Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 35 (2015) 2723–2731

www.elsevier.com/locate/jeurceramsoc

Enhanced electrical conductivity of silicon carbide ceramics by addition of graphene nanoplatelets

Benito Román-Manso [a], Eddy Domingues [b], Filipe M. Figueiredo [b,*], Manuel Belmonte [a], Pilar Miranzo [a,**]

[a] *Institute of Ceramics and Glass (ICV-CSIC), Kelsen 5, 28049 Madrid, Spain*

[b] *University of Aveiro, Dep. of Materials & Ceramic Eng., CICECO, Campus de Santiago, 3810-193 Aveiro, Portugal*

Received 13 February 2015; received in revised form 27 March 2015; accepted 30 March 2015
Available online 19 April 2015

Abstract

The paper describes the fabrication by liquid-phase spark plasma sintering (SPS) of composites of dense silicon carbide (SiC) with up to 20 vol.% graphene nanoplatelets (GNPs), and discusses the relationships between composition, microstructure and electrical conductivity. The structural integrity of the GNPs is preserved during the whole process, as observed by Raman spectroscopy. The effects of the applied pressure (50 MPa) during SPS result in the preferential orientation of the GNPs perpendicular to the pressing axis and anisotropic electrical behaviour. The electrical conductivity measured in the direction perpendicular to the SPS pressing axis is 4 to 6 times higher than the parallel counterpart. The conductivity increases up to three orders of magnitude with increasing GNPs fraction, reaching values of 4380 S m^{-1} at room temperature for materials with 20 vol.% GNPs. The conduction mechanism of the composite is analysed as a function of the GNPs content.

Keywords: SiC; Graphene nanoplatelets; Composites; Spark plasma sintering; Electrical conductivity

1. Introduction

Increasing the electrical conductivity of structural ceramics is key for applications that require, for instance, static charge dissipation in mechanical devices or manufacturing miniaturized complex components using the electro-discharge machining (EDM) technique [1–3]. Silicon carbide (SiC) is one of the most important structural ceramics. From the electrical conduction viewpoint, SiC is a semiconductor with fairly large band gap energies ranging from ~2.4 to 3.4 eV, depending on the structural polytype [4,5], thus exhibiting low electrical conductivity (σ) (close to 10^{-13} S m^{-1} [6]). However, SiC-based ceramics can be tailored to display very diverse σ values within a range from 10^{-9} to 10^{5} S m^{-1} [6–14], depending on the type of doping, often resulting from sintering additives. In this sense, the case of sintering additives containing nitrogen (N) is especially significant, since N atoms can be incorporated into the SiC lattice substituting for carbon (C) during sintering [15], creating a donor level within the bandgap. The highest σ reported for N-doped SiC (3×10^{4} S m^{-1}) was obtained using 19 wt.% yttrium nitrate ($Y(NO_3)_3{\cdot}4H_2O$) as sintering aid [7]. High conductivities are also obtained with additive systems based on AlN (*e.g.* 2×10^{3} S m^{-1} for AlN–RE_2O_3, RE = Y, Er [8,9]). Comparatively lower σ values (10^{-9}–10^{-1} S m^{-1}) were reported when employing only oxide additives such as Y_2O_3 and Al_2O_3 [6,10–12], depending on the dopant concentration and the nature, location and thickness of grain boundaries.

The incorporation of carbon nanostructures, such as carbon nanotubes (CNTs) or graphene, within ceramic matrices has led to important improvements in σ [16–24] as compared to the unfilled ceramics. Specifically, graphene nanoplatelets (GNPs) have been considered as an important filler candidate for ceramics due to the unique electrical properties of graphene [25], and the high resistance to structural damage of GNPs undergoing the elevated temperatures required for sintering.

* Corresponding author at: University of Aveiro, CICECO, Campus de Santiago, Aveiro, Portugal. Tel.: +351 234401464.
** Corresponding author at: Institute of Ceramics and Glass (ICV-CSIC), Kelsen 5, 28049 Madrid, Spain.
E-mail addresses: lebre@ua.pt (F.M. Figueiredo), pmiranzo@icv.csic.es (P. Miranzo).

http://dx.doi.org/10.1016/j.jeurceramsoc.2015.03.044
0955-2219/

Increments of up to 14 orders of magnitude in room temperature electrical conductivity have been reported for insulating Al_2O_3 and Si_3N_4 matrices, reaching 5.7×10^3 S m^{-1} in Al_2O_3 containing 15 vol.% GNPs [16], and 4×10^3 S m^{-1} for Si_3N_4 with 24 vol.% GNPs [17], where a percolation-type conduction mechanism was proved to occur. Moreover, when using finely exfoliated graphene oxide (GO) as a graphene source, σ values of as high as 700 S m^{-1} were achieved for just 7.2 vol.% reduced GO (rGO) [18]. Both GNP- and rGO-containing composites revealed electrical anisotropy due to a preferential orientation of the carbon nanostructures perpendicular to the SPS pressing axis [17,18], and to the lower conductivity in the *c*-axis as compared to the basal *ab*-plane of graphene [26].

