Simultaneous strengthening and toughening of reduced graphene oxide/alumina composites fabricated by molecular-level mixing process

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ABSTRACT
Reduced graphene oxide/alumina composite powders were prepared by mixing of graphene oxides and aluminum ions at the molecular-level. It was found that the composite consolidated from the powders showed that reduced graphene oxide were homogeneously dispersed and strongly bonded with the alumina matrix by oxygen atoms presenting at reduced graphene oxide/alumina interfaces. Both the hardness and the toughness of the composites were enhanced simultaneously by the addition of reduced graphene oxide, which act as bridges to restrain the propagation of cracks in the alumina matrix. It is clarified that graphenes can be utilized as promising reinforcements for enhancement in mechanical properties of ceramic materials when the molecular-level mixing process is applied.

1. Introduction
Ceramics are very attractive high strength materials due to their hardness and elastic modulus, which are superior to those of polymers and metals. However, their use in structural applications is often limited because of their fragile and brittle properties. In the last few decades, there have been many attempts to improve ceramics’ toughness by using the nano-structuring of grains and the addition of reinforcements. These methods have the similar aim of providing newly formed intrinsic grain boundaries or extrinsic interfaces that prohibit dislocation-movement but also make a long path for crack propagation [1–3].

For the purpose of enhancing the toughness by introducing a large boundary area, we focus on graphenes, which have a two-dimensional graphitic sheet structure, because they maximize the contact area with the matrix, whereas one-dimensional agents such as carbon nanotubes utilize only the outer surface of their structure when dispersed in a matrix. Furthermore, graphenes are also well known as ideal and promising nanomaterials in high-strength applications due to their outstanding aspect ratio, Young’s modulus, good flexibility, and strength in plane [4–7]. Thus, recently, a number of studies incorporating graphene into conventional materials such as polymers, metals, and ceramics have reported functional and structural property-improvement
Many polymers with graphenes demonstrate significantly enhanced mechanical [12–17] and electric properties [18–20]. Compared to the case of graphene/polymer composites, however, there have so far been few studies that have used graphenes as a reinforcement in bulk metals [21] or ceramics [22,23]. Several researchers, such as Walker et al., fabricated graphene platelet (GPL)/Si3N4 composites using a ball milling process; they confirmed that the hardness of Si3N4 was improved by graphene addition [22]. When a conventional powder metallurgy (PM) route was used for graphene/ceramic composites, the composite exhibited lower than expected mechanical properties because of the severe agglomeration of graphenes stemming from Van der Walls interactions between the graphitic layers [23]. Once graphenes have agglomerated in composites, they disturb the full densification of the matrix materials due to their large surface area, which prevents atomic diffusion. Hence, it is necessary to disperse graphenes in the ceramic materials in order to confirm the effect of graphenes.

Here, our approach to achieving homogeneously dispersed graphenes in a ceramic matrix is to utilize a molecular-level-mixing process (see Ref. [24] for the detailed processes). This process is a promising method to uniformly disperse carbon-nanomaterials in inorganic materials; however, it also creates a strong interfacial bond between oxygen-containing functional groups on the carbon materials and metal ions in solution [25]. We first synthesized graphene/ceramic composite powders in which a few graphenes were not surrounded on the surface but embedded in the matrix powders. If the graphenes are embedded in the ceramic matrix powders with good interfacial bonding, we can expect that the dispersion status of the graphenes in the matrix can be guaranteed even after sintering at elevated temperature.

In this study, we used functionalized graphene oxide (GO) prepared using the modified Hummer’s method [26], which is a novel process to exfoliate few-layered graphene sheets from graphite and to functionalize the surface of the graphenes with oxygen-containing functional groups. For comparison, aluminum oxide (alumina) nanopowders were fabricated using the same process without graphenes. In particular, the composite powders were consolidated and simultaneously crystallized into reduced GO/alumina composites using a spark plasma sintering (SPS) process.

2. Experimental section

2.1. Fabrication of GO powders

GO was synthesized from HOPG (highly oriented pyrolytic graphite) using the modified Hummers method [26]. Briefly, 1 g of HOPG was added to 40 mL of concentrated H2SO4 that was cooling in an ice-bath. After that, 3.5 g of potassium permanganate was slowly added to the HOPG solution over 15 min in an ice-bath. The mixture was maintained at 35 °C with stirring. 200 mL of water was added to the resulting mixture, and 10 mL of H2SO4 was added dropwise until bubbling finished, in the ice bath. During the process, the color of the mixture changed from green to brown. After filtering the solution using a glass filter, it was washed several times with 10% HCl aqueous solution. After drying in a vacuum oven below 50 °C, the dry form of GO was obtained.

