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Feature article

Anisotropy of functional properties of SiC composites with GNPs, GO and in-situ formed graphene

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ABSTRACT

This paper reports on anisotropy of functional properties of different silicon carbide-graphene composites due to preferential orientation of graphene layers during sintering. Dense silicon carbide/graphene nanoplatelets (SiC/GNPs) and silicon carbide/graphene oxide (SiC/GO) composites were sintered in the presence of yttria (Y_2O_3) and alumina (Al_2O_3) sintering additives at 1800 °C in vacuum by the rapid hot pressing (RHP) technique. It is found that electrical conductivity of SiC/GNPs and SiC/GO composites increases significantly in the perpendicular direction to the RHP pressing axis, reached up to 1775 S/m in the case of SiC/GO (for 3.15 wt.% of rGO). Also, thermal diffusivity was found to increase slightly by the addition of GNPs in the SiC/GNPs composites in the perpendicular direction to the RHP pressing axis. But, in the parallel direction, the addition of GNPs showed a negative effect. The formation of graphene domains was observed in reference sample SiC-Y_2O_3-Al_2O_3 sintered by RHP, without any addition of graphene. Their presence was confirmed indirectly by increasing electrical conductivity about three orders of magnitude in comparison to the reference sample sintered by conventional hot press (HP). Raman, SEM and TEM analysis were used for direct evidence of presence of graphene domains in RHP reference sample.

1. Introduction

Graphene is the thinnest known allotrope of carbon consisting of two-dimensional layers of sp^2 bonded carbon atoms. It was produced for the first time by Geim and Novoselov in 2004 [1]. Graphene has extraordinary combination of properties such as high tensile strength (130 GPa) and Young modulus (~1 TPa) [2], an extremely high thermal conductivity (3000–5150 W/m.K) [3–5], and high room-temperature intrinsic charge carrier mobilities (~200 000 cm^2/V.s) [6]. Graphene is used in the form of graphene nanoplatelets (GNPs) or graphene oxide (GO) as a filler in various ceramic matrices like B_4C [7–9], SiC [10,11], Si_3N_4 [12], Al_2O_3 [13], and yttria-stabilized zirconia [14] in order to improve both functional and mechanical properties. Considerable improvement and anisotropy of electrical conductivity of ceramic composites incorporated with graphene were reported by several authors [8,11,13]. The anisotropy of the electrical conductivity is demonstrated as a result of the intrinsic electrical anisotropy of graphite structures and preferential orientation of graphene after applying uniaxial pressure during sintering which leads to preferable formation of conductive networks of graphene basal planes in the direction perpendicular to the pressing axis. Tapasztó et al. [15] found that more than 80% of the GNPs were oriented within ± 15° deviation from a preferred orientation direction under uniaxial pressure during sintering. Under isotropic pressing, the orientation of graphene platelets in related ceramic composites was random.

This preferable orientation of graphene layers under uniaxial pressing also results in anisotropic thermal diffusivity which changes significantly with increasing the content of the graphene nanoplatelets [8,9,16]. Reduced graphene oxide (rGO) has a num-

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ber of structural defects such as nano-holes, nano-strips, vacancies, amorphous phase of rGO, microcraks, etc. which could negatively affect its thermal properties as well as those of the ceramics composites including it [17].

Addition of carbon nano-filler (carbon nanotubes CNTs, graphene nanoplatelets GNPs, graphene oxides GO) into silicon carbide (SiC) ceramics to enhance mechanical or functional properties hinders densification process and for that reason electrically-assisted techniques of sintering were widely used. Densification of SiC monoliths and composites was enhanced by using electrically-assisted sintering techniques compared to conventional sintering by hot pressing. In-situ formation of graphene domains in such sintered composites was observed. For example, Miranzo et al. [18] reported the formation of graphene in SiC:Y_2O_3:Al_2O_3 ceramics sintered by spark plasma sintering (SPS) as a consequence of thermal decomposition of SiOC/SiO_2 surface layer on the SiC grains. Other authors reported epitaxial growth of graphene on SiC single crystals due to thermal decomposition of SiC at high temperature under vacuum [19–21].

The aim of the present contribution was to investigate the influences of the GNPs and GO additions and the orientation of the graphene layers on the functional characteristics of SiC-graphene composites. The influence of the processing route (rapid hot pressing and hot pressing) on electrical and thermal properties of SiC composites was investigated. In-situ formation of graphene domains in the monolithic SiC samples during sintering was characterized.

