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Spark plasma sintering of layered γ-Al_2O_3/graphene reinforced nanocomposites

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Abstract. Multi-layered ceramic composites with alternation of grain sizes in layers were produced by adding thin interlayers of graphene-augmented alumina nanofibres (GAIN) between layers of monolithic α-Al_2O_3. The composite was mounted layer by layer directly in the graphite mould, using a vacuum filter system to precipitate alumina nanopowder and GAIN layers from the corresponding suspensions. The 30-mm diameter samples were consolidated by the spark plasma sintering technology at 1450 °C in nitrogen atmosphere at 50 MPa pressure. The effect of interlayers on the microstructure of alumina and on the thermal and electrical conductivity of the compact is studied.

Key words: nanofibre, hierarchical structures, nanocomposites, spark plasma sintering.

1. INTRODUCTION

Densification of ceramic composites is one of the most important factors influencing mechanical properties of products. In order to achieve full density, the relevant thermal and mechanical parameters have to be optimized so that sintering would be fully accomplished. In the meantime, if the total thermal and mechanical stresses exerted on the grains exceed a certain threshold, grain growth may occur, which will, in turn, affect the mechanical properties of the structure. Furthermore, in the case of ceramics, occurrence of transitions to other polymorphisms of the compound is not too far-fetched.

To achieve the lowest grain growth possible spark plasma sintering (SPS) is a suitable technique, allowing rapid heating and slow cooling rates. Among the wide family of ceramics, alumina plays an important role as a structural ceramic due to its exceptional properties, such as high hardness, oxidation resistance, and stability at high temperatures. As it was previously reported, grain growth in ceramic matrices could be inhibited by the incorporation of graphene-based fillers such as carbon nanotubes [1], graphene nanoplatelets [2,3], and reduced graphene oxide [4], whereby the inhibition depends on the amount of these additives. As previously reported in [5], graphene-augmented alumina nanofibres (GAIN or ANFC) used as additives in the alumina matrix also lead to a significant grain refinement. The approach of using a ceramic substrate for the graphene layers gives outstanding results with only a small amount of graphene (~0.3–1 wt%) dispersed in the composite. In addition, the graphene-augmented alumina fibres add new functionalities to alumina such as high thermal and electrical conductivities. Integrating functional layers into a ceramics structure offers a wide range of benefits from anisotropic thermal and electrical properties to the enhancement of fracture toughness of the structure.

An extraordinary approach to stop fracture propagation in ceramics structures is to delay the catastrophic failure using laminated ceramics. Laminated ceramic com-

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posites can be designed with weak interfaces in between the layers of the ceramic. In this case delamination and deflection of the crack in the 'weak interfaces' of lower fracture resistance will increase the work needed for the crack to break through all the layers [5]. It is worth mentioning that by decreasing the grain size in micro-grained alumina, fracture toughness firstly undergoes an enhancement before a decline to lower values than the initial point [6]. For the finer grained alumina (<~3 μm) the fracture toughness is reported to be independent of grain size and is considered as an intrinsic property [7]. Belmonte et al. [8] developed a layered structure of graphene and Si_3N_4 and detected an enhancement in toughness values (≈7.8 MPa $m^{1/2}$) together with an increase of the electrical conductivity by 16 orders of magnitude.

In this work, a new method of stacking alternating layers of alumina and graphene-augmented alumina nanofibres is introduced. A grain size refinement with a gradient in size in the functionally graded structure is reported. The obtained composites were consolidated using an FCT Systeme GmbH, Germany, spark plasma sintering furnace. A set of tests were performed to investigate the optimal sintering conditions taking into consideration the relative density of the sintered samples. The grain sizes in the composites were controlled by incorporating thin layers containing very small amounts of GAIN uniformly dispersed across the layer. The effect of the GAIN-containing layers on the microstructure and mechanical properties of the composites is discussed.

2. MATERIALS AND METHODS

Commercially available α-alumina nanopowder with an average particle size of 100 nm (TM-DAR, Taimei, Japan) was used as the inner and punching ceramics layers. A few layers of graphene-encapsulated alumina nanofibres were used as nanofillers applying the chemical vapour deposition (CVD) method, described in detail elsewhere [9,10]. The fibres of about 40 mm in length and average single fibre diameter of about 20 nm were manually ground in a mortar before further treatment and deposited directly into the graphite SPS mould. Two layers of monolithic alumina were added on the sides. The moulds were closed from both sides by graphite discs and graphite punches, and the sample was sintered with FCT Systeme GmbH spark plasma sintering at 1450 °C at 50 MPa pressure (Fig. 1) in N_2 atmosphere. The dwell time was 10 min, and a slow cooling rate of 50 °C/min was applied.

