



Fabrication and properties of reduced graphene oxide reinforced yttria-stabilized zirconia composite ceramics

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Abstract

Fully dense yttria-stabilized zirconia (YSZ) ceramics reinforced with reduced graphene oxide (RGO) were fabricated by spark plasma sintering (SPS), and their electrical, thermal, and mechanical properties were investigated. Graphene oxide (GO) was exfoliated by a short sonification in dimethylformamide (DMF)/water solution and uniformly mixed with ZrO_2 powders. The microstructure of the composites showed that undamaged RGO sheets were homogeneously distributed throughout matrix grains. The electrical conductivity of YSZ composites drastically increased with the addition of RGO, and it reached 1.2×10^4 S/m at 4.1 vol.%. However, the thermal diffusivity increased only 12% with RGO addition. The hardness decreased slightly with RGO addition, whereas the fracture toughness significantly increased from 4.4 to 5.9 $\text{MPa}^{1/2}$. The RGO pull-out and crack bridging contributed to the improved fracture toughness.

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1. Introduction

Carbon nanotubes (CNTs) are widely employed as reinforcements in polymers, metals, and ceramics, and CNT-reinforced composites have exhibited enhanced mechanical, electrical, and functional properties compared to monolithic materials.¹ However, the advantageous effects of CNT addition on the mechanical properties are sometimes contradictory, which has been attributed to the inhomogeneous dispersion of CNTs in the matrix, and damage to the CNTs during high temperature processing.^{2–5}

Graphene, a monolayer of sp^2 -hybridized carbon atoms arranged in a honeycomb lattice, has emerged as a promising alternative to CNTs in various applications because of its unusual electrical, thermal, and mechanical properties.^{6,7} The micromechanical cleavage of bulk graphite can produce a high-quality graphene, but the low productivity hinders the widespread use in large-scale applications such as composite fillers.⁸ A more promising technique for mass production is a wet chemical

route involving oxidation-intercalation, exfoliation, and reduction processes.^{9,10} This cost effective method yields graphene nanoplatelets (GNPs) or graphene nanosheets with thickness of up to 100 nm. GNP nanofillers offer the properties that are comparable or superior to those of CNTs,^{11–13} and have been successfully applied as a reinforcement for ceramic materials such as Al_2O_3 and Si_3N_4 to improve their electrical and mechanical properties.^{14–16}

Zirconia (ZrO_2)-based ceramics are technologically important and widely used in the structural and multifunctional applications such as solid oxide fuel cells, oxygen sensors, and ceramic membranes.^{17–19} However, GNP reinforced ZrO_2 composite have not yet been reported, although there has been a great effort to prepare ZrO_2 -CNT (or carbon nanofiber, CNF) composites, and to enhance the mechanical, electrical, dielectric, and thermoelectrical properties.^{2,4,20–23}

In this study, fully dense yttria-stabilized zirconia (YSZ) ceramics reinforced with reduced graphene oxide (RGO) were fabricated by spark plasma sintering (SPS), and their microstructural, electrical, thermal, and mechanical properties were investigated. The graphene oxide (GO) was prepared by the improved Hummers method,²⁴ and the composite powders were obtained by the chemical reduction of GO-YSZ dispersion with

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hydrazine. The uniform dispersion of GO-YSZ was achieved in a mixed solvent of dimethylformamide (DMF, $(\text{CH}_3)_2\text{NC}(\text{O})\text{H}$) and deionized (D.I.) water with sonification.²⁵

2. Experimental procedure

2.1. Preparation of RGO-YSZ composites

The starting materials were commercially available 3 mol% yttria-stabilized ZrO_2 powder (TZ-3YS, Tosoh Corporation, Japan), graphite flake (Sigma Aldrich), and KMnO_4 (Sigma Aldrich). Graphene oxide (GO) was prepared by adding a mixture of graphite flake and KMnO_4 into a mixed solvent of sulfuric acid (H_2SO_4 , Daejeong) and phosphoric acid (H_3PO_4 , Sigma Aldrich). The processing details are available elsewhere.²⁴ The synthesized GO was dispersed in a solution of 450 ml of DMF and 50 ml of D.I. water. The dispersed solution was sonicated for 30 min to exfoliate the graphene oxide. After that, 5 g of ZrO_2 was added into the dispersed solution with a repeated sonication. Finally, graphene oxide was reduced by hydrazine at 80°C for 12 h. After separating by centrifuge, the mixture was dried in an oven at 80°C for 12 h. Five kinds of composite powders (0, 0.6, 1.8, 3.0, and 4.1 vol.% RGO added YSZ) were prepared. For SPS, ~ 1.2 g of the composite powder was placed into a 10 mm diameter cylindrical graphite die and an electric current of ~ 1000 A was applied under a pressure of ~ 30 MPa. The ramping rate was $100^\circ\text{C}/\text{min}$ and the sintering was conducted at 1350°C (or 1450°C) for 5 min.

