Structural stability studies of graphene in sintered ceramic nanocomposites

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Abstract

The post-sintering structural stability of graphene in alumina nanocomposites synthesised by Spark Plasma Sintering (SPS) and Hot Pressing (HP) was compared. Raman spectroscopy, thermogravimetric analyses and electrical conductivity analyses were conducted to characterise degradation of graphene due to the utilisation of different sintering techniques and conditions. Scanning Electron Microscopy confirmed good dispersion of graphene in SPSed and HPed sample. Graphene in SPSed and HPed nanocomposite samples sintered using longer durations (60 min) were found to possess higher crystallinity, thermal stability and electrical conductivity as compared to SPSed samples sintered using shorter sintering durations (10–20 min). This was attributed to the thermally induced graphitisation caused by longer sintering durations, which was lacking in SPSed samples processed using shorter sintering durations and lower temperature. No additional effect of DC pulsed current on the structural stability of graphene for nanocomposites were observed for samples prepared by SPS.
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1. Introduction

The addition of graphene in ceramics is becoming a widely researched area because of its superlative nature and significant positive contribution to ceramics' performance. Over the past few years, graphene has attracted enormous research attention for its very mechanical and thermal properties and exceptionally high electron mobility [1]. Significant improvements in the mechanical, thermal and electrical properties of ceramics nanocomposites filled with graphene. Graphene has been added in ceramics likes cordierite [2], silicon carbide [3], silicon nitride [4], tantalum carbide [5], alumina [6], zirconium diboride [7], zirconia [8], boron nitride [9] to enhance not only electrical properties but also thermal conductivity, refractory, mechanical, antifriction, anticorrosive and biocompatibility properties for diverse applications [10]. For example, a remarkable 235% improvement in fracture toughness was reported for by the addition of only 1.5 vol% of graphene in silicon nitride [4]. Zhou et al. [2]

reported an increase of 8 orders of magnitude and 3.7 times in the electrical and thermal conductivity of cordierite ceramic respectively. Similarly, zirconium diboride filled with graphene, sintered at 1900 °C, was studied by Yadhukulakrishnan et al. [7] for possible high temperature barrier applications for space vehicles during the re-entry event.

Whilst much of the emphasis is on the improvement of thermal, electrical and mechanical properties, there is no research about the graphene's structural health after sintering. For carbon nanotubes, structural and chemical degradation of carbon nanotubes during non-SPS techniques has been widely reported in the literature due to the relatively long sintering time (3–10 h) and high temperatures involved (> 850 °C) in the sintering process [11–18]. Therefore, it is widely perceived in the ceramic community, that graphene would be degraded if non-SPS techniques are used for processing ceramic–graphene nanocomposites.

There are very few research papers reporting the use of non-SPS techniques for processing ceramic–graphene or ceramic–graphene oxide nanocomposites with improved characteristics [19–23]. For example, Rutkowski et al. [19] used conventional hot-pressing for

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processing silicon nitride–graphene nanocomposite and reported improvement in thermal properties [19]. Recently, Mehrali et al. [21] produced calcium silicate–reduced graphene oxide by Hot Isostatic Pressing (HIP). Adding reduced graphene oxide to pure calcium silicate increased the hardness of the material by similar to 40%, the elastic modulus by similar to 52%, and the fracture toughness by similar to 123% [21]. Kvetková et al. [22] compared gas pressure sintering and HIP for processing silicon nitride–graphene nanocomposites and reported mechanical properties of the sintered nanocomposites. Similarly, Tapaszto et al., prepared silicon nitride–graphene nanocomposites by SPS and HIP techniques [23]. In comparison to SPSed nanocomposites, lower elastic modulus, fracture toughness and Vickers hardness was observed for silicon nitride–graphene nanocomposites due to the presence of a weaker beta phase in HIPed sample [23]. However, in all these research papers [19–23], no comments were made on the structural and chemical stability of graphene in any of these reports.

In this study, Raman spectroscopy, Thermogravimetric analyses and electrical conductivity analyses were conducted to characterise degradation of graphene due to the utilisation of different sintering techniques and conditions. Particularly, Raman spectroscopy has been used previously by Centeno et al. [24] to study in detail the orientation of graphene in the graphene/alumina composites and to evaluate and optimise the in situ graphene thermal reduction process in the SPS. Similarly, Badaran et al. [20] characterised reduction of graphene oxide using Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR) for processing hydroxyapatite–graphene nanocomposite. However, no comments were made on the structural quality and crystallinity of graphene in these reports and no comparisons were made with other sintering techniques. To date, there is no report comparing the effect of sintering process on the structural and chemical stability of graphene after processing of ceramic–graphene nanocomposites. Therefore, in this study, we systematically compared the effect of processing techniques (i.e. SPS and HP) on the structural and chemical stability of alumina–graphene nanocomposites.

