

Grain size dependence of abrasive wear in boron carbide ceramics

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Abstract

Boron carbide ceramics are amongst the most exciting materials in the family of ultra-high hardness ceramics and they are used extensively in tribological applications. This research work is a pioneering contribution on the analysis of the abrasive wear resistance of boron carbide as a function of grain size and porosity. In contrast to most ceramics, it is concluded that grain size is not directly relevant to the wear resistance, whereas porosity and hardness play the main role. The absence of surface pullout by brittle fracture is a relevant experimental feature in this material which results in mild wear. Our results are rationalized in terms of the classical Rabinowicz model, which gives a reasonable description of the wear response.

Keywords: boron carbide, wear resistance, grain size, hardness

Introduction

Boron carbide is widely recognized for its excellent hardness and abrasion resistance. The combination of these with other promising properties like high melting point, low specific weight, high elastic modulus and good chemical inertness at room temperature make it a promising candidate for wear resistant components [1-6]. It is well-known that abrasive air-jet nozzles made of boron carbide with high relative density provides a longer life compared with those made of other materials [7-9]. Several of the main industrial applications of boron carbide are as wear resistant components e.g. blast nozzles, wheel dressing tools, bearings, mechanical seals and cutting tools.

However, despite the technological interest of boron carbide ceramics, its main drawback for extensive use is the difficulty of sintering fully-dense complex-shaped specimens, a consequence

of the very low self-diffusion coefficients. Up to now the key research on B₄C ceramics has been focused on processing of this ceramic to obtain fully dense ceramics with refined microstructure and improved mechanical properties like hardness and fracture toughness [2,10,11]. Quite recently, pure and fully dense B₄C ceramics have been prepared by means of spark plasma sintering (SPS). This novel technique has been reported to improve sintering and densification, particularly room temperature mechanical properties [12-17].

Although there is an increased demand of boron carbide ceramics for tribological applications, only a few studies have examined their tribological performance. Under abrasive wear, the effect of several additives on wear resistance of boron carbide-based ceramics has been studied [4], while the other studies were mainly focused on the impact erosion behavior of boron carbide ceramic nozzles in abrasive air-jet processes [7-9]. Moreover, to our knowledge there is no study exploring the role of microstructure, i.e. grain size or porosity, on wear properties of boron carbide. This study points out the importance of microstructure on the level of damage in boron carbide ceramics under abrasive wear. The abrasive wear mechanisms of B₄C ceramics are assessed by microstructural analysis and comparison with data reported for room-temperature mechanical properties.

Experimental procedure

Four sets of pure boron carbide ceramics with different average grain sizes (17.2 μm , 690 nm, 370 nm and 120 nm) were considered in this study. These B₄C ceramics were prepared by spark plasma sintering (SPS) different powders under various processing conditions giving rise to near fully-dense B₄C ceramics with the desired grain size distributions as explained elsewhere [15-17]. The sintering conditions are summarized in Table 1. Their microstructural characteristics, Vickers hardness values at 19.6 N (HV2) together with single edge V-notched beam (SEVNB) toughness measurements reported in a previous study [18] are listed in Table 1 for comparison with wear results.

A micro-scale abrasive wear tester (TE 66, Phoenix Tribology, UK) was used in this study. A schematic diagram of the tester is shown elsewhere [19]. A pre-conditioned chrome steel ball, 25 mm in diameter, was clamped between coaxial shafts and rotated by an electric motor. A flat and polished specimen was mounted vertically on a pivoted arm and was loaded against the ball by a 5 N dead weight hanging from a lever arm. Abrasive slurry, containing silicon carbide particles

(4.3 μm , grade F1200, Washington Mills, UK), suspended in distilled water was supplied to the contact interface between the specimen and ball, so that the contact zone was maintained in a small pool of slurry. The slurry supply was stirred continuously to prevent particle sedimentation, and was applied at a standard rate as drops to the surface of the rotating ball. The total sliding distance used in each test was 70 m (1000 ball rotations). The relative sliding speed was 0.2 m s⁻¹. The tests were interrupted at every 10 m of sliding distance, when the wear craters were examined by optical microscopy.