2.2. Characterization

The apparent density of the sintered specimens was measured using the Archimedes method in distilled water. The phases were determined by X-ray diffraction (XRD, M18XHF-SRA, MAC Science Co., Ltd.). The microstructure was observed by field emission scanning electron microscopy (FESEM, SU-70, Hitach and 7401F, JEOL) and transmission electron microscopy (TEM, Tecnai F20, FEI). The chemical status of RGO-YSZ composites was examined by Raman spectroscopy (T64000, HORIBA, Jobin Yvon).

2.3. Electrical, thermal, and mechanical testing

The electrical conductivity was measured at room temperature using a four-point probe (CMT-SR1000N, Chang Min Co., Ltd.), and the thermal diffusivity was measured by a xenon flash method (XFA 600 Linseis, Germany). The elastic modulus (E) was determined by an ultrasonic pulse echo tester. The hardness was measured using Vickers indentation on polished surfaces under a 3 kg load with a dwell time of 15 s, and fracture toughness was estimated from crack length measurement after 20 kg loading for 15 s.²⁶

3. Result and discussion

3.1. Characterization of RGO-YSZ composites

As-synthesized GO was stacked in layers, and the sheets were partially separated (Fig. 1(a)). The starting YSZ powder was composed of ~ 100 nm spherical nanoparticles (BET surface area: $9\text{ m}^2/\text{g}$). The size of GO was significantly reduced during the processing, and the dimensions of RGO were several hundred nanometers with wrinkled surfaces. The SEM micrograph of the composite powder indicated that RGO was relatively well-dispersed between YSZ nanoparticles (Fig. 1(b)). The mixed solvent of DMF/water and sonification were very effective to prepare the homogeneous dispersion of RGO and YSZ.²⁷ The sonification fully exfoliated the GO and the DMF solvent inhibited the coagulation of exfoliated GO possibly due to a high dipole moment.²⁵ GO and YSZ are expected to bond by van der Waals interaction and this bonding is sustained after the chemical reduction process, resulting in a uniform gray dispersion.

The fracture morphology of sintered RGO-YSZ composites is shown in Fig. 2. Nearly full densification was achieved by SPS. The relative density decreased slightly with increasing RGO content, but it was $\geq 98\%$ of the theoretical density at up to 4.1 vol.%. The theoretical density was obtained using the rule of mixtures with YSZ density of $6.1\text{ g}/\text{cm}^3$ and RGO density of $1.0\text{ g}/\text{cm}^3$.¹⁵ Above 4.1 vol.% RGO addition, the relative density was below 98% of the theoretical density, indicating that RGO impeded the densification of the YSZ ceramics. The monolithic ZrO_2 ceramics exhibited an equiaxed grain microstructure,

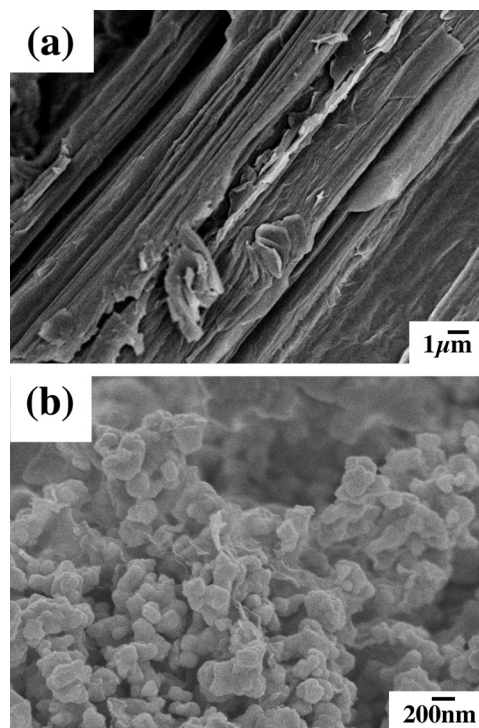


Fig. 1. FESEM images of (a) as-synthesized GO and (b) RGO-YSZ composite powder.

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