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Original Article

Tailoring the properties of spark plasma sintered SiAlON containing graphene nanoplatelets by using different exfoliation and size reduction techniques: Anisotropic electrical properties

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A B S T R A C T

Insulating SiAlON ceramics can be machined into complex shapes if the electrical conductivities can be increased with additives. Therefore, the microfluidization technique was used as an alternative to traditional sonication for exfoliation and homogenization of GNPs to investigate the effects of different exfoliation, size reduction and homogenization techniques on the microstructure, electrical conductivity and percolation threshold values of GNPs-SiAlON composites. 2.85, 5.70 and 11.40 vol. % sonicated and sonicated + microfluidized GNPs added into SiAlON matrix and were densified by using SPS technique. Due to their thinner and smaller platelet size, microfluidized GNPs dispersed more homogeneously compared to the sonicated GNPs in the SiAlON matrix. Electrical conductivities of the microfluidized GNPs-SiAlON composites were ~70–200% higher than sonicated GNPs-SiAlON in the both measured directions. Lower percolation thresholds were achieved when sonicated + microfluidized GNPs used in comparison to sonicated GNPs containing composites. Electrical conductivities in the in-plane direction were also higher than through-plane direction.

1. Introduction

Silicon-aluminum-oxynitride (SiAlON) ceramics are the solid solution of silicon nitride (Si_3N_4) containing Al_2O_3 and other metal oxides. SiAlON ceramics with good mechanical and thermal properties are widely utilized in emerging engineering applications such as wear components, high-speed cutting tools, gas turbine engine components, metal forming tools, seals and bearings, etc. [1,2]. In addition, they may have new and special applications such as functional components in micro-electro-mechanical systems if they can be machined in to complex shapes [3]. However, due to their high hardness, machining of the SiAlON ceramics into complex shapes by using traditional methods including diamond grinding or lapping is quite slow and expensive [4]. Meanwhile, highly precise complex shaped ceramic components can be easily obtained by using electrical discharge machining (EDM) provided that the electrical conductivity of the ceramic materials to be machined exceeds $1\,Sm^{-1}$ threshold value [5].

In recent years, graphene nanoplatelets (GNPs), which has outstanding electrical conductivity ($10^7\,Sm^{-1}$) [6], are accepted as the most promising candidate to give electrical conductivity to insulating ceramic matrices. Insulating engineering ceramics such as Al_2O_3 [7], Si_3N_4 [8], AlN [9] and ZrO_2 [10] etc. became electrically conductive even at low percolation threshold values with the addition of GNPs.

The homogeneous dispersion of GNPs without agglomeration in the matrix material is quite effective on improved properties and applications of composites. Since the dispersion of the GNPs depends on their size and thickness, the homogenization techniques applied to overcome the Wan der Waals bonds, which cause GNP agglomeration, become very important [11,12]. There are several studies investigating the effects of different GNPs homogenization techniques on the mechanical and thermal properties of ceramic matrix composites [11,12] but have not focused on the effects on electrical conductivity. On the other hand, the effects of GNPs addition and GNPs homogenization by different techniques such as sonication and microfluidization on the mechanical, thermal properties and microstructures of the SiAlON matrix composites were studied in our previous study [11]. We have reported that the microfluidization technique well exfoliated the GNPs in z- direction as well as reduced their dimensions in the x- and y- directions while the sonication process only de-agglomerates the GNPs. As a result, the microfluidized GNPs exhibited a more homogeneous distribution in the SiAlON matrix compared to the sonicated GNPs. Thus, the SiAlONs containing microfluidized GNPs had higher hardness and fracture toughness and lower thermal conductivities than the SiAlONs containing sonicated GNPs.

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Uniaxial pressure applied during sintering techniques such as spark plasma sintering (SPS) and hot pressing (HP) generally used to produce highly dense GNPs-ceramic matrix composites causes the basal planes of GNPs to be oriented perpendicular to the pressing axis and thus leads to anisotropic properties [8,13–15]. Therefore, the goal of this work was to determine the effects of the microfluidization technique as a new approach in the homogenization of GNPs, on the microstructure, electrical conductivity and percolation threshold values of the SPSed SiAlON matrix considering the anisotropy. In order to clearly demonstrate the effects of the microfluidization technique, GNPs have also been prepared by using traditional sonication method.

2. Materials and methods

The GNPs (Graphene Chemical Industries Company) used in this study has the following properties: 99.9% purity, ~120–150 m^2/g specific surface area, ~ 5–8 nm average flake thickness and ~5 μm average platelet diameter. The GNPs homogenized by two different techniques. As a first technique, GNPs were exposed to sonication (Sonics, 750 Vef) for 3 h. In the second technique, sonicated GNPs for 3 h were 16 times passed through a microfluidizer (Microfludics Corp.). Two differently treated GNPs were called as either sonicated GNPs or sonicated + microfluidized GNPs during the study.

The GNPs prepared by two different techniques and SiAlON matrix forming powders consisting of α-Si_3N_4 (UBE Industries Ltd., Japan), Al_2O_3 (Alcoa-A16SG), AlN (Tokuyama, H type, d50: 2–2.4 μm, Japan), Sm_2O_3 (99.9% purity, Stanford Materials Corp., USA), Y_2O_3 (99,9% purity, H.C. Starck Berlin, Germany), $CaCO_3$ (Reidel-de Haen, Germany) were mixed by using sonication followed by plenatary ball milling (Fritsch, Pulverisette) in the isopropanol medium. Then, the isopropanol removed from the GNPs-SiAlON powder mixtures in a rotary evaporator (Heidolph). Pure SiAlON and 2.85, 5.70 and 11.40 vol. % sonicated and 2.85, 5.70 and 11.40 vol. % sonicated + microfluidized GNPs containing SiAlON composites were produced by using SPS furnace. Sintering processes were carried out at 1875 °C and under uniaxial pressure of 50 MPa for 15 min. The details of production steps of the materials were reported in the previous publication [11].

