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Abstract

Fabrication and properties of CNT-, RGO-reinforced ceramic composites

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Ceramic materials has been extensively used in a various applications such as cutting tools, abrasive tools, gas turbine, constructions and dental applications owing to their outstanding mechanical properties and chemical, thermal reliability. However, the brittleness in nature of ceramic materials, friction problems in tribological applications due to the insulating feature and very low thermal conductivities are still an obstacle to limit their wide applications as high-performance ceramic parts or some functional applications. To overcome this problem, several attempt have been devoted to develop ceramic composite such as composite material, microstructure and composition optimization.

In this research, ceramic matrix composite was intensively studied and carbon nanotube, graphene nanoplatelets were introduced as an additive materials due to
high mechanical properties (hardness, toughness, elastic modulus) and electrical, thermal conductivities.

Two main topics will be discussed to investigate reinforcing mechanism and enhance their physical properties. 1) Fabrication and characterization of carbon nanotube reinforced ceramic, reduced graphene oxide reinforced ceramics and 2) Comparisons on the role of additive material (CNT, graphene)

First, fully dense yttria-stabilized zirconia (YSZ) ceramics reinforced with single wall carbon nanotubes (SWCNTs) were fabricated by spark plasma sintering (SPS), and their electrical and mechanical properties were investigated. Dimethylformamide (DMF) was used as a solvent and tip-sonicator was employed to disperse SWCNTs homogeneously throughout the matrix and reduce the damage on the SWCNTs during mixing. The microstructure of the composite ceramics indicated that undamaged SWCNT bundles were well distributed throughout the matrix with intimate contact with ZrO$_2$ grains without interlayer or amorphous carbon layer. The electrical resistivity of ZrO$_2$ ceramics drastically decreased with SWCNT addition and it reached 0.3 $\Omega$cm at 1.0 wt%. The SWCNT addition to ZrO$_2$ ceramics increased the fracture toughness from 4.4 to 5.2 MPa$^{1/2}$ at 1.0 wt%. The nanotube pull-out and crack bridging contributed to the improved fracture toughness. The frictional behavior was not affected, but the
wear resistance of ZrO₂ ceramics was significantly improved by SWCNT addition. Additionally, 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 ZrO₂ powders. The microstructure of the composites showed that undamaged RGO sheets were homogeneously distributed throughout matrix grains. The electrical resistivity of YSZ composites drastically decreased with the addition of RGO, and it reached 0.0081 Ωcm 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 MPa₁/₂. The RGO pull-out and crack bridging contributed to the improved fracture toughness.

Second, we fabricated CNT and RGO (Reduced graphene oxide) added alumina ceramic composite and compared their electrical, thermal and mechanical properties. The composite was prepared by SPS which is very similar method as mentioned before. Each specimen was consolidated above ~98%. However, RGO added composite exhibits relatively low density compared with that of CNT added composite. Elastic modulus and hardness were decreased in both CNT and RGO composite, and rapid decrease was confirmed in CNT added composite due to the low relative density. Fracture toughness of
the both composite was slightly increased and the increasing in RGO composite was more striking because of high surface area of RGO and 2-dimensional wrapping effect. It is believed that the toughening mechanisms were very similar with CNT-YSZ and RGO-YSZ composite.

The electrical conductivity of CNT and RGO composite was rapidly increased at a certain concentration. In point of view for electrical percolation, CNT has advantages in very small amount of additions, and it was also confirmed by simple simulations. Thermal conductivity was drastically decreased in both CNT and RGO composite. The residual carbon defects located intra-grains shorten the phonon mean-free path in CNT, RGO-ceramic composite.

Keywords: ceramic, composite, spark plasma sintering, carbon nanotube, graphene, mechanical property, physical property

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Chapter 1. General background

1.1. Ceramic matrix composites for toughening

To develop a tough ceramic materials for a wide applications, many kinds of composite like structures have been explored. For examples, ductile-phase toughening, transformation toughening, nano-composite and fiber toughening are the typical toughening mechanisms in ceramic composite materials.

1.1.1 Ductile-Phase Toughening

The addition of ductile phases to ceramic matrices has proven to be an effective toughening mechanism [1]. When the stress field around the crack tip can be released via adsorption of energy through the deformation of the ductile phase. Additional toughening can be done by ductile bridging ligaments in the crack wake, increasing extrinsic toughness. This occurs when the crack tip propagates past a ductile-phase grain that then bridges the crack wake and must be pulled to failure or debond from the surrounding matrix [Fig. 1a].
1.1.2 Fiber Toughening

If the fiber-matrix interface permits suitable relative deformation, with suitably strong fibers, partial or full bridging of cracks by the fibers may take place. This can result in considerable enhancement of the resistance of the composite to failure. The toughening effect is achieved when the fibers either shed load from the crack tip while remaining intact the interface debonds between the fiber and the matrix followed by pullout, and/or the individual fibers fracture, followed by energy adsorption through pullout of the broken fiber. These effects lead to increased extrinsic toughness. The mechanisms responsible for such whisker toughening include crack deflection and bridging, pullout within a zone immediately behind the crack tip (Fig. 1 b). Increases in toughness by extensive fiber pullout require minimization of the shear strength of the fiber-matrix interface. Fiber bridging requires at least modest interfacial strength to transfer load to the fiber and high fiber tensile strength to sustain the applied stress within the wake of the crack tip. [2]

1.1.3 Transformation toughening

Transformation toughening has been mainly studied in ceramics containing zirconia as a second phase. [3] It depends on the transformation
of zirconia from the tetragonal to the monoclinic phase under applied stress. This transformation occurs in the stress field around the crack tip, and the resultant strain involved in the transformation locally relieves the stress field and absorbs fracture energy. Figure 1c shows the resultant zone of transformed particles left in the crack wake. This will increase intrinsic toughness. The transformation toughening mechanism is directly affected by the stability of the tetragonal phase of the zirconia. The phase stability is dependent on dopant concentration, the grain size of the zirconia phase, and the testing temperature. Because of the fine balance of dopants and grain size.

1.1.4 Nanoceramic Toughening

In the field of composite nanoceramics, most of the work is concentrated on SiC nanoparticle-strengthened materials. The obvious enhancement in strength and toughness was reported and many mechanisms were suggested to understanding for the toughening in Al₂O₃/SiC micro-nano composites [4], a switch from inter-granular to trans-granular fracture because of the SiC particles, crack deflection by the internal stress around the intra-granular particles, crack bridging by SiC particles. Also, reduction in flaw size in the micro-nano composites is commonly accepted as an important reason for the strength increase.
1.2. CNT and Graphene reinforced composite

1.2.1 Fabrication and properties of carbon nanotube

Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure. Nanotubes have been constructed with very high aspect ratio [1]. These cylindrical carbon molecules have unusual properties, which are valuable for nanotechnology, electronics, optics and other fields of materials science and technology. In particular, owing to their extraordinary thermal conductivity and mechanical and electrical properties, carbon nanotubes find applications as additives to various structural materials. Carbon nanotube can be fabricated by arc-discharge, laser ablation, plasma torch and chemical vapor deposition. Among these methods, CVD is the most widely used method for the production of carbon nanotubes.[94] The metal nanoparticles are mixed with a catalyst support to increase the surface area for higher yield of the catalytic reaction of the carbon feedstock with the metal particles. One issue in this synthesis route is the removal of the catalyst support via an acid treatment, which sometimes could destroy the original structure of the carbon nanotubes. However, alternative catalyst supports that are soluble in water have proven effective
1.2.2 Fabrication and properties of graphene

Graphene is one of an allotrope of carbon in the form of a two-dimensional hexagonal lattice like a honeycomb structure. It is the basic structural element of other allotropes, including graphite, charcoal, carbon nanotubes and fullerenes. It has many outstanding properties. It is about 100 times stronger than steel by weight,[3] conducts heat and electricity with great efficiency and is nearly transparent.[4] Researchers have identified the bipolar transistor effect, ballistic transport of charges and large quantum oscillations in the material.

For fabrication of graphene, mechanical exfoliation through adhesive tape, reduction of graphite oxide, shearing, sonication and chemical vapor deposition (CVD) technique are well known. One of the typical fabrication method is CVD. High-quality sheets of few-layer graphene in area have been synthesized via chemical vapor deposition on thin nickel films using multiple techniques.

The growth of graphene on nickel films through chemical vapor deposition occurs in a few steps. First the thin nickel film is exposed to Argon gas at 900–1000 degrees Celsius. Methane is then mixed into the gas, and the carbon from the methane is absorbed into the nickel film. The nickel–carbon solution is then cooled down in argon gas. During the cooling process the carbon diffuses out of
the nickel to form graphene films.

