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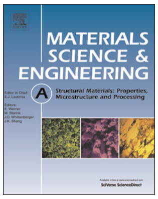

Fabrication and properties of graphene reinforced silicon nitride composite materials

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ABSTRACT

Silicon nitride (Si_3N_4) ceramic composites reinforced with graphene platelets (GPLs) were prepared by hot pressed sintering and pressureless sintering respectively. Adequate intermixing of the GPLs and the ceramic powders was achieved in nmethyl-pyrrolidone (NMP) under ultrasonic vibration followed by ball-milling. The microstructure and phases of the Si_3N_4 ceramic composites were investigated by Field Emission Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD). The effects of GPLs on the composites' mechanical properties were analyzed. The results showed that GPLs were well dispersed in the Si_3N_4 ceramic matrix. β-Si_3N_4, O′-sialon and GPLs were present in the hot-pressed composites while pressureless sintered composites contain β-Si_3N_4, Si, SiC and GPLs. Graphene has the potential to improve the mechanical properties of both the hot pressed and pressureless sintered composites. Toughening effect of GPLs on the pressureless sintered composites appeared more effective than that on the hot pressed composites. Toughening mechanisms, such as pull-out, crack bridging and crack deflection induced by GPLs were observed in the composites prepared by the two methods.

1. Introduction

Silicon nitride, an advanced ceramic material, is considered suitable for structural applications including high speed cutting tools, chemical and electrical insulators and various coatings due to its excellent mechanical properties at both room and elevated temperatures, good thermal shock resistance and excellent ablation resistance. However, because of the intrinsic brittleness of ceramic materials, it is crucial to improve the strength and toughness of silicon nitride ceramics to make them more reliable for engineering applications [1–6]. Reinforcing ceramic materials with appropriate nanofillers will significantly improve their strength and toughness, as well as electrical and thermal properties. These nanofillers can provide a variety of extrinsic toughening mechanisms [7–14].

For instance, carbon nanotubes (CNTs) with high tensile strength, good flexibility, and low density have been widely investigated as nanofillers to improve the electrical and thermal conductivity of the host materials with low filler contents. The enhancement of properties such as electrical conductivity and elastic modulus has been observed in polymer composites containing CNTs [11]. Balázsi et al. [12] fabricated the CNT–Si_3N_4 composites by spark plasma sintering (SPS) and a 25% increase in fracture toughness was achieved, compared to monolithic Si_3N_4. Bocanegra Bernal et al. [13] studied the effects of carbon nanotubes on the properties of ZrO_2 toughened Al_2O_3 (ZTA) composites and reported a 44% increase in fracture toughness over the pure ZTA.

Recently discovered graphene is a one atom thick 2-D layer of sp [2] carbon arranged in a honeycomb lattice [15,16], which has imposed itself with many unique outstanding properties. These properties make graphene a promising candidate of nanofiller material in various applications. The intrinsic mechanical properties of graphene reported so far, such as Young's modulus of 1 TPa and ultimate strength of 130 GPa, make it one of the strongest materials available [17–19,35]. Moreover, graphene is considered to have unusual electrical properties [20–22,35] and high thermal properties [23,24,35]. It has been shown that a single graphene layer is a zero-gap semiconductor with a linear Dirac-like spectrum around the Fermi energy, which manifests graphene in unusual phenomena such as an anomalous quantum Hall effect. Graphene has very high thermal conductivity *K*. The first experimental determination of the thermal conductivity of suspended monolayer graphene pegged the value at 5300 $W\,m^{-1}\,K^{-1}$ and a phonon mean free path of 775 nm near room temperature. Due to its remarkable properties, graphene has been selected as the nanofiller in a multitude of studies. It has been demonstrated in some studies that a relatively low addition of graphene to various

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ceramic based composites could result in a substantial improvement of electric, thermal and mechanical properties [25–34]. Liu et al. [31] used spark plasma sintering (SPS) to prepare Al_2O_3–graphene composite. A 27.20% increase in fracture toughness and a 30.75% increase in flexural strength were obtained with 0.78 vol% GPLs. Walker et al. [30] employed aqueous colloidal processing to obtain uniform and homogeneous dispersions of GPLs and Si_3N_4 ceramic particles which were then densified by SPS. The measured fracture toughness of monolithic Si_3N_4 (2.8 MPa $m^{1/2}$) increased to 6.6 MPa $m^{1/2}$ by 235% with 1.5 vol% GPLs.

In this study, we focus on the preparation of silicon nitride composites reinforced with GPLs by two different methods, hot pressed sintering and pressless sintering. Microstructures of the GPLs reinforced Si_3N_4 composites fabricated by the two methods were investigated and analyzed using Field Emission Scanning Electron Microscopy (SEM). Components of the composites were characterized using X-ray diffraction (XRD). Density and mechanical properties, including flexural strength and fracture toughness of the ceramic composites, were measured. The effect of GPLs contents on the mechanical properties of the ceramic composites prepared by the two methods was compared and discussed.

