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ScienceDirect

Ceramics International 41 (2015) 10755–10765

CERAMICS INTERNATIONAL

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Spark plasma sintering and toughening of graphene platelets reinforced SiBCN nanocomposites

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Received 30 March 2015; received in revised form 4 May 2015; accepted 4 May 2015
Available online 12 May 2015

Abstract

The possibility of incorporating graphene platelets (GPL) as nanofillers in SiBCN nanocomposites was studied to evaluate the potential improvement on mechanical properties. GPL-SiBCN mixed powders prepared by ball milling of graphene platelets and SiBCN amorphous powders with Al_2O_3 balls was consolidated by spark plasma sintering technique to form bulk samples with different contents of graphene platelets. The effect of added graphene platelets on the improvement of fracture toughness is particularly significant and the fracture toughness increases rapidly with increasing GPL content in the composites. Nearly 650% increase in fracture toughness of GPL/SiBCN ceramic with 5 vol % GPL content, reaching a maximum of 5.40 ± 0.63 MPa · $m^{1/2}$. Results show that the nanofillers in ceramic nanocomposites remained uniformly and survived at high temperature. Main toughening mechanisms in graphene platelets reinforced SiBCN ceramic are pull-out, bridging, crack penetration graphene and crack deflection.

Keywords: SiBCN composites; Graphene platelets; Spark plasma sintering; Toughness and toughening

1. Introduction

Structural ceramics, such as SiBCN ceramics and their composites with special structures and extraordinary high temperature performances, are identified as promising materials for aerospace and aviation industries [1]. They have amorphous structure and do not crystallize at temperatures even higher than 1700 °C [2–4]. SiBCN ceramics derived from polymer precursors have received a significant attention for their outstanding high temperature compression creep properties and lowest reported oxidation rate of any non-oxide material known to date [5]. Recently, mechanical alloying and hot pressing techniques were also employed to prepare SiBCN powder and ceramics [6]. Dense bulk ceramic can be fabricated at 1800–1900 °C under nitrogen atmosphere for 30 min with nanosized β-SiC, α-SiC and turbostratic BNC distributing in matrix [7]. However, low fracture toughness has limited the applications of SiBCN ceramics. A way to overcome this disadvantage is to fabricate it as composites. Various scales of reinforcing nano and submicron particles, such as SiC_p, ZrB_{2p} have been incorporated to form SiBCN based composites. These reinforcing particles uniformly distributed and dispersed in grains close to SiC and BNC may inhibit abnormal grain growth and enhance the strength of the materials.

Li *et al.* [8] employed the polyborosilazane (PBSZ may convert to amorphous SiBCN ceramics after sintering) as the sintering additive and fabricated the dense ZrB_2-SiBCN ultra-high temperature ceramic samples by hot pressing at 1900 °C. The mechanical properties and high temperature oxidation resistance of ZrB_2-SiBCN composites were improved along with the bending strength and fracture toughness reached to 241 ± 10 MPa and 4.47 ± 0.5 MPa · $m^{1/2}$, respectively. Ye *et al.* [9] used SiC nanoparticles with different contents (5–20%) mixed with liquid polyborosilazane to prepare SiC nanoparticle/polymer-derived SiBCN ceramics. Results showed that the

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http://dx.doi.org/10.1016/j.ceramint.2015.05.011
0272-8842/

Table 1
mechanical properties of SiBCN matrix composites by hot pressing.

Samples	Flexural strength/ MPa	Elastic modulus/ GPa	Fracture toughness/ $MPa \cdot m^{1/2}$
SiBCN	331.5 ± 30.4	139.4 ± 16.0	2.80 ± 0.90
C_f/SiBCN	64.4 ± 3.2	14.7 ± 7.4	1.47 ± 0.09
C_f/SiBCN+ZrO_2	112.5 ± 12.1	111.1 ± 23.3	2.94 ± 0.25
SiC_f/SiBCN[11]	284.3 ± 17.9	183.5 ± 11.1	2.78 ± 0.14

addition of SiC nanoparticles enhanced the thermal stability of SiBCN ceramics. The composites ceramics were found to have obviously increasing in permittivity and dielectric loss, yet the fracture toughness was not reported.

Another way to improve the fracture toughness of ceramics is to prepare fiber reinforced composites, which contributes to marked improvement in strength and toughness over monolithic ceramics [10]. Wang *et al.* [11] investigated the ablation mechanism and mechanical properties of SiC_f/SiBCN ceramic composites compared with C_f/SiBCN ceramics, and found that the mass ablation rate and linear ablation rate were much lower than the latter. The mechanical properties of SiC_f/SiBCN ceramics and C_f/SiBCN ceramics are showed in Table 1. The addition of SiC_f or C_f has greatly reduced the mechanical properties of SiBCN composites resulting from low relative densities compared to pure SiBCN ceramics.