1.2.3 Basic concept of CNT and Graphene reinforced composite

Since the discovery of CNT and graphene, they have been focus as a frontier materials. It has studied various areas of research for reinforcements in ceramic and metal composites in order to improve their mechanical, thermal and electrical properties [5,6]. However, the whole potential in this application has not been realized with experimental outcomes falling short of predicted values which demand an active insight in this field. Although ceramics have high stiffness, outstanding chemical and thermal stability with low density but their brittleness limits their use as structural materials. The combination of these nanotubes with a ceramic matrix could potentially create composites that have high temperature stability as well as exceptional toughness and creep resistance [7,8,9,10]. Also increased thermal and electrical conductivity of the composites even at low volume fractions might provide the thermal transport needed to reduce material operating temperatures and improve thermal shock resistance in applications like thermal elements and electrical igniters. The high temperature and high reactive environment during conventional fabrication methods of ceramics damage the carbon nanotubes and thus,
there is a need of alternate methods of processing the composites. Also, there is also a need of control of interface between nanotube and the matrix for better interfacial bonding. But the research is still in embryonic stage and there are a lot of challenges to be resolved before it is ready for use in varied industrial applications.

Among the carbon nanotubes, particularly ropes of single wall carbon nanotube are attractive materials for reinforcement of nanoceramics, and that the effective bonding of the ropes with the matrix plays a central part. There are the extraordinary mechanical properties and nearperfect structure of SWCN. MWCN are similar to SWCN, but contain more defects, which limit their properties. Furthermore, there are differences in the ability to transfer load from the matrix to the nanotubes. The internal shells of MWCN are unable to bond to the alumina matrix and therefore tensile loads are carried entirely by the external shell. This may account for the improvement in the toughening effect between SWCN in the present study and that observed. Fig. 2. Shows a typical microstructures of Al₂O₃/SWCNT and fracture toughness as a function of nanotube contents. [11]

In Graphene/Si₃N₄ system [12], by introducing aqueous colloidal processing methods, uniform and homogeneous dispersion of Graphene
plate and $\text{Si}_3\text{N}_4$ ceramic was fully densification using SPS (Fig. 3 (a)). ~235% increase in toughness for the nano composite over the monolith using only 1.5 vol% addition of graphene. The GPLs appear to be anchored or wrapped underneath the matrix grains and result in the formation of a continuous wall of graphene along the grain boundaries that arrest and forces cracks to propagate in not just two but in three dimensions in order to continue to propagate through the material. Fig. 3 (b)). Such fracture behavior in ceramics has not been reported. Graphene nanofiller reinforcement could potentially be used to enhance toughness for a range of ceramic materials enabling their wide spread use in high-performance structural applications.

1.3. **Spark plasma sintering (SPS)**

Spark plasma sintering is a newly developed process which makes the metal or ceramic sintering possible at low temperatures and short durations by applying high pulsed current throughout compacted powders and uniaxial pressing. SPS was invented based on the idea of using the plasma on electric discharge machine for sintering materials in the 1960s by Inoue et al. They expected that sintering assisted by plasma could help realize
advanced materials.

This method has recently become widespread in use and has attracted considerable attention, particularly in Japan [13,14]. In this method, a pulsed dc current is used simultaneously with a uniaxial pressure to primarily sinter powders. The success of the SPS method in sintering studies [15,16] has been attributed to the role of plasma that is generated between particles. The action of this plasma to eliminate surface impurities is reported to be the reason for the observed enhanced sintering. However, while the concept of plasma is plausible, there is no direct evidence of its existence and thus the role of the pulsed current remains not adequately understood.

The system consists of a SPS sintering machine with a vertical single-axis pressurization mechanism, specially designed punch electrodes incorporating water cooler, a water-cooled vacuum chamber, a vacuum/air/argon-gas atmosphere control mechanism, a special DC-pulse sintering power generator, a cooling water contl-01 unit, a position measuring unit, a temperature measuring unit, an applied pressure display unit and various interlock safety units. (Fig.4.) [17]

The current distribution in the SPS die is important because of its effect
on the distribution of heat generation and the intrinsic effects of the current on mass transport and other processes in materials [18-22]. The current distribution depends primarily on the die geometry and thermal and electrical conductivities of the die and sample materials. (Fig.5.)
Schematic illustrations of toughening mechanisms in ceramic-matrix composites: (a) ductile-phase toughening, (b) fiber toughening, (c) transformation toughening
Fig. 2. (a) Transmission electron micrographs (TEMs) of 5.7 vol% SWCN–Al$_2$O$_3$ nanocomposite and fracture toughness as a function of nanotube content.
Fig.3. (a) Fracture surface of the bulk sample indicates the presence of three-dimensional toughening mechanisms for the GPL-Si3N4 nanocomposite and toughness of the monolithic systematically increases with increasing GPL vol% from 0 to 1.5 vol% GPL (b)
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References

   L.S, Sigl et al Acta metallurgica 36(4) 1988 945


Chapter 2.

Synthesis of Zirconia ceramic composite reinforced with carbon nanotube and reduced graphene oxide.
2.1. Microstructure and mechanical properties of single wall carbon nanotube reinforced yttria stabilized zirconia ceramics

2.1.1. Introduction

Carbon nanotubes (CNTs) are widely used as reinforcements in polymers, metals, and ceramics to improve their mechanical and functional properties [1-3]. CNT has been considered as an ideal candidate for reinforcing/functioning elements because of small size, low density, high aspect ratio, and outstanding mechanical, electrical, and thermal properties [4-6].

Zirconia (ZrO$_2$) is a technologically important material and has a wide range of structural and multifunctional applications such as solid oxide fuel cells, oxygen sensors, and ceramic membranes because of its superior mechanical properties, good ionic conductivity, and high temperature stability [7-9]. Zirconia-CNT composites have been fabricated by hot pressing (HP) or spark plasma sintering (SPS), and their mechanical, electrical, dielectric, and thermoelectrical properties have been investigated [10-19]. The electrical and dielectric properties of the composites could be improved [19], but the positive effects of CNT (or carbon nanofiber, CNF) addition on the mechanical properties such as hardness and fracture toughness were still controversial [10-
Inhomogeneous dispersion of CNTs in the matrix, weak interfacial bonding between CNTs and ceramic grains, and damage of CNT during high temperature processing have been recognized as the main reasons [10-13,16-18]. Various attempts such as acid treatment, hetero-coagulation, and colloidal processing have been explored to overcome these problems [14,22-25]. In addition, the addition of CNTs in metal or alumina matrix composites improved the tribological properties by decreasing the coefficient of friction (COF) and/or increasing the wear resistance [26-28], but a very limited work on the wear properties of CNT-ZrO₂ composites has been performed [29].

In this study, fully dense yttria-stabilized zirconia (YSZ) ceramics reinforced with a various amount of single wall carbon nanotubes (SWCNTs) were fabricated by spark plasma sintering (SPS) and their microstructural, electrical, and mechanical properties were investigated. Dimethylformamide (DMF) was used as a solvent to disperse SWCNTs homogeneously throughout the matrix [30], and tip-sonicator was employed instead of ball milling or attrition milling to reduce the damage on the SWCNTs during mixing.

2.1.2. Experimental
Preparation of SWCNT-ZrO$_2$ composites

The starting materials were commercially available 3 mol% yttria-stabilized ZrO$_2$ powder (TZ-3YS, Tosoh Corporation, Japan) and single wall carbon nanotube (SWCNT, ASP-100F, Hanwha Nanotech). Four kinds of composite powders (0, 0.1 (0.4 vol. %), 0.5 (1.7 vol. %), and 1.0 wt% (3.4 vol. %) SWCNT added ZrO$_2$) were prepared in this study. Both ZrO$_2$ and SWCNT were dispersed in dimethylformamide (DMF, (CH$_3$)$_2$NC(O)H) using a tip sonicator for 30 min to form a stable suspension. After separating by centrifuge, the mixture was dried in an oven at 80 $^\circ$C for 24 h. 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 in N$_2$ flowing atmosphere. The ramping rate was 100 $^\circ$C/min and the sintering was conducted at 1350 $^\circ$C (or 1450 $^\circ$C) for 5 min.

Characterization

The zeta potentials of ZrO$_2$ and SWCNT in DMF were measured by electrophoresis method (ELS-8000, Otuska, Japan). The SWCNT-ZrO$_2$ mixture
before sintering was examined by transmission electron microscope (TEM, JEM-3000F, JEOL). The apparent density of the sintered specimens was measured using the Archemedes method in distilled water. The phases were determined by X-ray diffraction (XRD, M18XHF-SRA, MAC Science Co., Ltd.) and microstructure was observed by field emission scanning electron microscope (FESEM, 7401F, JEOL) and TEM. The chemical status of the sintered specimens was investigated by X-ray photoelectron spectroscopy (XPS, Model AXIS, KRATOS) with a Mg Kα radiation (1253.6 eV). The energy calibration was achieved by setting the hydrocarbon C1s line at 284.5 eV.

