Dense graphene nanoplatelet/yttria tetragonal zirconia composites: Processing, hardness and electrical conductivity

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ABSTRACT

Yttria tetragonal zirconia ceramic composites with 1, 2.5, 5 and 10 vol% nominal contents of graphene nanoplatelets (GNPs) were fabricated and characterized. First, the GNP dispersion in isopropanol was optimized to de-agglomerate the GNPs without damaging their structure. Then, submicrometric fully dense composites were obtained via spark plasma sintering (SPS) at 1250 °C with a 5 min holding time. The processing routine produced a nearly homogeneous GNP dispersion in the ceramic matrix, and the GNPs preferential orientation was perpendicular to the sintering compression axis. A ceramic grain refinement due to the GNPs was also detected. The Vickers hardness measured on the plane perpendicular to the sintering compression axis (basal plane) was lower than on the cross sections. This anisotropy increased with the increasing GNP content, while the average hardness decreased. The electrical conductivity was also highly anisotropic, up to seven times higher for the basal planes. The electrical percolation threshold for these composites was estimated to be between 2.2 and 4.4 vol% of the GNP measured content.

1. Introduction

Amongst advanced ceramics, 3 mol% yttria tetragonal zirconia polycrystals (3YTZP) stand out because of their hardness, high Young's modulus, chemical stability, low friction coefficient, high wear resistance, ionic conductivity, mechanical strength and high fracture toughness. This last attribute is due to the tetragonal-monoclinic martensitic transformation toughening, which impedes fracture propagation [1]. The 3YTZP is used as a biomaterial and in hip and knee joint replacements as a result of these excellent properties together with its high biocompatibility and low density [2].

The addition of carbon nanostructures in ceramics has become an interesting research topic due to the enhancement of the mechanical, thermal and electrical properties of the resulting carbon nanostructure/ceramic composites [3]. Since carbon is one of the most abundant materials on earth, these composites are an inherently sustainable and economical technology [4]. The two-dimensional character of graphene makes it a challenging candidate for engineering new materials because it can improve the interfacial contact with different phases [5]. The initial studies showed that graphene nanoplatelets (GNPs) (also called graphite nanoplatelets) could be used as a viable and inexpensive filler substitute for carbon nanotubes (CNTs) and were carried out on polymers [6]. This thesis was supported by the excellent in-plane mechanical, structural, thermal and electrical properties of graphite [7]. The graphene hexagonal structure is very stable due to strong in-plane bonds, while the different graphene layers in GNPs can easily delaminate into individual graphene sheets by applying mechanical stress due to the weak p_z bonding between the layers [8]. This allows graphene to be produced either by the top-down exfoliation of graphite stacks [9] or by the bottom-up assembly of smaller atoms and molecules [10,11]. As an advantage over carbon nanotubes, graphene can be produced at the ton scale without high temperature and metal catalysts, allowing relatively cheap production for large scale applications [12]. Graphene/ceramic composites have further advantages over carbon nanotube composite ceramics, such as the less restrictive processing conditions [4].

Pristine, single layered graphene has outstanding electrical, thermal and mechanical properties [8], including a high electron mobility at room temperature (2.5×10^5 cm^2 V^{-1} s^{-1}) [13] exceptional thermal conductivity (5000 W m^{-1} K^{-1}) [14] and superior mechanical properties with a Young's modulus of 1 TPa [15] due to the sp^2 hybridization. Therefore, graphene may greatly enhance the electrical conductivity of composites when added to an insulating ceramic matrix. The possibility of precise micromachining of electrically conductive hard ceramic

composites could be exploited in the fabrication of different devices, such as Micro Electro-Mechanical Systems (MEMS), for high temperature applications [16]. Although most of the extraordinary properties of graphene nanosheets are only associated with individual sheets, GNPs formed by the stacking of approximately 10 to 100 sheets, with a 5–10 μm planar dimension and a 10–100 nm thickness, also exhibit outstanding properties and are much less expensive alternatives, since achieving complete and homogeneous dispersion of individual graphene sheets in various solvents is a significant challenge. The high surface area makes graphene prone to form irreversible agglomerates [17] or to even restack to form graphite through Van der Waals interactions [8]. Several key issues must be addressed to obtain high performance graphene/ceramic composites, including the homogeneous dispersion of graphene with minimal restacking, the effective mixing with the ceramic and the understanding the interfacial structure and properties.

The limited existing studies on graphene/zirconia composites mostly used reduced graphene oxide (rGO), smaller and thinner than the GNPs used in this study, and point to a noticeable increase in the fracture toughness and electrical conductivity of the ceramic matrix [18,19]. An electrical conductivity of ~10^4 S/m was obtained for SPSed 3YTZP composites with a 4.1 vol% rGO (7–8 nm thick) by Shin & Hong [18], while the percolation threshold was estimated at 2.5 vol% rGO.