Graphene as one atom thick 2D layer of SP^2 carbon arranged in a honeycomb lattice is obtained great attention [12]. Graphene with its combination of large specific surface area, two dimensional high aspect ratio sheet geometry and outstanding mechanical properties [13–17] would contribute to application in ceramic matrix composites (CMCs). Moreover, graphene is considered to have super-electrical properties and very high thermal properties [18–20]. All these unique properties of graphene make it a potential nanofiller in composites materials. Current studies indicated that significant improvement of mechanical properties of polymer based composites with relatively low graphene fillers loading. However, to our knowledge, graphene-ceramic composites are not well studied till now. In recent work by Walker *et al.* [21], they reported an improvement of 235% in fracture toughness with only a 1.5 vol% loading of graphene in Si_3N_4 matrix by SPS. Wang *et al.* [22] employed spark plasma sintering to prepare graphene nanosheet/Al_2O_3 composites with a 53 vol% increment in fracture toughness with a 2 wt% loading of graphene. Various toughening mechanisms including graphene platelets pulled out and bridging were observed. The addition of graphene nanofillers in Al_2O_3 matrix resulted in grain size refinement. Tapaszto *et al.* [23] prepared CNT-Si_3N_4 and graphene-Si_3N_4 composites at the same processing conditions, respectively. They found that an enhancement of 10–50 vol% in mechanical properties, such as fracture toughness, hardness, bending strength and Young's modulus for graphene-Si_3N_4 composites compared to CNT-added composites with the same loading, but overall decreasing of both composites compared to monolithic Si_3N_4. Kun *et al.* [24] prepared graphene-Si_3N_4 composites by HIP with 1 and 3 wt% graphene addition. Study showed that graphene platelets may cause porosity in composites which resulted in decreasing both of Young's modulus and bending strength with increasing the amount of graphene platelets. However, Kvetkova *et al.* [25] found a contrary achievement in a similar research. They prepared 1 wt% graphene-Si_3N_4 composites with different contents of nanofillers by HIP and indicated an improvement in fracture toughness for all composites compared to pure Si_3N_4 ceramics, but deceased in hardness because of increasing residual porosity except for multilayer graphene composites. Pull-out of GPLs, crack bridging and crack deflection had been observed which could help to enhancement of fracture toughness. Liu *et al.* [10] fabricated the GPL reinforced zirconia toughened alumina (GPL/ZTA) by using SPS. The addition of only a 0.81 vol% graphene nanofillers into ZTA composites resulted in a 40% increasing in fracture toughness. Similar to the former works showed above, various mechanisms such as pull-out, bridging and crack deflection were observed.

Inspired by these pioneering works, and to minimize the possibility of structural damage to the GPL at high temperatures and pressures, we use SPS to densify GPL-SiBCN mixed powders for its advantages. In our current investigation, graphene platelets are used as nanofillers with different volume fractions to demonstrate the effect of graphene platelets on mechanical properties of SiBCN matrix, especially fracture toughness. The phase, mechanical properties and microstructures of different samples with or without graphene were intensively studied.

2. Experimental

2.1. Starting materials

In the current work, the starting raw materials were well crystalline cubic silicon powder (95% in purity, 45.0 μm, Beijing Mountain Technical Development Center, China), hexagonal boron nitride power (98.0% in purity, 0.6 μm, Advanced Technology & Materials Co. Ltd., Beijing, China) and graphite powder (99.5% in purity, 8.7 μm, Qingdao Huatai Lubricant Sealing S&T Co. Ltd., China). According to the literatures and our previous achievements, the chemical composition was set molar ratio of Si:BN:C as 2:1:3 and ball to powder mass ratio 20:1. Then the mixed powder was loaded into the silicon nitride vials along with identical component balls under argon atmosphere milled by a planetary ball mill (P4, Fritsch GmbH, Germany). The rotation speech of the main disk was set as 350 rpm, and the vials were 600 rpm in reverse. The machine was paused for 20 min every 40 min, and the effective milling time was 20 h. Graphene oxide was fabricated by oxidizing commercially available graphite powder used above by improving Hummers method. Graphene platelets were obtained through the reduction of graphene oxide using hydrazine hydrate as the reducing agent. The surface morphologies of the as-milled amorphous SiBCN powder and the obtained GPL were observed in SEM as shown in Fig. 1 (a) and (b), respectively.