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Effect of graphene platelets on tribological properties of boron carbide ceramic composites

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ABSTRACT

The friction and wear behaviour of hot pressed boron carbide/graphene platelets (GPLs) composites have been investigated using the ball-on-flat technique with SiC ball under dry sliding conditions at room temperature. The hardness and fracture toughness of the investigated materials varied from 18.21 GPa to 30.35 GPa and from 3.81 MPa·m$^{1/2}$ to 4.60 MPa·m$^{1/2}$, respectively. The coefficient of friction for composites were similar, however the wear rate significantly decreased ~77% in the case of B_4C + 6 wt.% GPLs when compared to reference material at a load of 5 N, and ~60% at a load of 50 N. Wear resistance increased with increasing GPLs content in regards to the present graphene platelets, which during the wear test pulled-out from the matrix, exfoliated and created a wear protecting graphene-silicon based tribofilm.

1. Introduction

Boron carbide (B_4C) is an interesting material because of its excellent hardness ~36 GPa, low density 2.52 g/cm^3, high melting point ~2450 °C, high Young's modulus ~445 GPa, and good chemical and wear resistance. Due to these outstanding properties, boron carbide ceramics are candidates for many structural applications as neutron absorber, abrasive and polishing media for hard materials and wear resistant components, armour, etc. [1–5]. For applications of B_4C materials under demanding working conditions where friction and wear processes predominate, an improvement of reliability and tribological behaviour is required. Over the last decade the fracture toughness and tribological characteristics of advanced ceramics have been improved through the development of ceramic–carbon based filler composites such as carbon nanotubes, carbon nanofibers, and graphene platelets [6–10].

Investigations in the field of processing and characterization of mechanical, tribological and fracture properties of ceramic + GPLs composites focused mainly on alumina, silicon nitride and silicon carbide matrix ceramics [11–14]. Reports concerning the mechanical, functional and fracture properties of B_4C + GPLs composites have been first published last year [15–18]. As regards the influence of GPLs on fracture toughness, Wang et al. [11] reported improved fracture toughness of GPL/Al_2O_3 composite thanks to toughening mechanisms such as nanosheets pull-out and bridging. Walker et al. [12] investigated the influence of GPLs addition on the fracture toughness of Si_3N_4 composites and reported 6.6 MPa·m$^{1/2}$ for material with globular grains and 1.5 vol.% of GPLs thanks to the toughening mechanisms in the form of graphene necking and crack bridging, crack deflection and graphene sheet pull-out. Similar results were presented by Kvetková et al. [13] for graphene platelets added to silicon nitride composites for which the indentation fracture toughness was significantly higher compared to the monolithic silicon nitride with the highest value of 9.9 MPa·m$^{1/2}$ in the case of composite reinforced by multilayer graphene nanosheets with the smallest dimension. Belmonte [14] prepared silicon carbide composites with 5 vol.% reduced graphene oxide with an increase in both the fracture toughness ~162% with a maximum value of 8.3 MPa·m$^{1/2}$, and strength by ~60% (600 MPa) when compared to monolithic SiC. In our previous work [15] we observed slight improvement of bending strength of B_4C + 0.5 wt.% GPLs. Rutkowski [16] studied thermal properties and he showed that anisotropy of thermal properties exceed 70% in the case of B_4C with 4 wt.% GPLs. Oxidation of B_4C started above 720 °C. Tan [17] fabricated electrically conductive

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B_4C composites via SPS with high toughness and hardness. A high value of fracture toughness (5.3 MPa·$m^{1/2}$) was obtained in B_4C + 4 vol.% GPLs. The main toughening mechanisms responsible for increased fracture toughness included crack deflection, crack bridging and GPLs pull-out [15,17]. Liu [18] used reduced graphene oxide (rGO) platelets to enhance the toughness of bulk boron carbide ceramics. Fracture toughness increased from 3.8 to 8.8 MPa·$m^{1/2}$ at 1.5 vol.% rGO platelets.

As regards the influence of GPLs on tribological properties of graphene/ceramic composites, only a limited number of works can be found [19–22]. The tribological properties of silica–GNP composites were investigated for the first time at room temperature by Porwal et al. [19]. GNPs addition reduced the coefficient of friction of the material by 20% for silica–GNP composites tested with alumina balls, while in the case of silica composites tested using BS balls, no change was observed. They reported an improvement of ~5.5 and ~8.5 times in wear resistance of the investigated composites. Llorente et al. [20] showed significantly improved wear resistance of SiC ceramics under dry sliding conditions with the addition of GNPs. According to them, this response is connected with the ability of the graphene fillers to be pulled-out and exfoliated, creating a wear protecting graphene-based tribofilm. GNPs have been found as the best graphene filler compared to rGO or in-situ grown graphene flakes because they are more easily removed, exfoliated, and crushed to create a protecting tribofilm. Balko [21] studied the wear behaviour of Si_3N_4 + MLG composites up to 700 °C. He found that graphene platelets did not participate in lubricating processes. The best performance at room temperature offers the material with 3 wt.% graphene platelets. Si_3N_4–GPLs composites containing 0.1 and 3 wt.% GPLs sintered by SPS and HIP methods were investigated and compared in terms of tribological performance by Maros et al. [22]. The wear resistance of SPS samples containing GPLs addition was improved for tribosystems with both SiC and Si_3N_4 sliding pairs. The effect of GPLs addition was indirect, through structural changes and wear mechanisms.

