BC_3$  ceramic, CDC coating by schedule A, and CDC coating by schedule B. < indicates the (002) peak of graphite. Small amount of graphite in  $Al_3BC_3$  ceramic.

The CDC coating is a highly porous coating of low density. The porosity of CDC is higher than 50% [5,6]. Therefore, it will not increase the density of the Al<sub>3</sub>BC<sub>3</sub> ceramic. In addition, the internal stress of the CDC coating is much lower than diamond-like carbon film, which represents an advantage over the diamond-like carbon film. This means that the thickness of the CDC coating can be as high as several millimeters without risk of peeling [6].

#### 4. Discussion

 $Al_3BC_3$  ceramic behaves like brittle ceramics (i.e., fracture of grains rather than plastic deformation) under tribological loading.  $Al_3BC_3$  ceramic is not a plausible lubricating material in vacuum at room temperature as well as at temperatures lower than 600 °C. Tribo-oxidation (glazed  $B_2O_3$ ) in oxidizing atmosphere renders  $Al_3BC_3$  ceramic with reduced friction and wear at 600 °C and 700 °C. Liquid lubrication by low-viscosity fluids and solid lubrication by carbon coating suggest that  $Al_3BC_3$  ceramic can be used as a tribological component, either by liquid lubrication or by surface modification. The surface chemistry of  $Al_3BC_3$  ceramic in various atmospheres and liquids is the key to understanding its tribological behavior. There are still many topics that deserve further investigation. For example,  $Al_3BC_3$  ceramic with a low-friction coating (e.g., diamond-like carbon film) can be a candidate material for fabricating gyro for space tribology.

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