The wear volume was calculated using the following formula [19]:

$$V = \frac{\pi b^4}{64R} \quad (1)$$

where b is the crater diameter and R the ball radius. This relationship assumes that the shape of the crater is conformal to the shape of the ball. The Archard wear law states that the wear volume follows the relationship:

$$V = w_r SP \quad (2)$$

where w_r is a constant (wear coefficient), S is the sliding distance and P is the applied load. Accordingly:

$$w_r = \frac{\pi b^4 / 64R}{SP} \quad (3)$$

Eq.(2) states a linear dependence of V versus SP , the wear coefficient being the proportionality constant. The wear resistance, defined as $1/w_r$, of each material was determined as the average of two series of tests, each with 70 m sliding distance. Microstructural analysis was performed on the worn surfaces by scanning electron microscopy (HITACHI S5200).

Results and Discussion

Figure 1 shows the wear volume (V) of each boron carbide specimen as a function of the product between sliding distance and normal load (SP). The values of both wear coefficient (w_r) and wear resistance ($1/w_r$) for each specimen are listed in Table. 1. It is evident that the highest wear coefficient is only ~50% greater than the smallest despite the fact that the grain sizes used cover over 2 orders of magnitude (from 17.2 μm to 120 nm). This is in marked contrast to many other ceramics such as alumina in which the wear rate is strongly influenced by the grain size [20]. A plot of the wear resistance of these four boron carbide ceramics as a function of the average grain

size is provided in Fig. 2, and shows no obvious correlation between these two variables, and the finest grain size does not exhibit the highest wear resistance. Therefore, it seems clear that other factors must have a stronger influence on the wear behavior of boron carbide ceramics. For instance, the presence of porosity may play a key role in reducing the wear resistance of finer boron carbide ceramics. Indeed, the lowest wear resistance in Table 1 ($6.9 \times 10^{13} \text{ Nm}^{-2}$) occurs in the specimen with the highest porosity (5.3%). Zorzi et al [4] reported a wear coefficient of $2.09 \times 10^{-14} \text{ m}^3 \text{ N}^{-1}$, corresponding to a wear resistance of $4.78 \times 10^{13} \text{ Nm}^{-2}$ for pure micrometric boron carbide ceramics with 95.5% of theoretical density. This is in good accordance with the results obtained in this study.

In order to investigate the wear mechanism, the worn surfaces of the four specimens were observed by HR-SEM and are displayed in Fig. 3. For all of the boron carbide specimens except for n° 4 (see Table 1), wear is relatively mild (i.e. there is little brittle fracture and pullout of the surface, as in “severe” wear). Since boron carbide specimens have high hardness (Table 1), comparable with that of the abrasive particles, the plastic deformation by the abrasive-surface interaction is limited. The observed cracks on the worn surface are normal to the sliding direction and therefore formed mainly as a result of the abrasive-surface friction. Under this condition, the cracks go straight down into the ceramic without linking up and so do not lead to severe wear as observed in Fig. 3 (a-c). One factor responsible for this is the transgranular fracture mode of these materials [15-18] which prevents the interlinkage of cracks by deflection along the grain boundaries. In the few material pullouts observed, where a discrete piece of material is removed by brittle fracture, the fracture responsible tended to be transgranular (Fig. 3 (a-c), red arrows). For coarse grains, pullouts can occur within the grains (Fig. 3 a-inset, red arrows). The nano boron carbide with high porosity displayed a rougher worn surface with more intense pullout. Pullouts were more extensive as cracks linked up between pre-existing pores, resulting in larger scale material removal which was also mainly transgranular (Fig. 3 d, blue arrows).

More precise SEM observation was performed on the most wear resistant boron carbide ceramic n° 2 (see Table 1). Regions with forests of fine cracks were observed (Fig. 4), inclined to the direction of the abrasion along with more pronounced interlinked cracks along the direction of abrasion. These are thought to have formed under the combined action of friction, surface pressure and plastic deformation. There was minimal lateral cracking around the wear scar. This

is likely to be because of the high hardness, which limits the depth of the plastic zone responsible for lateral cracking [22].

