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Original article

Enhancing toughness and strength of SiC ceramics with reduced graphene oxide by HP sintering☆

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ABSTRACT

In this paper, the silicon carbide-reduced graphene oxide (SiC/rGO) composites with different content of rGO are investigated. The hot pressing (HP) at 2100 °C for 60 min under a uniaxial pressure of 40 M Pa resulted in a near fully-dense SiC/rGO composite. In addition, the influence of graphene reinforcement on the sintering process, microstructure, and mechanical properties (fracture toughness, bending strength, and Vickers hardness) of SiC/rGO composites is discussed. The fracture toughness of SiC/rGO composites (7.9MPam$^{1/2}$) was strongly enhanced by incorporating rGO into the SiC matrix, which was 97% higher than the solid-state sintering SiC ceramics (SSiC) by HP. Meanwhile, the bending strength of the composites reached 625 M Pa, which was 17.3% higher than the reference materials (SSiC). The microstructure of the composites revealed that SiC grains were isolated by rGO platelets, which lead to the toughening of the composite through rGO pull out/debonding and crack bridging mechanisms.

1. Introduction

Silicon carbide is one of the most important structural ceramics with remarkable thermal, corrosive preventive and mechanical properties, as well as good oxidation resistance [1]. Due to those properties, SiC ceramics are used in many technological applications under severe working conditions, such as refractories, heat exchangers, cutting tools, and electronic substrates. However, the Achilles' heel of SiC ceramics is that its fracture toughness is relatively low, which hinders its further application [2,3].

Graphene [4] consists of a one-atom layer of carbon atoms arranged in a honeycomb lattice, which has attracted tremendous attention due to its exceptional electrical [5], thermal [6] and mechanical properties [7,8] characterized by 130 GPa tensile strength and 0.5–1 TPa Young's modulus values. However, it is difficult to obtain a high yield of single-layered graphene without subsequent layer agglomeration. In contrast to monolayer graphene, multilayer graphene (MLG) consists of several layers of graphene, which inherits these super properties. Lee [9] reported the exceptional mechanical properties of 10–100 nm thick MLG under extreme dynamic condition in Science. Kang [10] reported 0.695 T Pa Young's modulus of a graphene oxide (GO) film (50–60 nm thickness). Recently, MLG [11] in the form of GO [12–14] and graphene platelets (GPLs) [15] have been introduced into ceramic matrix [16,17] to enhance their properties because of their exceptional physical properties [18,19]. It has been shown that the presence of graphene improves the fracture toughness [13,20–23], electrical conductivity [24,25], thermal conductivity [26–28], as well as the tribological [29] properties of ceramic matrix composites.

SPS was widely used in fabricating Ceramic/MLG composites [19,28,30–32]. Bodis et al [33] reported that the fracture toughness increased by 20% for the 1 wt% GPL (15–20 nm thick) containing composite as compared to the monolithic SiC selected for reference material. Roman-Manso et al [28] obtained silicon carbide composites with highly oriented GPLs by SPS method. The GPLs used were 40–60 nm thick and 5–12 μm in the x–y plane. About 78–80% GPLs exhibit angles with respect to the plane perpendicular to the pressing axis within ± 15°. Recently, Belmonte [31] and Llorente [29] selected GPL (10–20 nm thick and 14 μm x–y dimensions)and rGO (thermal reduction from GO with 5 nm thickness and 5 μm x–y dimensions) as fillers to develop reinforced silicon carbide (SiC)/graphene composites. They reported that composites containing 5 vol% rGOs exhibited an outstanding mechanical performance, increasing both the fracture

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toughness by 162%, with a maximum value of 8.3 M Pa▪$m^{1/2}$ (surface crack in flexure method), and the strength by 60% (three point bending method) when compared to monolithic SiC (3.2 MPa▪$m^{1/2}$). Small bars of 15.0 mm × 2.0 mm × 2.5 mm were used to test mechanical properties. It seemed that rGO was a better MLG source in enhancing the mechanical performance than GPL by SPS sintering and thermal reduction of GO during SPS process was an effective way, though SPS process is not suitable for large size sample.

Li et al [20] reported SiC ceramics with different graphene contents by a solid state pressureless-sintering method. The highest bending strength of 434 M Pa was achieved corresponded to SiC samples with graphene content of 0.5 wt%. They found that pores in the samples increased with the increasing graphene content, which made it difficult for graphene to exert its superior mechanical properties. Thus, they suggested that pores could be fully eliminated by hot pressing method or by spark plasma sintering method.

Hot pressing sintering (HP) is a useful method to obtain ceramic/MLG composites [26,34–36].Very recently, Sedlak et al (37)prepared SiC/GPLs (12 nm thickness and 4.5 μm lateral particle size) composites by hot pressing technology. They found that both the bending strength and fracture toughness increased with increasing GPLs additives. The highest fracture toughness of 4.4 M P a▪$m^{1/2}$ (indentation method) was achieved at 6 wt% of GPLs addition, which was about 30% higher than the K_{IC} value of the reference material. The highest strength they reported was 290 M Pa, which was lower comparing with values from SPS literatures [29,31].