The morphological study of the obtained structures was performed by scanning electron microscope (SEM Zeiss EVO MA 15, Germany) equipped with an energy

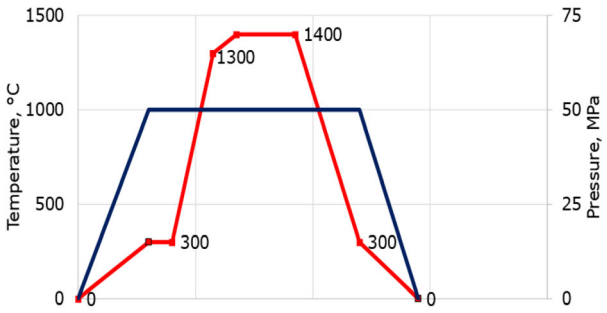

Fig. 1. Schematic diagram of the spark plasma sintering process for high-temperature sintering.

dispersive X-ray spectrometer (EDS) with voltage of up to 20 kV and magnifications up to 50 kX. The density of the sintered compacts was assessed using the Archimedes method with distilled water as the immersion medium. The rule of mixtures using the manufacturers' density specifications for alumina powder (3.95 g cm^{-3}) and alumina fibres (3.65 g cm^{-3}), a published density value for graphene (2.2 g cm^{-3}), and the target fillers volume was used to calculate the relative densities. Raman spectroscopy with a Horiba Jobin Yvon LabRAM 300 spectrometer equipped with a 633 nm laser wavelength excitation was used to determine the degree of structural perfection of sp^2 carbon and the presence of graphene in the sintered product. A steady-state thermal conductivity in-situ setup was used in order to investigate the heat conduction of the material. A two-probe DC electrical conductivity method was used to measure electrical properties of the structure.

3. RESULTS AND DISCUSSION

Figure 2 shows an SEM image of the sectional view of the sample after SPS. The image reveals that the area where GAIN fibres are concentrated is easily detectable in the sample, having a thickness of ~1.5 μm with a high porosity level, surrounded by an ~10 μm thick area where alumina grains are heavily refined. Outside the area influenced by the presence of GAIN, coarse alumina grains with an average grain size of 4.6 μm (largest up to ~9 μm) can be observed. This area is fully dense, and no porosity can be detected on the polished surface of the sample. In the higher resolution micrograph (Fig. 3) of the GAIN-containing layer, small particles with diameters of ~15–20 nm can be observed on the surface and in between the grains. These particles are residues of the GAIN that have disintegrated, supposedly, due to the phase transformation of γ-Al_2O_3 to α-Al_2O_3. Alumina grains in this area have a more oblate shape, having smaller dimensions in the direction perpendicular to

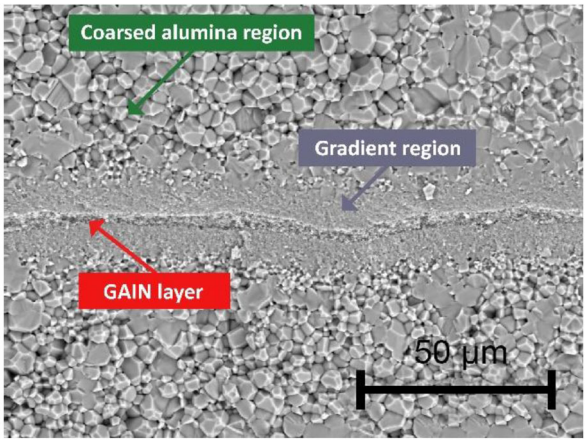

Fig. 2. SEM image of the cross-section of the sample after SPS demonstrating a single layer of graphenated fibres in between layers of monolithic alumina.

the plane of the layer. The layer is notably porous; this can be explained by the high concentration of fibres in between the grains, which at first prevented the alumina powder from compacting and then impeded grain growth during the sintering. The grains in the area around the GAIN-containing layer (~10 µm thick layer) show a gradual change in size, from ~0.25 µm in the vicinity of the fibres-containing layer, increasing to ~3 µm and larger toward the outside. In contrast to the GAIN-containing layer, in the area with rather unnoticeable porosity neither GAIN nor their residues can be observed in this region.