2.2. Fabrication of reduced GO/amorphous-alumina composite powders

GO was dispersed in distilled water by sonication to form a GO suspension. Al(NO3)3·9H2O was added to the suspension and stirred for 12 h. The solution was vaporized by heating to 100 °C and the powders that remained were oxidized at 350 °C for 1 h in an air atmosphere. The volume fractions of the graphenes were varied from 0 to 3 vol.%. For the reference data, GO powders were fabricated using the modified Hummers method, as noted above; amorphous-alumina powders were also fabricated in the same way as were our reduced GO/amorphous-alumina composites. GO and amorphous-alumina powders were planetary ball-milled for 12 h; the dried powder mixture was ground and sieved.

2.3. Fabrication of reduced GO/alumina composites

SPS was carried out with a Dr. Sinter 1500 SPS machine from Sumitomo Coal Mining Co. The composite powders were sintered for 10 min at a temperature of 1400 °C and vacuum pressure of 10−3 torr under a pressure of 50 MPa. The heating rate was fixed at 100 °C/min. The sintering process was performed in a graphite mold with a diameter of 15 mm; the sintered reduced GO/alumina composites have a cylindrical shape with a 15 mm diameter and 1 mm height.

2.4. Characterization of reduced GO-amorphous alumina and reduced GO/alumina composites

Microstructure characterization of the reduced GO/alumina composite powders and composites was carried out using scanning electron microscopy (Hitachi S-4800) and transmission electron microscopy (Tecnai G2 F39 S-Twin). FT-IR spectra were analyzed using the attenuated total reflectance (ATR) method (Jasco FT/IR-4100 type-A spectrometer); the XRD were measured using D/Max-IIIc (3 kW). Raman spectroscopy was analyzed using a high resolution dispersive Raman microscope (LabRAM HR UV/Vis/NIR, excitation at 514 nm). The volume fraction of the reduced GO in the reduced GO/alumina composites was determined using an element analyzer (ThermoQuest Elemental Analyzer EA1110-FIONS).

2.5. Mechanical properties alumina and reduced GO/alumina composite

The hardness of the reduced GO reinforced alumina matrix composite was measured using the Vickers indentation test under a load of 19.6 N and 10 s loading time. Vickers hardness (H) was calculated from the following Eq. (1):

\[ H = \frac{2P \sin \theta}{L^2} = \frac{1.854P}{L} \]  

(1)

where P is the applied load (kg), L is the average length of the diagonals (mm), and θ is the angle between opposite faces of the diamond tip (=136°). Using the Evans and Charles equation [22], fracture toughness was measured according to the
lengths of the cracks. A 3-point bending test was performed using an INSTRON 5583 under a crosshead speed of 0.2 mm/min. The dimensions of the specimens were 13.3 mm × 1.3 mm × 1 mm, based on ASTM 1161-02c. The 3-point flexural strength of reduced GO/alumina composites was evaluated using the following equation:

\[
\sigma_f = \frac{3PL}{2bd^2}
\]

(2)

where \( \sigma_f \) is stress on the specimen cross-section (MPa), and \( P \) is load at a given point on the load deflection curve (N), \( L \) is the length of support span (mm), with \( b \) and \( d \) being the width and thickness of the specimen, respectively.

3. Results and discussion

3.1. Synthesis of reduced GO/alumina composite powders by molecular level mixing process

Fig. 1(a) shows our strategy for fabricating reduced GO/alumina composite powders, in which reduced GOS are embedded and attached in the alumina matrix powders. The key feature of our strategy is that both hydroxyl (–OH), and carboxyl (–COOH) groups on the surface of GO and Al ions are mixed at a molecular level. As shown in Fig. 1(a), first, GOS and aluminum nitrate are dispersed as a stable suspension in a water-based solvent. Ultrasonic treatment provides thermal and vibrational energy to initiate a chemical reaction between Al ions and several functional groups on the surface of the GOS. Aluminum nitrates are thermally decomposed into Al-ions and nitrogen-containing organic materials [28]; then, the decomposed Al ions are heterogeneously nucleated on the functionalized GO surface. Once the Al-nuclei have formed on the GO surface, agglomeration of the GOS is prevented because \( \pi \)-electron-stacking between the graphene planes is weakened by the coating of the Al materials. The next step is to dry the solution by heating.