The results of this study suggest that the total microstructure, not simply the grain size, must be considered when determining the resistance of boron carbide ceramics to abrasive wear. Due to the mild wear without evidence of severe pullouts, the abrasive wear model proposed by Rabinowicz can be considered as follows [23,24]:

$$V=KP/H \quad (4)$$

Where V is the volume of material removed per unit sliding distance under a applied load P , H is the hardness of surface and K is a dimensionless constant depending on the geometry of particles and the fraction of material displaced by an abrasive particle that is removed. The load on the specimen and the mean velocity of the abrasive relative to the specimen were constant for all the tests.

A very modest improvement in wear resistance arises as grain size reduces by more than two orders of magnitude between specimens 1 and 4 (Table 1). On the other side, the porosity is a very important microstructural feature which has a contrary influence: the finest grained B₄C ceramic (120 nm) shows the lowest wear resistance and has the highest porosity. A similar decline was observed on the hardness values of boron carbide ceramics with the presence of porosity, while the fracture toughness is reported to be almost grain size independent [18]. Therefore, it seems that the wear behavior of boron carbide correlates most strongly with the hardness, as shown in Fig. 5 in agreement with the Rabinowicz model.

It is important to emphasize that this conclusion is referred only to abrasive wear under the experimental conditions reported in this work. It is possible that more severe conditions can induce large scale brittle fracture and chipping formation which change the wear mechanism consequently [7-9].

Conclusion

The wear response of a set of boron carbide specimens with various grain sizes (from hundreds of nanometers to tenths of microns) and near full density prepared by spark plasma sintering has been performed. The results show that the wear resistance is essentially unaffected by the grain

size. This was because the hardness was high and the fracture was intergranular; although small cracks form in the wear scar, lateral cracking and interlinkage to form pullouts did not occur. Instead, the main wear mechanism was mild, plasticity-controlled cutting and ploughing. The main microstructural influence was the extent of residual porosity through its effect on the hardness.

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Figure captions

Fig. 1. Wear volume versus sliding distance \times normal load for the set of six boron carbide specimens.

Fig. 2. Plot of the wear resistance as a function of grain size of the samples under study.

Fig. 3. SEM images of worn surfaced of boron carbide : (a) 17.2 μm , (b) 690 nm, (c) 370 nm and (d) 120 nm.

Fig. 4. Plastic deformation and crack opening of worn surface of boron carbides with mean grain size of 690 nm

Fig. 5. Wear resistance versus δ for boron carbide specimens.

Fig. 6. Plot of hardness as a function of the wear resistance for the boron carbide specimens.

Table caption

Table 1. Microstructural, mechanical and wear characteristics of boron carbide samples with several grain sizes.

Table 1.

Sample designation	SPS condition [#]	Density (%)	Mean grain size	Hardness (HV2) [18] (GPa)	Wear coefficient (w_r) ($\times 10^{-14} \text{ m}^2 \text{N}^{-1}$)	Wear resistance ($1/w_r$) ($\times 10^{13} \text{ Nm}^{-2}$)
1: B ₄ C220 ^{\$}	1800°C- 3 min	99.2	17.2 μm	29 \pm 2	1.24	8.08
2: B ₄ C500*	1700°C- 3 min	100	688 nm	34 \pm 2	0.96	10.42
3: B ₄ C220 ^{\$}	1700°C- 3 min	98.5	370 nm	33 \pm 1	1.17	8.52
4 :B ₄ C40 ^{&}	1200°C-10 min , 1600°C-1 min	94.7	120 nm	27 \pm 1	1.45	6.91

[#] SPS was done under pressure of 75 MPa with heating rate of 100 °C/min, * B₄C500 denotes sub-micrometric B₄C powders with average particle size of 500 nm [15], \$ B₄C220 denotes sub-micrometric B₄C powders with average particle size of 220 nm [16] and & B₄C40 denotes nano-metric B₄C powders with average particle size of 40 nm [17].