On the other hand, an indirect impact of fibres on the microstructure of the adjacent area during sintering cannot be omitted. In this case, the mechanism of the grain refinement in the adjacent area can be attributed to the fact that the GAIN fibres are electrically conductive; therefore, Joule heating and/or remote Joule heating occurs in the mould under the electrical discharge of SPS [11]. This phenomenon causes the local temperature in the areas surrounding the conductive layer to be relatively higher than in the far regions during the dwell time. However, a counterintuitive fact, which was addressed by Ghosh et al. [12], shows that the entropic contribution to the grain boundary energy causes the interfacial energy to fall as the temperature rises in a specific range of the electrical field in field-assisted approaches. Therefore, according to Raj et al., 'a local rise in grain boundary temperature can create a potential well, which opposes the migration of the boundary to the adjacent matrix where the temperature is cooler. This mechanism cannot apply at very high fields. The local pinning of grain boundaries is counterbalanced by high grain boundary diffusivity due to local Joule heating' [13]. In addition, due to the higher thermal conductivity of the GAIN fibres compared to alumina, heat extraction during the SPS cooling process is more efficient. Therefore, the grains in the vicinity of the layers release the thermal excitation faster than the regions of monolithic alumina. Room temperature thermal conductivity measured by a steady-state method was 55 $Wm^{-1}K^{-1}$ considering the entire cross-section of the sample. This value is an improvement on 30 $Wm^{-1}K^{-1}$ thermal conductivity of a monolithic alumina reference. However, considering the thin cross-section of the GAIN layers, the measurement suggests an incredibly high thermal conduction of 2160 $Wm^{-1}K^{-1}$. Indeed, the theoretical values for multiwall carbon nanotubes are as high as 3000 $Wm^{-1}K^{-1}$ [14] and for single-walled carbon nanotubes reach an incredibly high value of

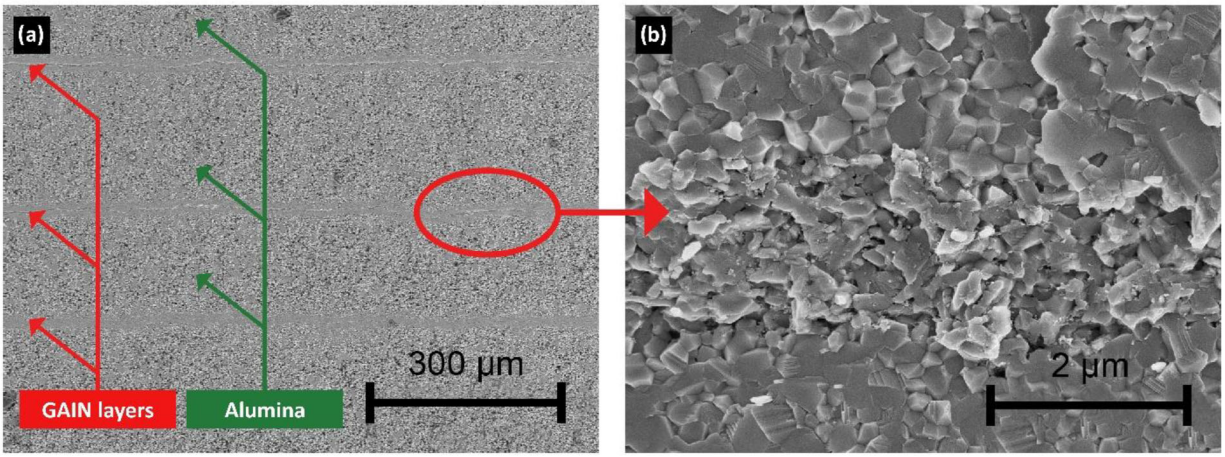

Fig. 3. SEM image of GAIN layers (a) and of the zoomed region demonstrating the grain size gradient (b).

6600 $Wm^{-1}K^{-1}$ [15]. Further thermal analysis is needed to confirm the GAIN fibers' contribution and transport mechanism in the as-developed structures.

