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Wear resistant boron carbide compacts produced by pressureless sintering

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ABSTRACT

Boron carbide compacts were produced by pressureless sintering at 2200 °C/2 h and 2250 °C/2 h in Ar atmosphere, using a starting powder with a particle size smaller than 3 μm. Effects of carbon addition (3.5 wt%) and methanol washing of the starting powder were investigated on the densification, Vickers hardness, and micro-abrasive wear resistance of the samples. The removal of oxide phases by methanol washing allowed the production, with no sintering additive, of highly densified (93.6% of theoretical density), hard (25.4 GPa), and highly wear resistant (wear coefficient $=2.9\times10^{-14}$ m^3/N.m) boron carbide compacts sintered at 2250 °C. This optimized combination of properties was a consequence of a reduced grain growth without the deleterious effects associated to the carbon addition. Methanol washing of the starting powder is a simple and general approach to produce, without additives, high quality, wear resistant boron carbide compacts by pressureless sintering.

1. Introduction

Boron carbide (B_4C) is a ceramic material of great technological interest due to properties as low theoretical density (*TD* =2.52 g/cm^3), high melting point (2450 °C), and high hardness, among others [1–6]. Besides the extensive use as abrasive media for hard materials, the industrial applications of boron carbide include the production of light-weighted armor plates and wear resistant components [1,7,8]. However, due to its strong covalent bonding character and the usual presence of an oxide film that involves the powder particles, the production of highly densified sintered bodies of stoichiometric boron carbide is extremely difficult. It is usually conditioned, in the literature, to the employment of pressure assisted sintering techniques and/or the use of additives [1,7–12]. The use of pressure assisted sintering techniques, besides the high cost, imposes important restrictions to the size and geometry of the sintered bodies. Many previous studies have reported the use of SiC, Al_2O_3, TiB_2, ZrO_2, Cr_3C_2, Al, rare-earth oxides and some transition metals to improve the densification rate and mechanical properties of B_4C [1,7–18]. However, some additives can also induce the formation of second phases that can deteriorate the mechanical properties and restrict the possible applications of the produced pieces.

Pressureless sintering of boron carbide has a lower cost compared to other techniques but the highest achievable densification is limited. Values greater than 90% *TD* are only possible using very high sintering temperatures (> 2200 °C) and fine particles (< 1 μm) [6]. The sintering behavior is significantly affected by the starting powder composition, in particular, the presence of oxide phases coating the particles surface and excess free carbon. The B_2O_3 (or H_3BO_3 as B_2O_3 is highly hygroscopic) coating hinders the densification as it avoids the direct contact between the B_4C particles until it is removed at high temperatures (> 1800 °C). In addition, particle coarsening has been associated to the presence of liquid or vapor phases formed by the oxide layer removing during sintering [3,5,6]. Using fine sized (median particle diameter ~0.8 μm) pure B_4C powder, highly densified compacts (> 90% *TD*) can only be obtained with a coarse microstructure (grain sizes up to about 100 μm) [6,10].

Carbon is the most widely used sintering additive to retard the coarsening of the particles by elimination of the oxide phases. It is commonly added in the form of phenol resin, which ensures a more efficient dispersion but demands an additional step of heat treatment before sintering [1,2,4,5,8–11]. High densities (~97–98% *TD*) associated to a fine grained microstructure can be achieved by addition of a little amount (3–5 wt%) of carbon [5,6]. However, some weak regions can remain in the sintered bodies as a result of gas (BO and CO) production by the oxide phases reduction reaction, as well as due to the presence of some non-reacted C in the microstructure [5,6,19,20].

Besides the addition of carbon, other approaches are proposed in

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the literature for the removing of the oxide coating from the boron carbide particles, as the sintering in a reducing atmosphere (H_2-He). However the high H_2 concentrations, needed to promote an efficient removal of the oxide layer, give place to the insertion of hydrogen in B_4C as an interstitial impurity. As a consequence, the vapor pressure of B_4C increases and densification is limited by grain coarsening [3].

Another approach is the elimination of the oxide phases before sintering by methanol washing of the boron carbide powder, as it was originally proposed by P. D. Williams [21]. Kim et al. [20] used pre-washed B_4C powder to produce compacts without additives by spark plasma sintering at 2000 °C/40 MPa. The removal of the oxide film (B_2O_3, HBO_2, H_3BO_3), formed on the surface of B_4C particles, decreased the onset sintering temperature from 1620 °C, for non-treated powder, to 1530 °C, for methanol washed powder, by the acceleration of lattice and/or grain boundary diffusion [3,5,19,20]. Very high and similar values of densification (> 99%) and hardness (~34 GPa) were obtained for the compacts produced with washed and non-washed powder. However, the grain growth was significantly reduced and the fracture toughness was improved for the sintered bodies produced using pre-washed powder. Despite the high potentiality of that approach, at our best knowledge, the paper of Kim et al. [20] is the only report in the literature where it is employed to produce well sintered B_4C compacts.