2. Experimental

2.1. Powders preparation

In this work, both commercially available GNPs (thickness < 3 nm, purity 99%, lateral size > 2 μm, by Cheap Tubes Inc., USA) and laboratory-synthesized GO were used. For the synthesis of the GO powder, we used a method slightly modififed from Marcano et al. [22]. A mixture of concentrated acids H_2SO_4:H_3PO_4 (180:20 ml, both p.a. quality) was prepared and stirred for 30 min. Then, 4 g of GNPs was added to the mixture and stirred. After that, 24 g $KMnO_4$ (p.a. quality) were added slowly in portions to the mixture to maintain the temperature of the solution below 30 °C. The solution was stirred for 6 h on a magnetic stirrer. The mixture was then poured into ice made of distilled water (500 ml) with 30% H_2O_2 (3 ml) and stirred 30 min. The mixture was filtered through nitrocellulose membrane filters (Pragochema, pore size 0.23 μm) and the collected solid was washed with 30% HCl and later with distilled water for several times. The obtained GO powder was dried at 80 °C overnight. The prepared GO powder was characterized by XRD, FTIR and TGA analyses.

SiC/GNPs composite powders with different contents of GNPs from 1 to 5 wt.% were prepared. Firstly, the appropriate amounts of GNPs were dispersed in isopropanol by intense ultrasonication (Sonopuls HD 3200, 20 kHz, Bandelin electronic GmbH, Germany) through a titanium probe (Ø 13 mm) for a duration of 100 min with a sonication power of 80 W. After that, the SiC powder (Superior Graphite, USA, β-SiC, d_{50} = 0.6 μm), Y_2O_3 (HC Starck, purity > 99.99%) and Al_2O_3 (Taimei Chemicals Ltd., α-Al_2O_3, purity > 99.99%, particle size 100 nm) in proportions of 93:5:2 wt.% were added into the suspensions and ball milled with SiC balls for 24 h. Isopropanol was removed from the homogenized suspensions by a vacuum rotary evaporator. The resulting composite powders were dried at 80 °C overnight and finally sieved through a 71 μm micro-sieve.

Also, SiC/GO composite powders with different contents of graphene oxide from 1 to 5 wt.% were prepared. The appropriate amounts of GO were dispersed in distilled water by intense ultrasonication for 100 min with 80 W. The SiC, Y_2O_3 and Al_2O_3 powders (in proportions of 93:5:2 wt.%) were added into the suspensions and ball milled with SiC balls for 24 h. The prepared suspensions were then sprayed into a liquid nitrogen and water was removed from the frozen powders by a freeze dryer for 24–48 h. Finally, the resultant composite powders were dried at 80 °C overnight and sieved through a 71 μm micro-sieve.

Reference powder composed of SiC-Y_2O_3-Al_2O_3 (93:5:2 wt.%) without any addition of graphene were prepared by ball milling in isopropanol with SiC balls for 24 h. Isopropanol was removed from the homogenized mixtures by using a rotary vacuum evaporator. The powders were dried at 80 °C overnight and then sieved through a 71 μm micro-sieve.

2.2. Sintering

For sintering, the composite and reference powders were placed in a graphite die lined with soft graphite paper (foil) to prevent direct contact between the material and the graphite die. Sintering is performed in rapid hot press (RHP) (DSP 507, Dr. Fritsch GmbH., Germany) in vacuum at 1800 °C for 5 min under a uniaxial pressure of 50 MPa. The heating rates was 100 °C/min. Rapid hot pressing is an efficient sintering technique which applies direct heating of the sample by passing DC current (without pulses) through the die and also sample if it is conductive. It is very similar method to the well-known spark plasma sintering (SPS) technique, however SPS is commonly utilized pulsed DC current. For comparative purposes, the reference powders were sintered by RHP as well as a conventional hot pressing (HP). It is worth noting that the RHP furnace operates with a vacuum level of approximately 5 Pa, while in the HP furnace, a vacuum level of approximately 1 Pa or less could be reached. Details of the RHP and HP sintering regimes are illustrated

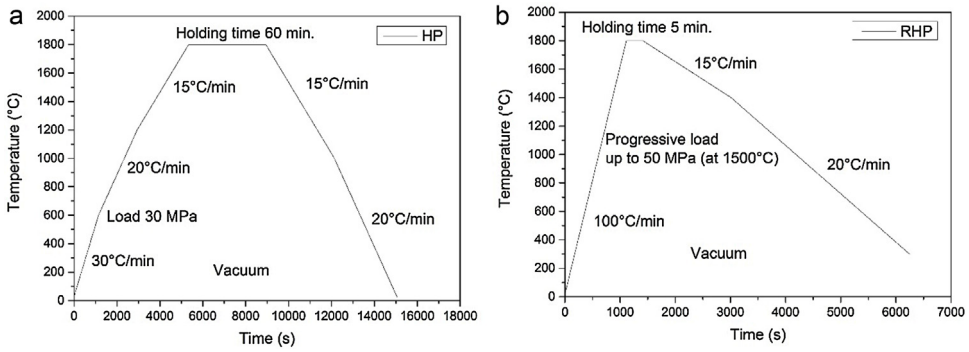

Fig. 1. Schema of sintering regime for (a) hot press and (b) rapid hot press.

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