*Electrical and mechanical testing*

The electrical resistivity was measured at room temperature using a four-point probe (CMT-SR1000N, Chang Min Co., LTD). The elastic modulus (E) was determined by an ultrasonic pulse echo tester. Hardness was measured using Vickers indentation on the polished surface under a 3 kg load with a dwell time of 15 s, and fracture toughness was estimated from the crack length measurement after 20 kg loading for 15 s [31]. A unidirectional ball-on-disk tribometer was used to evaluate the friction and wear characteristics of sintered specimens in ambient conditions (20±5 °C and 45±10% RH). The Si₃N₄ ball
(hardness: 13 GPa, surface roughness (Ra): 38 nm, SBB Tech. Co.) of 6.35 mm diameter was used as a counterbody material. Both Si₃N₄ balls and sintered pellets were ultrasonically cleaned with acetone before wear testing. Si₃N₄ balls were fixed in the ball holder and placed at the edge of the specimen to make a track diameter of 6 mm from the disk (specimen) axis, and the tests were conducted at a fixed rotational speed of 1500 rpm (linear speed of 0.47 m/s) for 15 min (total sliding distance of 424 m) [32,33,34]. The sliding tests were carried out at a 5 N load. During the test runs, frictional forces were recorded using an electronic sensor to generate the real time coefficient of friction (COF) data. Each experiment was repeated three times and the average values are reported. The microstructural characterization of the as-worn surfaces was conducted using SEM to determine the track width. Surface profiles of the worn surfaces were acquired using an alpha-step profilometer (Model 500, TENCOR) to measure the depth of the wear tracks. The wear track width and depth were further used in computing the wear volume (and subsequently wear rate).

2.1.3. Results and Discussion

Characterization of SWCNT-ZrO₂ composites
Fig. 1 shows the bright field TEM image of SWCNT-ZrO$_2$ mixture before sintering. The BET surface area of ZrO$_2$ was 9 m$^2$/g and the starting powder was the spherical nanoparticles of ~100 nm. SWCNTs were present as bundles of ~20 nm diameter and well-dispersed between ZrO$_2$ nanoparticles. It was clear from the micrograph that ZrO$_2$ and SWCNT were bonded together. DMF is a basic solvent (pH=9) [30], and the zeta potentials of ZrO$_2$ and SWCNT in DMF were determined to be $-10$ and $-70$ mV, respectively. The high surface charge density of SWCNTs is expected to prevent the agglomeration between nanotubes. It is expected that ZrO$_2$ and SWCNT were bonded (or adsorbed) by van der Waals interaction. Consequently, a well-dispersed SWCNT-ZrO$_2$ suspension was obtained in DMF.

XRD patterns of the sintered specimens with various amount of SWCNT are shown in Fig. 2. All the diffraction patterns were well matched with that of tetragonal ZrO$_2$ (JCPDS #42-1164) and no tetragonal to monoclinic phase transformation was observed during sintering. The graphite-like (002) diffraction peak at $2\theta=26.5^\circ$ from SWCNTs was not clearly detected [35]. The apparent and relative densities of sintered SWCNT-ZrO$_2$ composites are shown in Fig. 3. A nearly full densification ($\geq 98\%$ of theoretical density) was successfully achieved by SPS up to 1.0 wt% SWCNT addition, but the relative density gradually decreased with increasing the SWCNT content indicating that
SWCNT impeded the densification of the ceramics. The theoretical density was obtained using the rule of mixtures with ZrO\textsubscript{2} density of 6.1 g/cm\textsuperscript{3} and SWCNT density of 1.8 g/cm\textsuperscript{3} [36].

The fracture morphology of fabricated SWCNT-ZrO\textsubscript{2} composites is shown in Fig. 4. The monolithic ZrO\textsubscript{2} ceramics exhibited the equiaxed grain microstructure and the average grain size determined by linear intercept method was 390 nm (Fig 4(A)). The fracture mode was dominantly intergranular. SWCNTs were well distributed throughout the ZrO\textsubscript{2} matrix and the number of nanotubes exposed on the surface increased with SWCNT content (Fig. 4(B)~(D)). The unbroken, entangled SWCNTs and trace of pulled out SWCNTs were clearly seen in the micrographs. SWCNTs remained as bundles similar to the mixture before sintering. The average grain size (ZrO\textsubscript{2}) was 380, 350, and 280 nm in 0.1, 0.5, and 1.0 wt% SWCNT added ZrO\textsubscript{2} composites, respectively. Thus, the ZrO\textsubscript{2} grain size was gradually reduced with SWCNT addition similar to the previously reported multiwall carbon nanotube (MWCNT)/ZrO\textsubscript{2} composites [16]. The microstructure of 1.0 wt% SWCNT added ZrO\textsubscript{2} composite was further investigated by high resolution TEM (Fig. 5). A typical bright field image revealed that the SWCNT bundles were distributed along the grain boundaries encompassing the ZrO\textsubscript{2} grains to form the network structure (Fig. 5(A)). Intimate contact was observed between SWCNT bundle and ZrO\textsubscript{2}
grain without interlayer or amorphous carbon layer, indicating that SWCNTs were not damaged during the consolidation by SPS (Fig. 5(B)). SWCNT bundles were randomly distributed in the composite, and the longitudinally and cross-sectionally embedded SWCNT bundles were simultaneously observed (Fig. 5(C)). The cross-sectional image showed that ~25 nanotubes were in a bundle and the diameter of nanotubes was in the range of 1.2~1.4 nm confirming the nature of SWCNT.

The chemical status of sintered composites was examined by XPS and the core level C1s spectra were shown in Fig. 6. As-received SWCNTs showed a strong peak with a shoulder at higher binding energy. The shoulder could be attributed to presence of sp3 C-C, C-O, and >C=O bonds based on the previous work [37]. In addition, there was a broad peak centered at 290.4 eV, which is likely to be carboxylate O-COO- functional group resulting from the post acid treatment. SWCNT-ZrO$_2$ composites exhibited the extra peak at 288.2~288.5 eV, which can be assigned to the carboxyl group (–COO). This result presents a strong evidence for the chemical adsorption between SWCNT and ZrO$_2$ via the formation of ester-like bonding (COOZr) [35,38].

Electrical and mechanical properties of SWCNT-ZrO$_2$ composites
The electrical resistivity of SWCNT-ZrO$_2$ composites is shown in Fig. 7. The electrical resistivity of monolithic ZrO$_2$ ceramics was so high that the exact value was not possible (beyond the limitation of equipment: $\sim10^{12}$ $\Omega$cm). The resistivity of composites decreased to $\sim100$ $\Omega$cm even at 0.1 wt% SWCNT addition revealing that the nanotubes were well dispersed forming the interconnected percolation network through the insulating ZrO$_2$ matrix. The minimum resistivity of $\sim0.4$ $\Omega$cm was achieved at 1.0 wt% SWCNT and this value is comparable to the previously reported values in ceramics-CNT composites [10,13]. The percolation threshold was determined to be 1.7 wt% in MWCNT/3Y-TZP composites [19], but the threshold value in this study appears to be much smaller.

Fig. 8 shows the variation of Vickers hardness and indentation fracture toughness as a function of SWCNT content. It is evident that the hardness gradually decreased, whereas the fracture toughness slightly increased with increasing the SWCNT content. The increase of hardness in ceramics-CNT composites was commonly attributed to the grain size reduction [27,39]. In this study, the matrix grain size was reduced with SWCNT addition, but the hardness decreased with SWCNT addition. Thus, the decrease of hardness appeared to be related to the decrease of the apparent density (residual porosity) with SWCNT addition [12,18]. The indentation fracture toughness of
monolithic ZrO$_2$ was relatively low (4.4 MPam$^{1/2}$) because of smaller grain size (~300 nm) [34], but the SWCNT addition increased the fracture toughness to 5.2 MPam$^{1/2}$ at 1.0 wt%. In MWCNT/ZrO$_2$ composites, the increase of indentation fracture toughness with MWCNT addition was reconfirmed by the fracture toughness measured by the single edge V-notch beam (SEVNB) method [16]. In this study, the bending test could not be performed because the specimen dimension was too small, but it is speculated that the fracture toughness increased with SWCNT addition.

Fig. 9 shows the SEM micrographs of indentation-induced cracks on the surface of monolithic ZrO$_2$ ceramics and 1.0 wt% SWCNT added ZrO$_2$ composite. The monolithic ZrO$_2$ ceramics exhibited the typical crack propagation (Fig. 9(A)), but in the composite, the SWCNTs were untangled and stretched between the crack surfaces, which bridged the gap. The toughening effects in alumina-CNT composites have been attributed to formation of entangled network [36] and nanotube pull-out, crack deflection, and crack bridging [39,40]. Similar toughening mechanisms are believed to be operative in SWCNT-ZrO$_2$ composites. The phase transformation toughening can be attributed to the increase of fracture toughness, but it was reported that the propensity to undergo the phase transformation in ZrO$_2$ decreased with addition of MWCNT due to the reduction of grain size [16]. Thus, the increase of
fracture toughness in SWCNT/ZrO$_2$ composites can be attributed to the SWCNT.