2. Experimental procedure

2.1. Preparation process

The starting powder mixture used for the fabrication of composite materials consists of α-Si_3N_4 powder (supplied by Xingrongyuan Technology Co. Ltd., Beijing, China) with a purity of 99.9% and an average particle size of 2 mm, sintering additives (5 wt% Y_2O_3, 2 wt% Al_2O_3 and 1 wt% MgO) and filler material graphene (G-100, purchased from Shanghai Simbatt Energy Technology Co. Ltd.). N-methyl pyrrolidone (NMP) solvent from Aladdin Industrial Corporation was also purchased. The powders were blended to obtain mixtures containing 0, 0.2, 0.5, 1, 2, 5 and 10 wt% of GPLs. The GPLs and α-Si_3N_4 particles were dispersed in NMP solvent by bath sonication for half an hour, followed by a ball milling procedure at 400 rpm in a planetary ball mill for 12 h. Such a high filling of the milling chamber aimed at well dispersing and destroying graphene agglomerates. The milled slurry mixture was extracted through the sintered-glass filter funnel to pump out the solvent and then the as-received mixture was dried under 120 °C in an oven for 24 h. Finally the dried powder mixture was ground and sieved using a 120 mesh sieve.

Bulk composite samples were sintered through hot pressed sintering process and pressureless sintering process respectively. In the process of hot pressing, the powder mixtures were poured into a graphite mold of 70 mm in diameter. Graphitic papers with 1 mm thick were placed between the powder and the mold or punch and the powder for easy removal of the sintered samples. The preforms in the graphite mold were heated to 1200 °C for 1 h and then elevated to the maximum temperature of 1750 °C in 1 h. Next the composites were heat treated at 1750 °C for 1 h and then cooled down to the room temperature with the furnace. The whole process was carried out in a nitrogen flow under a uniaxial pressure of 20 MPa. Sintered composites with a dimension of 30 mm × 40 mm × 5 mm were obtained. The temperature was measured and controlled using an optical pyrometer. Shrinkage, displacement, heating current, and voltage were also recorded during the sintering processes.

In the process of pressureless sintering, the powder mixture were cold-pressed into the preforms with a dimension of 40 mm × 40 mm × 5 mm which were then packaged, vacuumized and cold isostatically pressed at 150 MPa in the cold isostatic press (KJYS-200). After that, the preforms were sintered in a nitrogen flow at atmospheric pressure. The temperature program of the pressless sintering was the same as hot pressing process. Sintered specimens with a dimension of 40 mm × 40 mm × 5 mm were obtained.

2.2. Characterization and tests

Density of the ceramic composites was measured by Archimedes' method and relative density was calculated by dividing bulk density with the theoretical density of the powder mixture. Microstructure and morphology of the surfaces and fractures of Si_3N_4–graphene composites were observed by scanning electron microscopy (SEM, Sirion200). X-ray diffraction (XRD, ADVANCED D8) were carried out in order to obtain the components of the obtained ceramic composites.

Flexural strength of the composites was measured via three-point bending test (WDW-100) with a span length of 30 mm and a loading speed of 0.5 mm/min and, five rectangular specimens with a dimension of 35 mm × 4 mm × 3 mm were tested to obtain an average strength. Fracture toughness (K_{IC}) of the composites was measured by single edge notched beam method. Five specimens with a dimension of 30 mm × 2.5 mm × 5 mm were tested to obtain the average toughness.

3. Results and discussion

3.1. Microstructure characterization

The high stability exhibited by GPLs/NMP dispersions allows the homogeneous mixing of GPLs (<5 nm in thickness) with Si_3N_4 powders via sonication and ball milling. Following the solvent extraction through sintered-glass filter funnel, the Si_3N_4–graphene intermixing was preserved, as illustrated in Fig. 1a, which shows that the graphene flakes were well dispersed in the matrix powders.

The sintered ceramic composites were fractured and their micro-structures were examined. Fig. 1b–d show the SEM images of fracture surfaces of the composites with GPLs. Upon hot pressing, the graphene sheets remain relatively flat (see inset in Fig. 1b). Meanwhile, there were often two or more GPLs stuck closely together. These multi-platelets tended to be distributed intergranuarly in the matrix grain boundaries and were often connected with some porosity, which can prevent the migration of the grain boundaries. While in the process of pressureless sintering, single graphene sheets were tucked and wrapped around the matrix grains, as is shown by the arrows in Fig. 1d. Besides, pores were frequently observed and the edges of the graphene platelets tend to scroll, even formed tubular structures (see inset in Fig. 1c and d). The two-dimensional structures of graphene have been postulated to be intrinsically unstable because long-wavelength fluctuations destroy the long-range order of 2-D crystals according to the Mermin–Wagner theorem [35]. It is the intrinsic microscopic undulations that have contributed to the stability of the suspended 2-D graphene sheets. Therefore, this kind of 2-D crystal embedded in 3-D space has a tendency to crumple [35]. Thus, in the process of pressureless sintering, ubiquitous tubular structures within the residual pores as well as the undulations imposed by the Si_3N_4 substrate surface morphology can be observed. Compared to the pressureless sintering process, the load applied to the die containing the Si_3N_4–graphene mixtures during hot pressing enabled the stability of the flat morphologies, thus leading to less porosity and avoiding the scrolling of the graphene sheets edges. In addition, the homogeneous distribution of the GPLs was well preserved by the constant load throughout densification.