Regarding the mechanical properties, the hardness of rGO/3YTZP composites decreased gradually with the increasing rGO content, while the fracture toughness increased 34% with respect to the monolithic 3YTZP for composites with 4.1 vol% rGO [18]. This increase in the fracture toughness is significantly larger than that of zirconia composites with similar percentage of carbon nanotubes (CNT). Some authors have used pressureless sintering (PLS) to produce graphene/zirconia composites. Yin et al. [20] used PLS in Ar to fabricate rGO/3YTZP composites with a high graphene content from GO, and obtained a fine microstructure with pores due to the GO pyrolization. Ramesh et al. [21] used PLS in air to fabricate GO/3YTZP composites and obtained the enhanced densification, hardness and fracture toughness with minimal GO additions (< 1 wt%). The PLS is a simple sintering method that results in composites that exhibit lower anisotropy and lower density than those sintered by methods involving uniaxial pressures. The study of graphene/3YTZP composites is also challenging because graphene may influence the tetragonal to monoclinic and cubic phase ratios in the matrix [22], which could affect the fracture toughness. However, reports indicate the negligible effect of GO on the tetragonal to monoclinic transformation by low temperature degradation for GO/3YTZP composites [21].

Minimal studies have been published concerning 3YTZP reinforcement with GNPs. Chen et al. [23] reported a 61% increase in the fracture toughness in GNP/3YTZP SPSed composites with a very low GNP content (0.01 wt%). The GNPs used in their study were 0.5–2 μm in diameter and 0.8–1.2 nm thick, so they could instead be considered as few layered graphene (FLG). The use of such a small GNP content may be sufficient to benefit the matrix reinforcement, but it does not affect the electrical conductivity of the composites. The problem with using a higher GNP loading is aggregation, necessitating research on the homogeneous dispersion of graphene during processing. There is a recent study on a GNP/3YTZP system (15–25 μm diameter, 6–8 nm thickness GNPs) by Markandan et al. [24] who used PLS to obtain composites with electrical conductivity of 0.28 × 10^4 S/m with 2 wt% GNP.

In this work, the fabrication of submicrometric fully dense and highly anisotropic conductive composites with different competitive GNP contents and homogenous GNP distribution in a 3YTZP ceramic matrix is pursued. Wet powder mixing and spark plasma sintering was used as the processing and sintering techniques. Before mixing, optimization of the GNP de-agglomeration was also performed. The presence of tetragonal, monoclinic and cubic phases in the ceramic

matrix was determined by X-ray diffraction, And the GNP structural integrity was evaluated by Raman spectroscopy after de-agglomeration treatments both before and after sintering the composites. Distribution of GNPs into the ceramic matrix was assessed by microstructural characterization of the composites via scanning electron microscopy (SEM). The influence of the GNP content on the composites' hardness and on their electrical conductivity has also been evaluated and compared to a reference monolithic 3YTZP sample sintered under the same conditions.

2. Experimental

2.1. Processing and sintering

2.1.1. GNPs de-agglomeration

GNPs with ≤ 5 μm planar diameter and 50–100 nm thicknesses were supplied by Angstron Materials (Dayton, Ohio, EEUU). The GNPs can form agglomerates [17] which complicate their dispersion in the ceramic matrix, and instead producing an inhomogeneous distribution in the final sintered composite. Therefore, different treatments prior to sintering have been applied to different GNP suspensions to determine the most effective method to avoid these agglomerates. One method is the ultrasonic agitation of the GNP suspensions in isopropanol with different energies and for different periods of time. Isopropanol was chosen as an effective dispersion medium for GNPs compared to other solvents [25,26]. The first dispersion treatment was a 1 h agitation in an ultrasonic bath. The second and third agitation treatments were performed using a higher power (750 W maximum power) ultrasound probe KT-600 (Kontes, Inc., Vineland, NJ) at 20 kHz and 95% amplitude, for two different total durations of 20 and 40 min, in time intervals of 5 min to avoid heating of the suspension to over 30 °C.

2.1.2. GNP/3YTZP ceramic composite

To evaluate the effect of GNPs in the ceramic matrix, monolithic 3YTZP was prepared from ceramic 3YTZP powders sized at 40 nm supplied by Tosoh Corporation (Tokyo, Japan). The as-received powders and powders annealed at 850 °C for 30 min in air [27] were used to sinter the monolithic 3YTZP ceramics by SPS in a furnace model 515 S, Dr. Sinter, Inc. (Kanagawa, Japan) at 1250 °C and 75 MPa for 5 and 7 min, with 300 and 50 °C/min heating and cooling ramps, respectively. Graphite moulds of 1.5 cm inner diameter coated with graphite paper were used, in addition to graphite rods. Graphite tissue surrounded the moulding system to avoid heat losses. Approximately 3 g of powder were used for each pellet. Sintered cylindrical pellets of 15 mm diameter were manually sanded with P80 sandpaper to remove graphite from the SPS moulding system.

Composites with 1, 2.5, 5 and 10 vol% GNP content were prepared by adding the corresponding quantity of 3YTZP ceramic powder to the isopropanol GNP sonicated dispersion. The mixtures were further sonicated for 5 min with the probe and then dried on a hot plate with continuous magnetic stirring. The resulting powders were homogenized in an agatha mortar and sintered by SPS using the conditions described above.

2.2. Characterization of the starting powders and sintered specimens

Elemental microanalysis (Elemental Analyzer TruSpec micro LECO) was performed to evaluate the composite powders prior to sintering to assess the total C content (and consequently, the measured GNP content) in the composites. Approximately 1–3 mg of the composite powders from each composition were placed in Sn capsules and completely burned in a pure oxygen environment at temperatures between 100 and 1000 °C. The combustion product (CO_2) was quantified by an infrared cell. This study was performed at Microanalysis General Service; Centros de Investigación, Tecnología e Innovación de la Universidad de Sevilla (CITIUS).