When subjected to unlubricated sliding against Si$_3$N$_4$ balls, all sintered SWCNT-ZrO$_2$ composites exhibited an almost identical evolution of coefficient of friction (COF) with time regardless of the SWCNT content. The average steady state COF was in the range of 0.50~0.56 (Fig. 10) and was not significantly affected by SWCNT addition. In the previous report [29], the friction coefficient of ZrO$_2$ decreased from 0.5 to 0.35 by addition of 1.07 wt% carbon nanofiber under a 5 N load, and the lower friction coefficient was ascribed to the smearing of carbon-based transferred films over the contact area, which permits easy shear and helps to achieve a lubricating effect during sliding. The different friction behavior might be related to the nature of reinforcing elements and degree of densification; carbon nanofibers of 80-150 nm diameter and 90% of theoretical density in the previous study and SWCNT bundles of ~20 nm diameter and 97% of theoretical density in this work, respectively. It has been reported that the thin-walled CNT composites had the similar frictional properties as the matrix (alumina), but the thick-walled CNT composites exhibited much lower coefficient of friction [41]. Lim et al. demonstrated that alumina-CNT composites with lower density had much lower friction coefficients than the one with higher density at the same CNT content.
It appears that a small amount of SWCNT does not provide a lubricating effect, but further confirmation is required. The experimentally determined wear rate of monolithic ZrO$_2$ ceramics $1.3 \times 10^{-4}$ mm$^3$/Nm and the wear rate was continuously reduced with addition of SWCNT and the wear resistance was significantly enhanced (Fig. 10). The lowest wear rate of $9.6 \times 10^{-6}$ mm$^3$/Nm was measured for 1.0 wt% SWCNT added ZrO$_2$ composite. According to the modified equation proposed by Yang and Wei [43], the removed volume (wear rate) is a strong function of grain size, hardness, and fracture toughness [34,44]. The high wear resistance of SWCNT-ZrO$_2$ composites is attributed to the smaller grain size and higher fracture toughness when compared to monolithic ZrO$_2$ ceramics. Fig. 11 represents the SEM images of worn surfaces after wear test. The monolithic ZrO$_2$ ceramics showed the severe lateral cracks (Fig. 11(A)). In SWCNT added specimens, the debris particles were compacted to form the layer and the wear surface was rather smooth (Fig. 11(B), (C)). The surface cracks and pulled out grains were observed in 1.0 wt% SWCNT added ZrO$_2$ composite (Fig. 11(D)). As mentioned earlier, the wear rate decreased with increasing the SWCNT addition and thus, the severity of wear sequentially increased by forming the surface crack, grain pull-out, compact layer, and lateral crack. It appears that the addition of SWCNTs increased the wear resistance of ZrO$_2$ ceramics by reducing the formation of compact layer and/or
severe lateral crack.

2.1.4. Conclusions

A marked improvement on mechanical and wear property was reported in SWCNT-ZrO₂ composite, and the chemical bonding, SWCNT bridging, and SWCNT pull-out were suggested as the toughening mechanisms. The SWCNTs were uniformly distributed in ZrO₂ matrix and rarely damaged by high sintering temperature. The solvent (DMF) and surface potential of ZrO₂ and CNT were very important factors for homogeneous distribution and SPS was highly effective for consolidation of SWCNT and ZrO₂ powder mixtures. The SWCNTs entangled the matrix grains and were strongly trapped between grain-boundaries. This microstructure improved the fracture toughness and made the composite very tough against the tribological conditions.
Fig. 1 (A) TEM micrograph of SWCNT-ZrO$_2$ powder mixture and (B) high magnification image of (A).
Fig. 2 X-ray diffraction patterns of (A) 0 wt%, (B) 0.1 wt%, (C) 0.5 wt%, and
(D) 1.0 wt% SWCNT added ZrO$_2$ composite ceramics.

Fig. 3 Apparent and relative density of developed SWCNT-ZrO$_2$ ceramics.
Fig. 4 FESEM micrographs of fractured morphology for the developed (A) 0 wt%, (B) 0.1 wt%, (C) 0.5 wt%, and (D) 1.0 wt% SWCNT added ZrO$_2$ ceramics.
Fig. 5 HRTEM micrographs of 1.0 wt% SWCNT added ZrO$_2$ ceramics.

Fig. 6 XPS spectra of (A) as received SWCNT and (B) 0 wt%, (C) 0.1 wt%, (D)
0.5 wt%, and (E) 1.0 wt% SWCNT added ZrO$_2$ ceramics.

Fig. 7 Electrical resistivity of developed SWCNT-ZrO$_2$ composite ceramics.
Fig. 8 Hardness and indentation fracture toughness of developed SWCNT-ZrO$_2$ composite ceramics.

Fig. 9 FESEM micrographs of indentation induced crack morphology in (A) monolithic ZrO$_2$ and (B) 1.0 wt% SWCNT added ZrO$_2$ composite ceramics.
Fig. 10 Average coefficient of friction (COF) and wear rate of the developed
SWCNT-ZrO$_2$ composite ceramics.
Fig. 11 SEM micrographs of worn surface for (A) 0 wt%, (B) 0.1 wt%, (C) 0.5 wt%, and (D) 1.0 wt% SWCNT added ZrO$_2$ ceramics.

References


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

2.2.1. 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 sp2-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. 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. A more promising technique for mass production is a wet chemical route involving oxidation-intercalation, exfoliation, and reduction processes. 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, and have been successfully applied as a reinforcement for ceramic materials such as Al2O3 and Si3N4 to improve their electrical and mechanical properties.

Zirconia (ZrO2)-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. However, GNP reinforced ZrO2 composite have not yet been reported, although there has been a great effort to prepare ZrO2-CNT (or carbon nanofiber, CNF) composites, and to enhance the mechanical, electrical, dielectric, and thermoelectrical properties.
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,\textsuperscript{25} and the composite powders were obtained by the chemical reduction of GO-YSZ dispersion with hydrazine. The uniform dispersion of GO-YSZ was achieved in a mixed solvent of dimethylformamide (DMF, (CH\textsubscript{3})\textsubscript{2}NC(O)H) and deionized (D.I.) water with sonification.\textsuperscript{26}

\textbf{2.2.2. Experimental}

\textit{Preparation of RGO-YSZ composites}

The starting materials were commercially available 3 mol\% yttria-stabilized ZrO\textsubscript{2} powder (TZ-3YS, Tosoh Corporation, Japan), graphite flake (Sigma Aldrich), and KMnO\textsubscript{4} (Sigma Aldrich). Graphene oxide (GO) was prepared by adding a mixture of graphite flake and KMnO\textsubscript{4} into a mixed solvent of sulfuric acid (H\textsubscript{2}SO\textsubscript{4}, Daejeong) and phosphoric acid (H\textsubscript{3}PO\textsubscript{4}, Sigma Aldrich). The processing details are available elsewhere.\textsuperscript{25} 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 °C/min and the sintering was conducted at 1350 °C (or 1450 °C) for 5 min.

*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, FESEM, 7401F, JEOL) and transmission electron microscopy (TEM. Tecnai F20, FEI). The chemical status of RGO-YSZ composites was examined.
by Raman spectroscopy (T64000, HORIABA Jobin Yvon).

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.27

2.2.3. Results and Discussion

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 m$^2$/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.\textsuperscript{28} The sonification fully exfoliated the GO and the DMF solvent inhibited the coagulation of exfoliated GO possibly due to a high dipole moment.\textsuperscript{26} 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 ≥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 g/cm$^3$ and RGO density of 1.0 g/cm$^3$.\textsuperscript{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, and the fracture mode was a mixture of intergranular and
intragranular (Fig. 2(a)). RGO was well distributed throughout the ZrO$_2$ matrix, and the amount of RGO protruding out of the fracture surface increased with the RGO content (Figs. 4(b)~(e)). The protruding RGO was platelets which ran along the grain boundary of the matrix. The grain size, determined by a linear intercept method, decreased from 345 to 315 nm with the addition of RGO, but the reduction of the YSZ grain size was not significant, in contrast to RGO-Al$_2$O$_3$ system. In RGO-YSZ composites, the fracture mode became predominantly intergranular. At this stage, it is not clear whether the change of the fracture mode is due to the weakened interphase boundaries or crack deflection, and further confirmation is required. The microstructure of 4.1 vol. % RGO added YSZ composite was further investigated by TEM (Fig. 3). In a typical bright field image, it was difficult to identify the RGO (Fig. 3(a)). Thus, an electron energy loss spectroscopy (EELS) analysis was carried out, and the resulting EELS mapping showed that carbon (C) was located along the grain boundaries encompassing several ZrO$_2$ grains (Fig. 3(b)). The high resolution TEM image clearly revealed the presence of RGO between ZrO$_2$ grains, and intimate contact was observed without an interlayer or amorphous layer, indicating that RGO was not damaged during the consolidation by SPS (Fig. 3(c)). The thickness of RGO was estimated to be 7~8 nm, which corresponds to ~7 layers of graphene.
XRD patterns of the sintered RGO-YSZ composites showed that all the diffraction peaks were well matched with that of tetragonal ZrO$_2$ (JCPDS #42-1164), and no tetragonal to monoclinic phase transformation was observed during consolidation (Fig. 4). The graphite-like (002) diffraction peak at 20=26.5° from RGO was not clearly detected. Raman study was performed to characterize the structure of RGO in the composites after consolidation by SPS (Fig. 5). The Raman spectrum of as-received graphite displayed a strong peak (G band) at 1582 cm$^{-1}$ and a weak peak (D band) at 1367 cm$^{-1}$ (Fig. 5(a)). In the case of as-synthesized GO, the G band significantly broadened and shifted to higher frequency, and the D band grew in intensity (Fig. 5(b)). Both the G and D bands were observed in the spectra of sintered RGO-YSZ composites and their intensity increased with increasing RGO content (Fig. 5(c)~(f)). The obtained results confirmed that RGO was present in the composite with sheet-like structure.