As one of the main applications of boron carbide is the production of wear resistant components, several tribological studies, including erosive and abrasive resistance evaluation of this material are reported in the literature [22–29]. However, the comparison between the available results is not straightforward as the authors employ different experimental geometries, investigate different wear mechanisms, and study samples produced by different sintering techniques. This difficulty is observed even in the scarce literature on micro-abrasive wear resistance of boron carbide [14,23,28,29], which was investigated in the present work. Sonber et al. [29] measured the wear coefficient of hot pressed sintered boron carbide using a ball-on-flat reciprocative sliding wear geometry. They report a specific wear rate of the order of 10^{-15} m^3/N.m, using a counter body of WC-Co. Several authors employed the ball cratering method [28,30,31], a three-body geometry where an abrasive silicon carbide slurry is dripped between a rotating sphere and the sample surface. They reported the following specific wear rates for boron carbide produced by different methods: 2.09×10^{-14} m^3/N.m (for pressureless sintered compacts) [14]; $\sim2.5\times10^{-14}$ m^3/N.m (for hard, 36.3 GPa, compacts with no reference to the sintering method) [23] and $6–7\times10^{-13}$ m^3/N.m (for coatings produced by CVD) [28].

The wear resistance of a material strongly depends on the wear mechanism and results of a combination of several properties as hardness, toughness and chemical inertness, which in the case of sintered materials are strongly dependent of microstructural features as grain size, porosity level and the presence of second weak phases. Taking that into account, and considering the technological interest in the development of alternative sintering approaches for the production of wear resistant B_4C compacts, in the present work we have compared the influence of carbon black addition (3.5 wt%) and/or previous methanol washing of the carbide powder on the microstructure and mechanical properties (density, hardness and micro-abrasion wear resistance) of boron carbide compacts produced by pressureless sintering under inert atmosphere (Ar).

2. Experimental procedure

2.1. Materials

Commercial available boron carbide powder (Grade HS supplied by H. C. Starck, Germany, particle size < 3 μm) was used in this study. Table 1 shows the main characteristics of this powder taken from the manufacturer's data sheet. Carbon black powder (Printex 60, Degussa AG., Frankfurt, particle size ≈20 nm) was used as a carbon source. Methanol P. A. (99.8%) was used for washing the boron carbide powder.

Table 1
Boron carbide powder characteristics (Grade HS, H. C. Starck).

Specific surface area	15–20 m^2/g
Particle size	D 90% of particles: 3.0 μm D 50% of particles: 0.8 μm D 10% of particles: 0.2 μm
Impurity levels	Max. 1.7 wt% of O Max. 0.7 wt% of N Max. 0.05 wt% of Fe Max. 0.15 wt% of Si Max. 0.05 wt% of Al Max. 0.5 wt% of other
Total boron	75.65 wt%
Total carbon	21.8 wt%
B/C molar ratio	3.7–3.8

Four different starting powder compositions were used for the sintering studies:

(1) S: pure HS powder as received;
(2) ST: pure HS powder previously treated by methanol washing;
(3) SC: mixture of HS powder, as received, plus 3.5 wt% of carbon black;
(4) STC: mixture of HS powder, previously treated by methanol washing, plus 3.5 wt% of carbon black.

For the methanol washing, boron carbide powder was ultrasonicated in methanol (3 ml/g) for 1 h. After washing, the powder was dried in air for 24 h at room temperature. The mixtures with carbon black were done using a Planetary Milling (Retsch PM100), operated at 100 rpm for 30 min. Three tungsten carbide balls (ϕ =10 mm) and the powder mixture were put in a tungsten carbide jar (125 ml) in a mass ratio of 1:1.23, in order to have a volume ratio of about 1:2.

2.2. Sintering and characterization

Cylindrical shaped compacts (15.4 mm in diameter and ~ 3–7 mm in height) were produced by uniaxial pressing (100 MPa) at room temperature. The pressureless sintering was performed in inert atmosphere (Argon flow of 0.8 l/min) using a resistive furnace with graphite heating elements (Thermal Technological Inc., Santa Rosa, CA). Temperature was monitored using a pyrometer (Model MA1SC, Raytek Co., Santa Cruz, CA) sighted on the graphite casing which enclosed the samples. The pieces were sintered at 2200 °C/2 h and the temperature was raised following a heating rate of 30 °C/min. This sintering temperature was chosen to avoid the abnormal grain growth, reported in the literature at higher temperatures [1,4,6,19]. For compacts produced with pre-washed starting powder (compositions ST and STC), the effect of a higher sintering temperature (2250 °C/2 h) was also investigated.

Samples surfaces were polished using diamond paste down to 1 μm following standard metallographic procedures. In order to observe the grain growth behavior the samples were electrochemically attacked using 1% KOH solution at 30 V for 10 s [24]. Sintered bodies densities were measured by the Archimedes method using distilled water. For the starting powder and the sintered compacts, the phase composition was analyzed by X-ray Diffractometry (Siemens, Kristalloflex D500 operated with a Cu X-ray tube, $\lambda_{K\alpha} \cong 1.5418$ Å, and a graphite monochromator). Scanning electron microscopy (JEOL JSM 6060) was used to investigate the samples microstructure. The mean Vickers hardness was determined from an average of 10 indentations in each sample. A Shimadzu type M microhardness tester was used with a 9.8