To the best of our knowledge, the tribological properties of B_4C/GPLs composites have not been reported, yet. Therefore, the aim of the present contribution is to investigate the influence of the addition of graphene platelets on the tribological behaviour of B_4C/GPLs composites.

2. Experimental materials and methods

2.1. Experimental materials

The B_4C/GPLs composites were sintered from commercial powders: micron boron carbide powder (H.C. Starck, AB 134566 HS B_4C; D50 = 1 μm) and graphene Gn(12) of Graphene Laboratories, Inc., USA with the following parameters: purity: 99.2%, average flake thickness: 12 nm (30–50 monolayers), average particle (lateral) size: ~4.5 μm (1.5–10), specific surface area: 80 m^2/g. To avoid graphite contamination graphene was added as a sintering additive instead of resin precursor. All experimental materials, containing 4 wt.% GPLs as a sintering additive and from 0 wt.% (reference sample) to 6 wt.% GPLs as reinforcing phase.

The prepared compositions were homogenized in a high-energy rotary-vibratory mill using tungsten carbide-cobalt (WC–Co) milling media in an isopropanol alcohol environment. The milling time was only 2 h due to minimizing the contamination of powder mixtures by WC–Co impurities coming from milling media. The homogenized and dried mixtures were hot-pressed (Thermal Technology LLC) at 2100 °C for 1 h under 25 MPa in argon flow. The heating rate was 10 °C/min. Sintered bodies with a diameter of 50 mm were obtained.

2.2. Experimental methods

Specimens for microstructure examination were prepared and by routine ceramographic procedure they were cut, ground and polished to a 1 μm finish. The phase composition of the sintered materials was analysed by XRD diffraction (Phlips with X-Pert HighScore software). The microstructural characterization was determined by scanning electron microscopy (FIB-SEM ZEISS AURIGA Compact). Transmission electron microscopy (JEOL JEM 2100F UHR) was used for observation of the B_4C grain/GPL particle interactions. The EDS analysis was used for identification of the chemical composition of microstructures in connection with FIB-SEM at polished surface, at worn surface, in the wear track cross section, and by TEM on thin foil. Raman spectroscopy (Horriba Yvon Jobin LabRAM HR) was used for identification of graphene presence on the polished surface and also in the wear track. Apparent densities of the sintered samples were calculated by the Archimedes method in distilled water.

Mechanical characterization was performed in terms of measurement of basic mechanical properties of bulk materials such as hardness and fracture toughness using indentation methods. Hardness was determined by Vickers indentation (Wolpert Wilson 432 SVD Vickers Hardness Tester) under a load of 9.81 N with a dwell time of 15 s. In order to determine the indentation toughness at least 10 Vickers imprints per specimen were introduced with the load 98.07 N. The indentation toughness was calculated from the lengths of radial cracks and indents diagonals using a formula (Eq. (1)) valid for semi-circular crack systems as proposed by Anstis et al. [23].

$$K_{IC} = 0.016 \cdot \left(\frac{E}{H}\right)^{1/2} \cdot \left(\frac{P}{c^{3/2}}\right) \quad (1)$$

where K_{IC} – indentation toughness (MPa·$m^{1/2}$); 0.016 – material-independent constant for Vickers-produced radial cracks; E – Young's

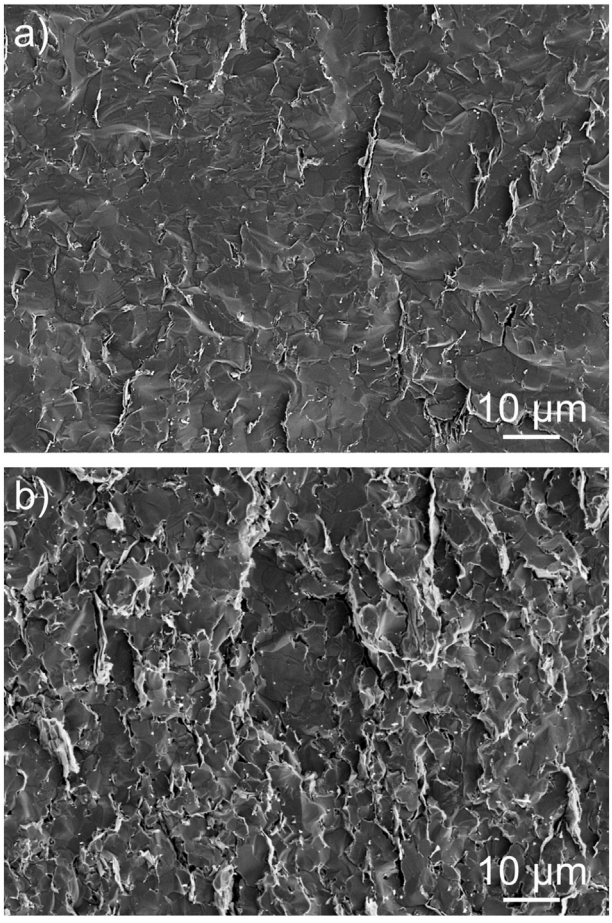

Fig. 1. SEM microstructural observations: a) fracture surface of B_4C + 1 wt.% GPLs, b) fracture surface of B_4C + 6 wt.% GPLs.

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