Electrical, thermal, and mechanical properties of RGO-YSZ composites

The electrical conductivity of RGO-YSZ composites is shown in Fig. 6. The electrical conductivity of monolithic ZrO$_2$ ceramics was beyond the
limitations of the equipment ($<10^{-10}$ S/m). The conductivity of the composites increased rather slowly with the addition of RGO, reaching $\sim5\times10^{-7}$ S/m at 1.8 vol. %. Further increase in the RGO content drastically improved the electrical conductivity, and a maximum conductivity of $\sim10^5$ S/m was achieved at 4.1 vol. % RGO addition. The obtained conductivity was at least one order of magnitude higher than that of graphene-$\text{Al}_2\text{O}_3$ (15 vol. %) and SWCNT-$\text{ZrO}_2$ (1 wt. %) composites.$^{13,24}$ Thus, RGO was well dispersed, forming an interconnected percolation network and providing electrical conducting pathways through the insulating $\text{ZrO}_2$ matrix.$^{31}$ The percolation threshold was $\sim2.5$ vol. %, which was comparable to that observed in graphene-$\text{Al}_2\text{O}_3$ composites.$^{13}$ The thermal diffusivity of RGO-YSZ composites is plotted in Fig. 6. Compared to the monolithic $\text{ZrO}_2$ ceramics, the thermal diffusivity of RGO-YSZ composites increased slightly, but the increment was limited to 12%. It appears that the amount of RGO was not high enough to improve the thermal property noticeably.$^{32}$

The Vickers hardness and indentation fracture toughness of RGO-YSZ composites are shown in Fig. 7 as a function of RGO content. It was found that the hardness gradually decreased, whereas the fracture toughness increased with increasing RGO content. The increase of hardness in the composites is commonly attributed to grain size refinement.$^{33}$ The matrix grain size in this
study slightly decreased with RGO addition and thus, the decrease of hardness appears to be partially related to the decrease of the apparent density (residual porosity) with RGO addition.\textsuperscript{34} The significant drop of hardness has also been observed in graphene-$\text{Si}_3\text{N}_4$ composite.\textsuperscript{15} The fracture toughness of monolithic $\text{ZrO}_2$ was relatively low (4.4 MPam$^{1/2}$) because of smaller grain size,\textsuperscript{35} but the RGO addition increased the fracture toughness to 5.9 MPam$^{1/2}$ at 4.1 vol. %. With similar additive content, the improvement of fracture toughness was more significant in RGO-YSZ composite than in SWCNT-$\text{ZrO}_2$ composite, probably due to the 2-dimensional sheet wrapping.\textsuperscript{13} In MWCNT-$\text{ZrO}_2$ composites, the increase of indentation fracture toughness with CNT addition was reconfirmed by the fracture toughness measured by the single edge V-notch beam (SEVNB) method.\textsuperscript{36} In this work, the bending test could not be carried out because the specimen dimensions were too small, but the tendency of the improved fracture toughness with RGO addition can be said based on the previous report.\textsuperscript{36} Fig. 8 shows the SEM micrographs of indentation-induced cracks on the surface of monolithic and 4.1 vol. % RGO added YSZ composites. The monolithic $\text{ZrO}_2$ ceramics exhibited typical crack propagation (Fig 8(a)). Closer examination of the crack in the RGO-YSZ composite revealed pulled-out RGO and bridging RGO marked in the image (Fig. 8(b)). Thus, it is believed that the toughening mechanisms in RGO-YSZ composite are sheet wrapping, sheet pull-out, and
crack bridging similar to the previously reported graphene-Si$_3$N$_4$ composite.\textsuperscript{15} The phase transformation toughening can also be attributed to the increase of fracture toughness. However, it was reported that the propensity to undergo the phase transformation in ZrO$_2$ decreased with the addition of MWCNTs due to the reduction of grain size.\textsuperscript{36} Thus, the contribution of phase transformation to the increase of fracture toughness appears to be negligible.

\textbf{2.2.4. Conclusion}

Fully densified RGO-YSZ composite ceramics with nano-grain size were successfully fabricated by spark plasma sintering. The 2-step sonification and chemical reduction in combined DMF/D.I. water solvent were very effective for RGO distribution, and significant improvements of the electrical and mechanical properties were observed. The interconnected electron pathway through the RGO provides enhanced the electrical conductivity, and the RGO pull-out, crack bridging, and 2D RGO wrapping contribute to the improved fracture toughness.
Fig. 1 FESEM images of (a) as-synthesized GO and (b) RGO-YSZ composite powder.
Fig. 2 FESEM micrographs of fractured morphology for (a) 0, (b) 0.6, (c) 1.8, (d) 3.0, and (e) 4.1 vol. % RGO added YSZ ceramics.
Fig. 3 (a) Bright field image, (b) EELS (C) mapping of (a), and (c) high resolution TEM image of 0.7 wt% RGO added YSZ ceramics.
Fig. 4 X-ray diffraction patterns of (a) 0, (b) 0.6, (c) 1.8, (d) 3.0, and (e) 4.1 vo. % RGO added YSZ composite ceramics.
Fig. 5 Raman spectra of (a) commercial graphite, (b) GO (c) 0.6, (d) 1.8, (e) 3.0,
and (f) 4.1 vol. % RGO added YSZ composite ceramics.

Fig. 6 Electrical conductivity and thermal diffusivity of RGO-YSZ composite
ceramics.
Fig. 7 Hardness and indentation fracture toughness of RGO-ZrO$_2$ composite ceramics.

Fig. 8 FESEM micrographs of indentation induced crack morphology in (a) monolithic YSZ
References


4. Sun J, Gao L, Iwasa M, Nakayama T, Niihara K. Failure investigation of


Chapter 3.

Fabrication and properties of alumina ceramic composite reinforced with carbon nanotube and reduced graphene oxide
3.1. Introduction

Alumina is one of the more widely used ceramic material in the industrial applications such as abrasive, jewel, crucible, catalyst. Due to the excellent mechanical property, it is also suitable for structural applications. To improve the mechanical or multifunctional properties, various researches have been conducted and the fabrication of ceramic matrix composite is extensively studied. Various types of composites which is fiber reinforced composite [1,2], nano particle reinforces composite [3,4] and other composites were investigated. In this manner, the carbon nanotube and graphene have been focused as next generation additive materials due to their outstanding mechanical, thermal, electrical properties[5~10]. Recently, the CNT, RGO added ceramic composite was extensively studied and the improvement of mechanical property
(especially in fracture toughness) and electrical property were reported. [11~14]

However, only a limited studies [15] for comparisons between CNT composite and RGO composite in a same matrix and sintering method have done except some polymer matrix composite[16, 17] and demand on intensive investigation of interfacial phenomena or bonding characteristic have arisen. At the point of mechanical property or electrical, thermal conductivity, iasadfasf

In this study, fully dense alumina ceramics reinforced with reduced CNT and GNP(graphene nano platelet) were fabricated by spark plasma sintering (SPS), and their microstructural, electrical, thermal, and mechanical properties were investigated. High quality of SWCNT was used and the graphene oxide (GO) was prepared by the improved Hummers method, [18] and the composite powders were obtained by the chemical reduction of GO- $\text{Al}_2\text{O}_3$ dispersion with hydrazine. The uniform dispersion of CNT- $\text{Al}_2\text{O}_3$ and GO- $\text{Al}_2\text{O}_3$ were achieved in a mixed solvent of dimethylformamide (DMF, $(\text{CH}_3)_2\text{NC(O)}\text{H}$) and deionized (D.I.) water with sonification. [19]

3.2. Experimental

The starting materials were commercially available $\text{Al}_2\text{O}_3$ (Sumitomo, Japan),
SWCNT (Hanhwa chemical), graphite flake (Sigma Aldrich), and KMnO₄ (Sigma Aldrich). Graphene oxide (GO) was prepared by adding a mixture of graphite flake and KMnO₄ into a mixed solvent of sulfuric acid (H₂SO₄, Daejeong) and phosphoric acid (H₃PO₄, Sigma Aldrich). The processing details are available elsewhere. [18]

For CNT-Al₂O₃ composite powders, both Al₂O₃ and CNT were dispersed in dimethylformamide (DMF, (CH₃)₂NC(O)H) using a tip sonicator for 30 min to form a stable suspension. After separating by centrifuge, the mixture was dried in an oven at 80 °C for 24 h.

For RGO-Al₂O₃ composite powders, 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 Al₂O₃ 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.

Four kinds of composite powders (0, 0.1, 0.5, and 1.0 wt% SWCNT added Al₂O₃) were prepared for each of the SWCNT and GNP respectively.