Recently, conducting ceramic composites were fabricated by the *in-situ* formation of graphene-like layers [27,28]. In particular, an aluminosilicate/graphene composite with an in-plane conductivity of 700 S m^{-1} was obtained by carbonization of polyaniline layers [27]. Likewise, SiC/graphene composites with $\sigma \approx 100$ S m^{-1} (~6 orders of magnitude larger than monolithic SiC ceramics) were obtained by some of the present authors growing epitaxial multilayers of graphene (~4 vol.%) *in-situ* at the SiC grain boundaries during the spark plasma sintering (SPS) process[28].

To the best of our knowledge, the addition of pristine GNPs as fillers for the controlled electrical functionalization of SiC ceramics has not been reported so far. In the present study, novel SiC/graphene composite materials have been manufactured by SPS with GNPs additions of up to 20 vol.%. A complete set of electrical conductivity measurements was performed in the two distinct directions to the SPS pressing axis to elucidate the electrical anisotropy and electric transport mechanisms of such complex ceramic systems.

2. Experimental

2.1. Composites manufacture

Different SiC/GNPs composites were prepared varying the content of GNPs from 0 to 20 vol.%. Commercially available GNPs (Angstron Materials Inc., USA, N006-010-P), with 10–20 nm thickness and ~14 μm in the *x*–*y* plane, were first dispersed in isopropyl alcohol by sonication for 1 h in an ultrasonic bath. Simultaneously, powder mixtures of β-SiC powders (BF-17A, H.C. Starck, Germany, mean diameter of 0.5 μm) together with Y_2O_3 (Grade C, H.C. Starck, Germany) and Al_2O_3 (SM8, Baikowski Chimie, France) in the proportions of 93:5:2 in wt.%, respectively, were attrition milled for 2 h in isopropanol using alumina grinding media. The resulting ceramic slurry was mixed with the GNPs suspension and, then, stirred and sonicated for 1 h to obtain a homogeneous mixing of all components. The process follows by evaporating the solvent in a rotary-evaporator at 93 °C, drying at 120 °C and sieving through a 63 μm mesh. For the case of the monolithic material (0 wt.% of GNPs), the isopropanol was directly evaporated from the ceramic slurry.

Subsequently, the powders were placed in the middle of a symmetric SPS graphite die and punches set-up, surrounded by a graphite foil to avoid direct contact between the sample and the graphite. Specimens were thus sintered in a SPS furnace (SPS510CE, SPS Syntex Inc., Japan) at 1800 °C, under moderate vacuum (~6 Pa), using a heating rate of 133 °C min^{-1}, a dwelling time of 5 min, and uniaxial pressure of 50 MPa. The temperature during the SPS process was controlled with a pyrometer focalized in a half-through-thickness hole drilled at the centre of the lateral surface of the graphite die.

2.2. Microstructural characterization

The relative densities were determined by the Archimedes' method using distilled water as the immersion medium. The theoretical density (ρ_{th}) for the monolithic material was estimated as 3.24 g cm^{-3} [28], considering the formulated composition of the raw powders, the oxygen content in the starting SiC converted to silica (1.9 wt.%), and the amount of *in-situ* synthesized graphene (~4 vol.%). In the case of the composites, ρ_{th} was estimated assuming the values for the matrix (3.24 g cm^{-3} as the monolithic material) and for the added GNPs (2.2 g cm^{-3}), which led to 3.19, 3.13 and 3.03 g cm^{-3} for the composites containing 5, 10 and 20 vol.% GNPs, respectively (Table 1).

The microstructural characterization was carried out by field-emission scanning electron microscopy (FESEM; S-4700, Hitachi, Japan), X-ray diffractometry (XRD; Bruker D5000, Siemens, Germany) and confocal micro-Raman spectroscopy (model Alpha300 WITec GmbH, Germany). Fracture surfaces of the composites were imaged by FESEM to check the actual dispersion and orientation of GNPs within the ceramic matrix. Also, the median size and aspect ratio of the SiC grains were estimated from various FESEM micrographs by measuring at least 400 grains using Image J. XRD patterns were collected in step-scanning mode with Cu-*K*α radiation, in a range of detection $10° < 2\theta < 80°$, with a scanning rate of 2° min^{-1} in steps of 0.05°. Raman maps of 10×10 μm^2, with a resolution of 60×60 pixel, and an acquisition time of 20 ms per spectrum, were recorded on the pristine GNPs and on the composites using a laser wavelength excitation of 532 nm. The intensity ratios between the D, 2D and G bands of graphene, as well as the full-width-at-half-maximum (FWHM) of those bands, were evaluated.

2.3. Electrical characterization

Samples machined into bars of $15.0 \times 3.5 \times 2.5$ mm^3 were used to measure the electrical conductivity using a tubular support of alumina employed as holder and placed into a furnace in order to perform the measurements under variable temperature (278–523 K) in an air atmosphere. Data were collected both during heating and cooling to verify the stability of the samples and electric contacts during the measurements. Platinum wires ensured the electrical connections between the samples and the measuring instrumentation. The σ for the directions parallel ($\sigma^{||}$) and perpendicular ($\sigma^{\perp}$) to the SPS pressing axis was measured with 2-probe *ac* and 4-probe *dc* methods, respectively (Fig. 1). The *ac* conductivity data were obtained by collecting impedance spectra (potentiostat/galvanostat/frequency response analyser Autolab PGSTAT20, Netherlands) in the frequency