To the best of our knowledge, the enhancing toughness and strength in SiC with reduced graphene oxide (rGO) by HP sintering has not been reported so far. In addition, the reported bending strength of the composites fabricated by HP method is lower, comparing with the value of traditional SSiC ceramics. In this study, in order to improve mechanical properties of SiC ceramic so as to extend the application in severe environment, we propose one method to introduce GO into SiC ceramic by in situ thermal reduction of graphene oxide during hot pressing process. The aim of this contribution is to take the lead in investigating the effects of rGO contents on the bending strength, fracture toughness, micro-hardness, and microstructure evolutions of the composites in detail.

2. Experimental

2.1. Experimental materials

α-SiC powders(Saint-Gobain), GO powders (Changzhou, the Sixth element company), B_4C(Mudanjiang, Jingangzuan Boron Carbide) and Carbon Black (Aladdin) were used as raw materials. The average grain size of SiC powder was 0.2 μm, GO nano-platelets were about 12 nm thick, and the average lateral particle size was around 10 μm. In these composites, 0.6 wt% B_4C and 1.0 wt% Carbon Black were used as sintering additives. The amount of rGO was 0, 1, 2, 4, 6, and 10 wt% of the total composites.

Firstly, GOs were ultrasonic processed in alcohol media, for 1 h, meanwhile the alcohol based SiC slurry was attrition milled for 2 h with SiC balls (5 mm in diameter) with a rate of 300 rpm. SiC balls were used to avoid the contamination from the milling media. Then, GOs were poured into SiC slurry. All suspensions were attrition milled for 4 h with SiC balls with a rate of 400 rpm, dried at 120 °C, and sieved through a 74 μm mesh.

Finally, block shaped specimens of 40 mm × 40 mm × 4 mm were HP sintered at Ar atmosphere. A uniaxial pressure of 40 MPa was applied throughout the sintering cycle. The process was started by raising the temperature to 1200 °C at a rate of 20 °C/min. Then the sintering temperature was increased to 2100 °C at a rate of 10 °C/min. A 60 min soaking time was used during the sintering. The temperature was measured and controlled using an optical pyrometer.

2.2. Experimental methods

Apparent density of the composites was measured by the Archimedes method with deionized water as the immersion medium. The theoretical density of the composites was calculated by the rule of mixtures using densities of 3.2, 2.1, 2.5 and 2.1 g/cm [3] for SiC, rGO, B_4C and Black carbon, respectively. The relative density was obtained from dividing the bulk density by the theoretical density.

The microstructures of the composites were characterized by scanning electron microscope (S4800, Hitachi). The nanostructure was further examined by means of a high resolution transmission electron microscope (HRTEM; JEM-2100 F, JEOL, Japan). The degree of rGO was investigated by the laser Raman spectrophotometer (XploRA ONE-532), with 633 nm laser wavelength excitation and 17 mW laser power. The phases of the raw materials and the composites were determined by X-ray diffraction (Rigaku D/max 2550 V).

For the mechanical tests small bars of 36 mm × 4 mm × 3 mm were machined. Bending strength was determined by three point bending tests using an outer span of 30 mm and a displacement rate of 0.5 mm/min. Vickers hardness was carried out on the polished surface of the bar, using a load of 49 N for 15 s. The fracture toughness was measured by a three point loading and single edge notched beam (SENB) technique [38] with a notch of 0.1 mm width and 1.5 mm depth on a face perpendicular to HP direction, a span of 24.0 mm and a speed of 0.05 mm/min. Seven bars of each sample were tested to obtain an average value. The fracture toughness was then calculated by the following equations:

$$K_{IC} = (PS/BW^{1/2}) f(a/W) \tag{1}$$

$$f\left(\frac{a}{W}\right) = \frac{3(a/W)^{1/2}[1.99 - (a/W)(1 - a/W)(2.15 - 3.93a/W + 2.7a^2/W^2)]}{2(1 + 2a/W)(1 - a/W)^{3/2}} \tag{2}$$

Where K_{IC}-fracture toughness, P-fracture load, B-specimen thickness, W-specimen width, S-span distance, a-average crack length.

The fracture toughness of the samples was also measured by Vickers indentation on both faces perpendicular and parallel to HP direction at a load of 49 N in order to study the anisotropy of the composites. KIC was calculated by Eq. (3). [39]:

$$K_{IC} = P(\pi c)^{-3/2} \cot\beta \tag{3}$$

Where K_{IC} is fracture toughness, 2c is the length of crack and P is the applied force and β = 68°.

3. Results and discussion

3.1. Processing condition

The synthesis route of SiC/rGO composites is illustrated in Fig. 1. In brief, GO sheets and SiC particles were mixed without assistance of surfactant. Then the composites were hot pressing sintered at 2100 °C, under 40 M Pa pressure. In order to obtain uniform microstructures, GO was used rather than reduced graphene oxide as precursor to aviod the aggregation of graphene caused by an additional reduction process [12,14]. After ball milling, well dispersed matrix composition with homogeneous distribution of sheet like structure was prepared. SiC particles were scattering in GO petals, for the size of SiC particles was much smaller than the lateral size of GO, Fig. 2.

Thermal treatment had been found to be one of the most effective way to reduce GO. Fig. 3 shows the Raman spectra and the microstructure of the GO powder before and after sintering at 2100 °C. The significant structural change occuring during the sintering process from GO to rGO is reflected in Raman spectra. It is known that there are two important bands linked to carbonaceous species: (i) the D−band 1360