For SPS, 5 g of the composite powder was placed into a 20 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 °C/min and the sintering was conducted at 1350 °C (or 1450 °C) for 5 min.

**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, FESEM, 7401F, JEOL) and transmission electron microscopy (TEM. Oxford INCA cr stall). The chemical status of RGO-YSZ composites was examined by Raman spectroscopy (T64000, HORIZABA Jobin Yvon), XPS (Sigma Prove, Thermo Fisher Scientific) and carbon contents was measured by Elemental (C,N,S) analyzer (Thermo electron corporation, Flash EA 1112)

**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)
and thermal conductivity was calculated via thermal diffusivity, density and heat capacity. The elastic modulus (E) was determined by an ultrasonic pulse echo tester. The hardness was measured using Vickers indentation on polished surfaces under a 1 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.[20] The bending strength was measured using 3-point bending method.

3.3. Results and discussion

In order to obtain uniform and densified microstructures for composites, colloidal process was used. Both CNT and RGO were dispersed in DMF (dimethylformamide) solvent and sonicated. After Al₂O₃ addition, the suspension was sonicated again. Based on our previous works and other reports, DMF solvent and sonication through tip-sonicator were very effective for dispersion and making homogeneous composite powder.[19, 21]

Bulk quantity of RGO was fabricated via exfoliation of GO and chemical reduction. Chemical status and quality of RGO were characterized using XPS and raman spectroscopy. XPS results showed different degree of oxygen functional groups in graphite, graphite oxide and RGO. Fig.1 shows the C1s peaks which consists of four kinds typical components arising from
C=C/C-C (sp2 and sp3, ~284.6 eV), C-O (hydroxyl, ~286.7 eV), C=O (carbonyl, ~288.3 eV) and O-C=O (carboxyl, ~290.1 eV). The presence of the carbonyl and carboxyl groups in GO decreased dramatically (Fig. 1. (a,b)), which was attributed by chemical reduction conditions. Hydroxyl groups (C-O) were relatively increased due to the formation of the GO layers by exfoliation of graphite oxide, as shown in (Fig 1. (a,c)). Raman spectra of graphite, graphite oxide and RGO were shown in Fig.2. D and G peaks were confirmed at all specimens. D and G peaks were generated from vibration of in-plane C-C bonding and structural defects (or reduced domain size), respectively. In graphite, G peak is very dominant compared to D peak. However, when it once oxidized, defect density (D peak) increased drastically (Fig.2.(b)) and did not recovered after reduction. (Fig.2.(c)). The D peak in this work is quite higher than CVD driven graphene [22] and these results are inevitable in every chemically driven graphene [23] because chemical oxidation and reduction generate structural defects even though the oxygen and oxygen related functional groups were almost eliminated.

A typical density table with fabricated conditions is shown in Table.1. Most of the sintered body was fully densified (above ~97%) except 1wt% CNT added composite. Generally, the sintering behavior slowed down when secondary phase (CNT, RGO) was added. CNT can be partially agglomerated due to their
high surface area unlike RGO and for this reasons, CNT composite exhibits lower density compared with that of RGO composite.

XRD patterns of the sintered composites showed that all the diffraction peaks were well matched with that of alpha-Al₂O₃ and other secondary phase or impurity phase were not observed during consolidation (Fig.3). Also, the graphite-like (002) diffraction peak at \(2\theta=26.5^\circ\) from RGO was not clearly detected.[24] FE-SEM micrographs of as-purchased alumina powder and fractured morphology for monolithic Al₂O₃ and composites are shown in Fig. 4. As purchased alumina powder exhibited spherical shape with average powder size of a few hundred nanometers. (Fig. 4.(a)) Sintered Al₂O₃ ceramic contains large amount of abnormal grains and the grain size was significantly decreased with the addition of CNT and RGO. The pinning effect of the additive materials with large surface area which distributed between the alumina grain boundaries inhibit the grain growth during the sintering and causes grain refinement. The unbroken, pulled out CNTs and trace of pulled out CNTs were clearly shown in the micrographs (Fig. 4(c)–(d)). RGOs were well distributed throughout the Al₂O₃ matrix, and the amount of pulled-out RGOs on the fracture surface increased with the RGO content (Figs. 4(e)–(f)). The microstructure of 1.0 wt% CNT and RGO added Al₂O₃ composite was further investigated by high resolution TEM (Fig. 5).
A typical bright field image and electron energy loss spectroscopy (EELS) spectrums were shown in Fig. 5. The intimate contact was observed between CNT bundle and Al$_2$O$_3$ grain without interlayer or amorphous carbon layer, indicating that CNTs were not damaged during the consolidation by SPS (Fig. 5(a)). It was also clearly revealed that there is a RGO layers sandwiched between the Al$_2$O$_3$ grains at grain boundary and intimate contact was observed without an interlayer or amorphous phase (Fig. 5(c)). The thickness of RGO was estimated to be ~7 nm. [25].

As shown in (Fig. 5 (b, d)), Carbon pi peak was decreased, whereas oxygen peak (~540eV) was newly generated in interfacial area. The hybridization of C atoms in a carbon sheet, as well as the effective sheet orientation with respect to the direction of the incoming electron beam, is known to modify the relative contribution of spectral features associated with 1s-pi transitions to the recorded EELS. The pi-ratio is therefore, in case of unchanged orientation, a measure for the degree of hybridization of the C atoms; an increased pi-ratio indicates an increase in sp2 character and a decrease in pi-ratio indicates an increase in sp3 character. Which means the sigma bonding in the interface was increased and chemical status was changed from sp2 hybridization to sp3 hybridization. It is speculated that the additional sigma bonding in sp3 hybridization and oxygen peak in interface area are clear evidence for chemical bonding between carbon
and alumina ceramics. For additional evidence on chemical bonding, chemical status was characterized by X-ray photoelectron spectroscopy (XPS). Fig. 6 shows C1s and O1s peaks. Unlike monolithic alumina, C1s peaks of Al₂O₃/CNT, Al₂O₃/RGO composite revealed another carboxyl like peak (-CO) and additional oxidized binding energy was detected in Al₂O₃/CNT, Al₂O₃/RGO composite (Fig. 6. (d,f)). The oxidized binding energy is also detected in CNT oxidized by oxygen plasma [43]. From EELS and XPS data, we figure out that the chemical bonding between carbon and matrix is formed during sintering.

Typical elastic modulus were shown in Fig. 7. Based on outstanding elastic modulus of CNT and graphene, it was expected that CNT and graphene containing ceramic composites will exhibit superior elastic modulus. However, actually measured elastic modulus decreased in composites and one of the most contributing factor was porosity. We can estimate the elastic modulus of pore containing composite by following equation. (The ideal elastic modulus of SWCNT bundle is ~1TPa. [26]

\[ E = E_0(1-1.9P+0.9P^2) \]

P=porosity, E=elastic modulus, E₀=theoretical elastic modulus

A larger decrement in CNT composite is mainly related with relative density (residual porosity). CNT has a possibility of partial aggregation cause of very
high surface area, and the pore containing structural problem (hollow bundle structure) prohibits the modulus improvement. In case of RGO, It has been already reported that the single layer graphene has extremely high elastic modulus of ~1 TPa. [8] However, chemically driven graphene (GNP, RGO) has relatively low value (~0.25 TPa) compared with that of the single layer graphene fabricated by CVD because of the defect status and disordered carbon structure [27] and also, we confirmed the similar problems by raman spectroscopy in our specimens. For these reasons, elastic modulus of RGO added alumina ceramic was also slightly decreased as increasing the amount of RGO.

Fig. 8 shows the variation of Vickers hardness and indentation fracture toughness as a function of CNT and RGO content. The hardness gradually decreased, whereas the fracture toughness slightly increased with increasing the additive content. The increase of hardness in ceramics composites was mainly attributed to the grain size reduction [28,29]. In spite of the matrix grain size reduction with CNT and RGO addition, the hardness decreased. Thus, the decrease of hardness appeared to be related to the decrease of the apparent density (residual porosity) with CNT and RGO addition [30,31]. As shown before in Fig. 7, decreasing behavior of CNT and RGO added composite was quite similar with that of the elastic modulus. Thus, the lower apparent density
of CNT composite leads lower elastic modulus and hardness. Contrary to hardness, both of the composite have a tendency to improve the fracture toughness. With similar additive content, the improvement of fracture toughness was more significant in RGO composite, probably due to the 2-dimensional sheet wrapping effect. [32,33] Also, based on Atkins equation, lower elastic modulus of CNT composite constrain the improvement of toughness. However, this values are controversial to compare because the Atkins’s method still has many arguable problems. So the one thing to notice here is that the fracture toughness can be improved by CNT and RGO addition.

Fig. 8 shows the indentation-induced crack propagation on the polished surface for composites. It is clearly shown that the bridging CNTs and RGO retain its typical one-dimensional and sheet-like structure and was lying down parallels to the fracture surface, when a crack propagates and face with CNT or RGO, they can act as a bridge to interrupt the widening of the crack. The bridging requires more additional energy to open up the crack, and subsequently leads to toughening.