Since the GNPs orientations in particular directions through the SiAlON matrix resulted in the anisotropic microstructures and properties, the measurements were performed in the both through-plane (//) direction which is parallel to the SPS pressing axis and in-plane (⊥) direction which is perpendicular to the SPS pressing axis [14]. After cutting, an automatic polisher (STRUERS, TegraPol-25) was used to prepare a sample from pure SiAlON whereas argon ion polisher (CP, Jeol SM-09010) was preferred for the GNPs containing composites due to the pull outs and fractures of GNPs during mechanical polishing [11]. The backscattered electron images (BSE-SEM) of the pure SiAlON and GNPs-SiAlON composites were taken in the scanning electron microscope (SEM-Zeiss, SUPRA 50 VP).

The Lotgering factor (LF) values of the GNPs were calculated by using equation developed by Lotgering [16]. XRD peak intensities of GNPs from sintered and powder forms of composites were used for LF calculations and details were explained somewhere else [11].

Electrical conductivities of the samples in the through-plane and in-plane directions were measured with a digital micro-ohmmeter by using two point method (Agilent, 4294 A). All samples were cut to dimensions of 5 mm × 5 mm × 2 mm (l*w*h) to eliminate the effects of different sizes on the measurements. Before electrical conductivity measurements, surfaces to be measured were prepared by sputtering a thin Au-Pd film. At least ten measurements were taken from each sample and the average values were used.

3. Results and discussion

3.1. Microstructural investigations

BSE-SEM images of the only sonicated and sonicated + microfluidized GNPs given in a previous work [11] demonstrated that the traditional sonication only de-agglomerates the GNPs whereas microfluidization technique successfully exfoliate and thin the GNPs in the z-direction. Furthermore, the microfluidized GNPs were smaller and have a narrower platelet size distribution compared to the only sonicated GNPs. Raman analysis of untreated, sonicated and sonicated + microfluidized GNPs were also given in a previous work showed that untreated and only sonicated GNPs were mostly multilayered structures and some of them were few layered. On the other hand, it was determined that the microfluidization process led to few layered GNPs with predominantly less than 3 layers.

As an example, Fig. 1 shows the BSE-SEM images of the pure SiAlON, 2.85 vol. % sonicated and 2.85 vol. % sonicated + microfluidized GNPs containing SiAlON matrix composites. The sonicated GNPs were dispersed inhomogeneously (Fig. 1c, e) whereas sonicated + microfluidized GNPs exhibited a more homogeneous dispersion in the microstructure of the SiAlON matrix due to the smaller and thinner platelet size (Fig. 1d, f). Additionally, it was obvious from Fig. 1 that GNPs addition caused grain size reduction of SiAlON matrix and the details were discussed elsewhere [11].

The Lotgering factors (LF) of GNPs in the through-plane (//) direction were calculated using XRD peak intensities to investigate the effect of GNPs orientation on the properties of resulting materials (Table 1). As the LF value approaches 0, random orientation increases, while closer to 1 perfect orientation is achieved. The LF of the only sonicated GNPs for the same quantities were higher than sonicated + microfluidized GNPs. As a result of having a smaller platelet size, the sonicated + microfluidized GNPs were less oriented in through-plane direction throughout the SiAlON microstructure compared to the only sonicated GNPs. On the other hand, when the quantity of GNPs increased, the LF also increased for both type of GNPs. The highest LF value was obtained for 11.40 vol. % sonicated GNPs containing SiAlON.

3.2. Electrical properties

The room temperature DC electrical conductivity values of the pure SiAlON and GNPs-SiAlON composites in the through-plane (//) and in-plane (⊥) directions were measured and given in Table 1. Also, these values are plotted as a function of GNPs content in Fig. 2. Pure SiAlON exhibited electrically insulator behavior with exceptionally low conductivity value of $\sim 10^{-9}\,Sm^{-1}$ (Table 1). However, the electrical conductivity value of the SiAlON sharply increased to around $10^{-1}\,Sm^{-1}$ with the addition of 2.85 vol. % GNPs prepared by both techniques. After this point, the increment in the electrical conductivities of the composites declined with the further increase of the GNPs. Fig. 2 clearly shows that both through-plane and in-plane directions electrical conductivities of all composites containing sonicated + microfluidized GNPs were higher than those containing only sonicated GNPs at the same GNPs content, thereby, indicated the positive effects of preparing the GNPs by microfluidization technique on the improvement of the electrical conductivities of ceramic matrices. Fig. 2 also exhibited the conductivity differences between sonicated and sonicated + microfluidized GNPs containing SiAlON composites and the electrical conductivities of composites containing sonicated + microfluidized GNPs were from ~70% to more than 200% higher than SiAlON containing only sonicated GNPs.

On the other hand, the electrical conductivity values of the composites were displayed anisotropic behavior due to orientations of the GNPs in the SiAlON matrix microstructure and were higher in the in-plane (⊥) direction compared to the through-plane (//) direction