Two-probe electrical conductivity measurement revealed 100 S m^{-1} at room temperature. Raman spectrum of the graphene-augmented fibres before and after SPS is shown in Fig. 4a and 4b, respectively. In the former case, the appearance of D and D′ peaks indicates the existence of defected graphene layers. Meanwhile, the 2D peak provides evidence of the existence of multi-layered graphene [16]. A detailed analysis on the Raman spectra of the GAIN fibres was done previously by Ivanov et al. [10]. In the latter case (Fig. 4b), it is evident that the carbon structure is preserved as all the peaks are present. It is worth noting that wide and low intensity properties of the 2D peaks in this case can be a result of anisotropy. In fact, complex 2D peak shapes are expected to occur for the graphene layers formed by CVD, which can significantly change the band structure of carbon layers.

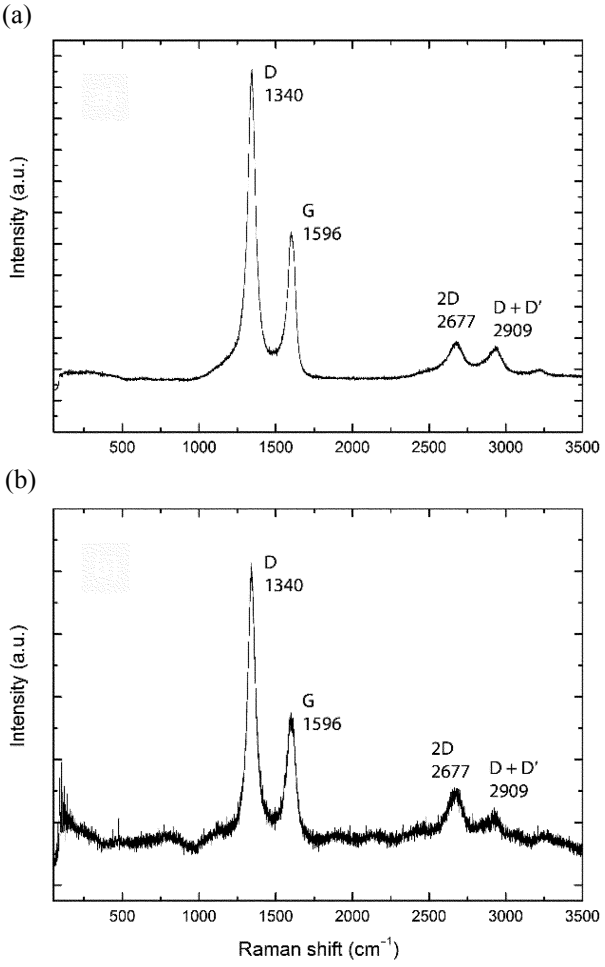

Fig. 4. Raman spectrum of the GAIN before SPS (a), and after SPS (b).

4. CONCLUSIONS

In this work, a functional layered structure of graphene-augmented alumina nanofibres and monolithic α-Al_2O_3 was developed with the help of spark plasma sintering. The layers were directly put into a graphite mould of the SPS, and sintering at 1450 °C with 10 min of dwell time resulted in a full-density sample. A gradient in the grain size was observed with the smallest submicron grains in the vicinity of the electrically and thermally conducting interlayers. However, a coarser grain structure gradually formed in the direction of the monolithic alumina. Thermal and electrical conductivity measurements provided promising data. Nevertheless, a more thorough study of the properties is essential in order to understand the thermal conduction mechanisms and the contribution of the graphene-augmented fibrous structure to the composite.

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Alumiiniumgrafeenkomposiitide kihtstruktuuri sädeplasmapaagutus

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Valmistati α-Al_2O_3 mitmekihilised, grafeenitud (grafeenpinnatud) alumiiniumoksiidsetest nanokiududest vahekihtidega komposiidid. Komposiit moodustati kiht-kihilt grafiitvormis, kasutades vaakumfiltersüsteemi Al_2O_3 nanopulbri ja grafeenitud alumiiniumoksiidi kihtide sadestamist vastavatest suspensioonidest. Katsekehad läbimõõduga 30 mm konsolideeriti sädeplasmapaagutuse (SPS) tehnoloogia teel nende edasiseks iseloomustamiseks. Uuriti vahekihtide mõju alumiiniumoksiidi baasil materjali mikrostruktuurile ja soojus- ning elektrijuhtivusele.