Flexural strength of CNT and RGO added alumina composite was shown in Fig. 10. It is expected that improving the fracture toughness may result in improved mechanical strength. As a consequence, strength will be directly related to toughness. Indeed, Munro et al analyzed data from the literature and concluded
that many polycrystalline ceramics showed a linear relation between toughness and strength at the similar grain size and density. [34]. In our results, increases in strength were shown in both CNT and RGO added composites. It is speculated that the large amount of increasing in CNT composite compared to that of RGO added composite is related with structural difference of additive materials. The flexural strength is strongly depends on critical flaw size. Therefore, if the partially agglomerated CNT or RGO act as a micro flaws when external stress induced, 2-dimentional RGO will generate much larger flaw compared to 1-dimentional CNT. Weak out-of-plane physical bonding would be another problem. It can be easily slide shear direction by induced stress. Also, When the stress is applied, the bonding strength between matrix and additives, and the difference of bonding area affect the mechanical strength and it is speculated that the larger surface contact area of CNT contribute the superior mechanical property than RGO by load sharing.

For this reasons, flexural strength of RGO composite increases less than that of CNT added composite. On the other hand, it was slightly increased in CNT addition up to 0.5wt% and start decreasing while continuously increased in RGO composite. This rapid plunge may be due to the sparsely dotted agglomerated CNTs or graphitic impurities. (Fig. 11. (a,b)).

Measured and simulated electrical conductivity of two composite were shown
in Fig. 12. The electrical conductivity of monolithic Alumina ceramics was beyond the limitations of the equipment ($< 10^{-10}$ S/m). The conductivity of the RGO composites increased rather slowly with the addition of RGO. Further increase in the RGO content drastically improved the electrical conductivity, and a maximum conductivity of $~10^0$ S/m was achieved at $~2$ vol. % RGO addition. Otherwise, the conductivity of the CNT composite rapidly increased at the initial stage with addition of CNT $~0.2$ vol% and saturated. It is believed that the different percolation behavior is generated due to their structural feature. To confirm their electrical conductivities characteristic, following PCW model was introduced. [35]

$$
\sigma_e = \sigma_0 + c(1 - \bar{T}S_d\sigma_e^{-1})^{-1}\bar{T}
$$

$$
\bar{T} = \left(\frac{1}{3}\right)\left(\frac{1}{s_{11}} + \frac{1}{s_{22}} + \frac{1}{s_{33}}\right)
$$

$$
S_{11} = S_{22} = \frac{\alpha}{2(\alpha^2 - 1)^{\frac{1}{2}}} \left[\alpha(\alpha^2 - 1)\frac{1}{2} - cosh^{-1}\alpha\right] (\alpha > 1)
$$

$\sigma_0 =$ conductivity of matrix, $\sigma_e =$ conductivity of composite $T =$ diagonal component of the orientation average, $\alpha =$ aspect ratio, $c =$ filler contents (vol.%)

There are two assumptions in calculation. First, the current path could only be generated through CNT and RGO. Second, the additive materials (CNT, RGO)
are uniformly distributed within grain boundary. Based on the simulation, we
find out that the most important factor in electrical percolation is aspect ratio. In
high aspect ratio, percolation occurred at low vol% in both CNT and RGO
composite. Also, it was predicted that the wire type is more appropriate for fast
percolation than plate type and actual measured conductivities showed similar
result. We could also estimate the aspect ratio of CNT (about 100) and RGO
(above 1/100) inversely.

Thermal conductivity and relative results were shown in Fig. 13. Unexpected
rapid thermal conductivity drop was observed in both of the composite. To
understand the decrease in thermal conductivity, simple model for composite
material is introduced and their interfacial thermal resistance was calculated by
following equation.[36]

\[
K_e = K_m \left[ \frac{3 + V_f (\beta_x + \beta_z)}{3 - V_f \beta_x} \right]
\]

\[
\beta_x = \frac{2[d(K_c - K_m) - R_k K_c K_m]}{d(K_c + K_m) + R_k K_c K_m}, \quad \beta_z = \frac{L(K_c - K_m) - 2R_k K_c K_m}{L K_m + 2R_k K_c K_m}
\]

**K_e**: effective thermal conductivity, **K_c**: thermal conductivity of CNT and GNP,
**K_m**: thermal conductivity of matrix, **V_f**: volume fraction (vol%) **L_x, L_z**: geometric
factor, **R_k**: interfacial thermal resistance
At the given 0.5 wt% addition, the calculated interfacial thermal resistance of CNT and RGO composites were $1.4 \times 10^{-8}$ and $8.8 \times 10^{-7}$ m$^2$K/W respectively. (Fig.13(c)) This value is relatively high compared with other polymer matrix composite or solvent system. [37] Based on Wiedemann-Franz law, the ratio $K/\sigma T$ ($T=300$ K) for those composite is around $\sim10^{-2}$ (WΩ/K$^2$), which is several order of magnitude larger than the free electron Lorenz number of $\sim2.45\times10^{-8}$ (WΩ/K$^2$). Therefore, the measured $K$ essentially reflects the phonon’s contribution in the composite [38]. This calculation also corroborates the assumption that phonon contribution is dominant in the specific heat capacity. Thus, applying the classical relation $K=Clv$ and assuming a characteristic sound velocity ($\sim10^4$ m/s)[39], the calculated phonon mean-free-path was only a few angstroms, and became smaller as increasing the content of CNT or RGO. These phenomena is very disappointing results considering the very long phonon mean-free path of additives [40]. A high thermal barrier can be constructed at the interface between the additives and matrix by lattice mismatch and a stress generated by thermal expansion mismatch. However, it is difficult to consider interface problems because the calculated phonon mean-free path was much smaller than average grain size ($\sim$ a few hundred nanometer). More probable problem would be defects generated during consolidation. We measured the carbon contents of as pulverized powder and additive eliminated
powder by heat treatment. (Table. 2) By direct observation, the color of specimen was became white after heat treatment at 700°C. However, carbon was also detected even after we eliminate the CNT and RGO. The carbon contents was gradually increased as increasing the amount of carbon additives (CNT, RGO) and it is believed that the residual carbon diffused from CNT, RGO and graphite mold during consolidation was distributed throughout the matrix. The possibility of carbon diffusions into alumina was already suggested [41]. High residual carbon contents of RGO composite is speculated that the features of plate like structure of RGO and unstable dangling carbons during chemical oxidation and reduction processes are easy to diffuse [42]. Al₄O₄C and Al₄O₂C₂ compounds can be formed by reaction between alumina and carbon but in a point of view of thermodynamic kinetics, temperature is too low to react so the residual carbon would be connect with amorphous phase or partially segregate in matrix. Eventually, these carbon defects scatters phonons and reduce the thermal conductivity.

3.4. Conclusion

Fully densified CNT, RGO-Alumina composite ceramics were successfully
fabricated by spark plasma sintering. The chemical bonding between alumina matrix and additives (CNT, RGO) was confirmed and significant improvements of the mechanical properties were observed. RGO composite showed much higher strength and high contact area of chemical bonding contribute to the improved mechanical strength. The interconnected electron pathway through the additive material provides enhanced the electrical conductivity and 1D structure was more effective in percolation but, reduced phonon mean-free path by carbon contaminations inhibits their improvement of thermal conductivity.
<table>
<thead>
<tr>
<th>Sintering condition (°C-min)</th>
<th>Additive (wt.%)</th>
<th>Relative density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1350-5</td>
<td>-</td>
<td>97.9</td>
</tr>
<tr>
<td>1350-5</td>
<td>CNT-0.1</td>
<td>97.5</td>
</tr>
<tr>
<td>1350-5</td>
<td>CNT-0.5</td>
<td>97.4</td>
</tr>
<tr>
<td>1350-5</td>
<td>CNT-1</td>
<td>96.2</td>
</tr>
<tr>
<td>1350-5</td>
<td>GNP-0.1</td>
<td>98</td>
</tr>
<tr>
<td>1400-5</td>
<td>GNP-0.5</td>
<td>99</td>
</tr>
<tr>
<td>1400-5</td>
<td>GNP-1</td>
<td>98.2</td>
</tr>
</tbody>
</table>

Table 1. Density table
Table 2. Carbon contents of $\text{Al}_2\text{O}_3$, $\text{Al}_2\text{O}_3$/CNT and $\text{Al}_2\text{O}_3$/RGO ceramic composite

<table>
<thead>
<tr>
<th></th>
<th>$\text{Al}_2\text{O}_3$</th>
<th>$\text{Al}_2\text{O}_3$/CNT (0.1wt)</th>
<th>$\text{Al}_2\text{O}_3$/CNT (0.5wt)</th>
<th>$\text{Al}_2\text{O}_3$/CNT (1wt)</th>
<th>$\text{Al}_2\text{O}_3$/RGO (0.1wt)</th>
<th>$\text{Al}_2\text{O}_3$/RGO (0.5wt)</th>
<th>$\text{Al}_2\text{O}_3$/RGO (1wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grounded powder</td>
<td>0.01</td>
<td>0.07</td>
<td>0.44</td>
<td>0.77</td>
<td>0.1</td>
<td>0.45</td>
<td>0.87</td>
</tr>
<tr>
<td>After heat treatment</td>
<td>0</td>
<td>0.01</td>
<td>0.015</td>
<td>0.025</td>
<td>0.02</td>
<td>0.031</td>
<td>0.043</td>
</tr>
</tbody>
</table>