2. Experimental details

Alumina and alumina–3 vol% graphene nanocomposites were sintered. Graphene nanopowder (chopped nanoribbons flakes produced by the CVD pyrolysis of a solution containing ethanol, ferrocene and thiopene as reported in [25]) were dispersed in dimethylformadie, DMF [26] using high power tip ultrasonication for 45 minutes and then hand-mixed with alumina nanopowder (Sigma-Aldrich, UK: gamma phase; particle size < 50 nm; surface area 35–43 $m^2 g^{-1}$; melting point 2040 °C; and density 3.97 g cm^{-3}) for 10 min. The liquid mixture was rotation ball milled for 8 h. It was then dried at 65 °C for 12 h using a rotary drier containing milling media (4 mm alumina balls), followed by vacuum oven drying at 100 °C for 60 h. To avoid re-agglomeration of graphene during lengthy drying, the alumina balls (milling media) was added during rotary drying. The dried nanocomposite powder was ground and sieved at 150 mesh and then placed again in

the vacuum oven at 100 °C for another 60 h to thoroughly extract the solvent. Nanocomposite pellets (diameter 20 mm and thickness 4 mm) were prepared by Spark Plasma Sintering (SPS), which is an advanced rapid processing technique for sintering advanced ceramic systems [27]. LABOX 350 (Sinter Land Inc., Japan) furnace was used for SPS. A pressure of 10–70 MPa was applied concurrently with the heating (rate 25–50 °C min^{-1}) and released at the end of the sintering period, which was 8–60 min. Sintering temperature for all nanocomposites were in the range 1250–1450 °C. For comparison, the prepared nanocomposite powders were also hot pressed at 10 MPa in a graphite die (20 mm in diameter) for 45–60 min. For SPS, a pulsed DC current with 5 μs ON and 5 μs OFF was used without any pause. Uniaxial hot press furnace, supplied by OXY-GON (USA) was used and to achieve optimal samples for comparison, the hot pressing temperature was in the range of 1250–1550 °C. Alumina samples were also fabricated using the same SPS and hot pressing procedures but without any addition of graphene.

All of the sintered samples were ground using SiC paper down to 4000 grit. The density of the ground samples was measured using the Archimedes' water buoyancy method and also verified by a manual Heliulm multipycnometre (Quantachrome UK). All samples were then thoroughly dried in an oven for 24 h and then diamond polished using 1 μm paste. Sintered nanocomposite samples were gently fractured and their micro structures were examined in an FE-SEM. Cross-sectional surfaces were gold coated and observed in an ultra-high resolution analytical FE-SEM (Hitachi, SU-70) using 20 keV. The Raman spectra were obtained on a Kaiser HoloLab 5000 system with an Nd:YAG laser excitation source of 532 nm (2.33 eV). The Raman laser was focussed on different areas of fracture surfaces, avoiding the near surface regions. Spectra were detected with an imaging photomultiplier (1024 × 1024) with 5 cm^{-1} resolution. Typical collection time was 70 min for each sample and at least 5 locations/ sample were examined for accurate quantification of the ratios of the intensities for different bands (i.e. D, G and G′). Thermogravimetric analysis (TGA) was conducted for all nanocomposites to evaluate graphene oxidation temperature using TA Instruments SDT Q600. Q500 (TA instruments) was used with a heating rate of 5 °C/min to 1000 °C in air. All specimens were examined on platinum pans in the range 30–1000 °C. A heating rate of 5 °C/min in flowing air (at 180 ml/ min) was used. Sample masses ranged from 40 to 50 mg and at least 3 samples were oxidised for each composition of selected nanocomposites. For evaluating electrical conductivity, a bar (dimensions: $18 × 3 × 4$ mm^3) was cut from each sintered pellet using precision and deformation-free cutting machine (Accutom-50). At least 5 bars were produced for each composition and around 500 μm of material was removed from all surfaces of sample by fine grinding. Four-point method [6] was employed by using a resistivity/ Hall measurement system (Quantum Design, PPMS, Model 6000) for measuring electrical conductivities of nanocomposites. For pure alumina samples, high resistance metre (HP 4329A) was used to measure the conductivity. The connecting wires in the