Table 2. Carbon contents of $\text{Al}_2\text{O}_3$, $\text{Al}_2\text{O}_3$/CNT and $\text{Al}_2\text{O}_3$/RGO ceramic composite
Fig. 1. XPS spectra of graphite (a), GO (b) and RGO (c)
Fig. 2. Raman spectra of graphite (a), GO (b) and RGO (c)
Figure 3. X-ray diffraction patterns of (a) as purchased, (b) sintered Al₂O₃, (c) 0.5 wt% CNT added, and 0.5wt% RGO added Al₂O₃ composite ceramics.
Figure 4. FESEM micrographs of as purchased alumina powder (a) and fractured morphology for (b) monolithic, (c) 0.5 wt% CNT, (d) 1 wt% CNT
added and (e) 0.5 wt% RGO, (f) 1 wt% RGO added alumina composite

Figure 5. (a) Bright field image of 1 wt% RGO added alumina ceramics (b) EELS data of (a), (c) Bright field image of 1 wt% CNP added alumina ceramics and (d) EELS data of (c)
Figure 6. XPS data of Al$_2$O$_3$ (a), (b), Al$_2$O$_3$ /CNT (c), (d), Al$_2$O$_3$ /RGO (e) and (f).

Figure 7. Elastic modulus of CNT and RGO-Alumina composite ceramics.
Figure 8. Hardness and indentation fracture toughness of CNT and RGO-Alumina composite ceramics.
Figure 9. FESEM micrographs of indentation induced crack morphology in (a) 1wt% CNT added and (b) 1wt% RGO added alumina composite ceramics
Figure 10. Flexural strength of CNT and RGO-Alumina composite ceramics.
Figure 11. FESEM micrographs of fractured morphology for (a) 1wt% CNT added and (b) 1wt% RGO added alumina composite ceramics.
Figure. 12. Electrical conductivity of CNT and RGO-Alumina composite ceramics.
Figure 13. Temperature dependence of thermal conductivity (a) CNT added, (b) RGO added, (c) interfacial thermal resistance considered thermal conductivity,
and phonon mean free path (d).

References


10. Superior Thermal Conductivity of Single-Layer Graphene, Alexander A. Balandin, Suchismita Ghosh, Wenzhong Bao, Irene Calizo, Desalegne Teweldebrhan, Feng Miao § and Chun Ning Lau, Nano lett, 8(3) 902-


27. Elastic Properties of Chemically Derived Single Graphene Sheets


42. Reaction between aluminum oxide and carbon- The Al$_2$O$_3$-Al$_4$C$_3$ phase diagram, Foster L.M, Long G, Hunter M.S., J. am ceram soc, 39(1) 1 (1956)

국 문 초 록

세라믹재료는 우수한 기계적 특성과 화학적, 열적 안정성으로 인하여 절단용구, 연마재, 가스터빈, 건축자재, 치아재료 등의 산업 전반에 걸쳐 다양한 용도에 맞추어 사용되고 있다. 그러나 세라믹재료 자체가 가지는 취성은 고기능성 세라믹재료나 가혹한 환경에서 사용하기에 제약으로 작용해오고 있고, 절연특성으로 인한 마찰전기 축적의 문제, 낮은 열전도성 등의 문제를 해결하기 위하여 미세구조 최적화, 복합체 제작등의 다양한 시도가 이루어져 왔다.

그 중에서도 복합체에 관한 연구는 오랜 시간 동안 점차재의 조성, 구조, 형태 등 여러 가지 측면에서 이루어져 왔다. 최근에 관심을 가지게 된 물질 중에서 탄소나노튜브와 그래핀은 우수한 기계적,
전기적, 열적 특성으로 인해 차세대 첨가제로 그 가능성을 매우 높이고 있는 상황이다.

본 연구에서는 세라믹 복합체에 관하여 심도 깊은 연구를 진행하고자 한다. 탄소나노튜브와 그래핀이 첨가제로 선정되었고 첨가제의 강화기구 규명과 복합체의 물성평가에 관하여 논하고자 한다.

첫 번째 주제 에서는 완전히 치밀화 시킨 YSZ-SWCNT 복합체를 통한 활성 소결법으로 제작하고 전기적, 기계적 특성을 평가하였다. Dimethylformamide (DMF) 를 용매로 선정하였고 tip-sonicator 를 이용하여 탄소나노튜브를 모재에 데미지 없이 분산할 수 있었다. 제작된 복합체의 미세구조를 살펴보았을 때, 균일하게 분산된 SWCNT 번들이 모재와 깨끗하게 결합되어 있는 것을 볼 수 있었고 비정질의 탄소층이나 이중의 층이 만들어지지 않은 것을 확인할 수 있었다. ZrO$_2$ 세라믹의 전기 저항은 CNT 를 1.0 wt% 첨가했을 때 0.3 $\Omega$cm 까지 급격하게 감소함을 확인할 수 있었다. 또한 SWCNT 가 1.0 wt% 첨가되었을 때 복합체의 파괴인성이 4.4에서 5.2 MPa$^{1/2}$ 까지 증가함을 확인할 수 있었다. 이는 탄소나노튜브의 pull-out, crack bridging 으로 인한 영향으로 생각된다. 복합체의 마찰계수는 크게
변화하지 않았으나 마모율은 급격하게 감소하여 탄소나노튜브가 내마모특성을 향상시키는 것으로 판단되며 이는 기계적 특성 향상에 근거한 것이라고 생각된다.

추가적으로, 완전히 치밀화된 reduced graphene oxide (RGO)가 첨가된 YSZ 복합체를 통전활성소결 방법으로 제작하고 전기적, 열적, 기계적 특성을 평가하였다. Graphene oxide (GO)는 DMF/water 용매에서 짧은시간 초음파처리를 이용하여 박리시켰고 ZrO₂ 분말과 고르게 혼합하여 복합분말을 제작하였다. 소결된 복합체의 미세구조에서 RGO 가 균일하게 모재사이에 분포됨을 확인하였고 별다른 구조적 결함은 관찰되지 않았다. 복합체의 전기저항이 RGO 4.1 vol%에서 0.008 Ωcm 수준으로 급격히 감소함을 확인하였다. 또한 열확산계수가 미세하게나마 증가함을 확인하였고 경도 감소와 파괴인성 증가를 확인할 수 있었다. 이는 앞의 SWCNT 복합체와 유사하게 RGO pull-out 과 crack bridging 효과 때문인 것으로 생각된다.

두 번째로, 알루미나 모재에 CNT 와 RGO (reduced graphene oxide)를 각각 첨가하여 전기적, 열적, 기계적 특성을 평가하고 비교하였다. 각각의 복합체는 앞선 CNT-YSZ, RGO-YSZ 복합체와 유사하게
통전활성 소결방법을 이용하였으며 98%이상으로 치밀화됨을 확인하였다. 그러나 CNT 복합체의 경우 RGO 복합체에 비하여 다소 낮은 밀도를 나타내었다. 기계적 특성에서, 탄성계수와 경도가 두 복합체에서 모두 감소함을 보였고 RGO 복합체에서 더 큰 폭의 감소를 나타내었다. 이는 RGO 복합체의 밀도가 가장 큰 영향을 미친 것으로 생각된다. TEM-EELS 분석을 통하여 미세구조 및 모재와 첨가제 사이의 결합이 존재함을 화학적 상태가 sp2에서 sp3 hybridization으로 변화함을 통해 확인할 수 있었고 있었다. 파괴인성의 경우 두 복합체 모두 증가하는 경향을 나타내었고 pull-out, crack bridging 등에 의한 영향으로 생각된다. 기계적 강도는 두 복합체 모두 증가함을 보였으나 CNT 복합체에서 더 우수한 강도값을 보였다. 이는 CNT 가 가지는 더 넓은 표면적이 더 많은 결합영역을 제공하여 load sharing을 통해 증가되었다고 판단되어 진다. 전기적 특성에서는 두 복합체 모두 일정 첨가제 농도 이상에서 급격히 전기 전도성이 향상됨을 보였다. Electrical percolation 측면에서는 CNT 가 훨씬 빠른 것을 알 수 있었으며 이는 CNT 가 가지는 구조적 특성(1D structure) 때문인 것으로 시뮬레이션 결과로 알 수 있었다. 열전도율은 두 복합체 모두 급격히 감소하였으며 이는 CNT, RGO 혹은
탄소몰드에서 확산된 탄소가 모재 내에서 결함으로 작용하여 phonon mean free-path 를 감소시켜 나타난 결과라고 판단된다.

주 요 어 : 세라믹, 복합체, 동전 활성 소결, 알루미나, 지르코니아, 탄소나노튜브, 그래핀, 계면 결합, 기계적 특성, 전기전도성, 열전도성

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