As the water solvent is evaporated, the concentration of Al increases in the solution until the Al nuclei are continuously precipitated and reacted with oxygen atoms supplied by the water solvent or the external air-atmosphere. During this step, Al nuclei on the GOS are transformed into Al oxide materials by the vigorous oxidation process; the residual functional groups of GOS are reduced by the additional oxidation process. By varying the oxidation time and temperature, the size and shape of the alumina powders are changed. In particular, since our aim is to make graphene-embedded-alumina composite powder, the reaction conditions were

Fig. 1 – Fabrication process of reduced GO/alumina composite powders by molecular level mixing process. (a) Schematic design for fabricating reduced GO/alumina composite by molecular level mixing process; (b and c) AFM and TEM images of fabricated GO; (d and e) SEM and TEM images of reduced GO/amorphous-alumina composite powders after removal of the solvent and heat treatment; (f) FT-IR analysis of reduced GO/amorphous-alumina (red line) and pure amorphous-alumina powders. (A colour version of this figure can be viewed online.)
optimized in order to ensure that most of the reduced GOs were covered by alumina materials, as schematically shown in Fig. 1(a).

Fig. 1(b) provides an AFM image of the GO prepared using the Hummer’s method. The size and thickness of the fabricated GO are revealed to be a few micrometers in-plane and only a few layers, respectively (see the Supporting information in Fig. S1). Fig. 1(c) provides a TEM image of the GO showing a hexagonal selected area electron diffraction (SAED) pattern, which indicates clear graphite diffraction and the pattern of the few-layered GOs. Fig. 1(d) provides a TEM image of the GO showing a hexagonal selected area electron diffraction (SAED) pattern, which indicates clear graphite diffraction and the pattern of the few-layered GOs. The morphology of the reduced GO/alumina composite powders, obtained after the calcination process, confirms that the reduced GOs are surrounded by alumina powders, as shown in Fig. 1(d). Fig. 1(e) provides a TEM image of the reduced GO/alumina composite powders; reduced GO sheets can be clearly observed among the amorphous-alumina powders. In addition, it was found that severe agglomeration among reduced GOs had not occurred even after the chemical reaction was induced by the heat treatment process.

Fig. 1(f) shows the Fourier transform-infrared (FT-IR) data for both the reduced GO/alumina composite powders and the pure alumina powders without graphenes. Two characteristic peaks of the composite powders are observed at 1380 and 1100 cm\(^{-1}\). One is C–C stretching at around 1380 cm\(^{-1}\); another peak, at around 1100 cm\(^{-1}\), corresponds to Al–O–C bonding \[29–31\]. This bonding implies that our process induces the formation of chemical bonding between reduced GOs and the alumina matrix.

There can be several mechanisms which form the chemical bonds between Al ions from Al(NO\(_3\))\(_3\) and functional groups such as –COOH and –OH at the GO surfaces. Basically, it is possible to make chemical bonding between hydroxyl radical present at the surface of graphene oxide and Al ion. A high-energy ultrasonic process accelerates this chemical reaction \[32\]. The thermodynamic equations are simply expressed as follows \[33,34\]:

\[
\text{Al}^{3+} + 3(\text{OH}^-) \rightarrow \text{Al(OH)}_3^-, \quad \Delta H = 61.3 \text{kJ/mol at } 273 \text{ K} \quad (3)
\]

\[
\text{Al(OH)}_3^{\text{\lambda}} \xrightarrow{\Delta} (1/2)\text{Al}_2\text{O}_3 + (3/2)\text{H}_2\text{O}, \quad \Delta H = 101.89 \text{kJ/mol} \quad (4)
\]

\[
\text{Al}_2\text{O}_3^{\text{\lambda}} \xrightarrow{\Delta} \gamma - \text{Al}_2\text{O}_3 \xrightarrow{\Delta} \alpha - \text{Al}_2\text{O}_3 \quad (5)
\]

As shown in Eq. (3), the hydroxyl group (OH) bonded with carbon atom of GO is firstly reacted with Al ions and then the bonded Al–OH on the carbon atom is transformed into Al\(_2\)O\(_3\) phase by heating process resulting in the reductant of H\(_2\)O. Thus Al–O–C bonds at the reduced GO/alumina interface is newly formed and small amount of the bonds is observed in the FT-IR results. The synthesized Al\(_2\)O\(_3\) amorphous phase is crystallized by heating energy supplied from further sintering process as shown in the above Eq. (5).

3.2. Consolidation and microstructures of reduced GO/alumina composites

The reduced GO/alumina composite powders were crystallized and simultaneously consolidated using a SPS process.

Fig. 2 – Spark plasma sintering and microstructures of reduced GO/alumina composites. (a) Schematic illustration of SPS process of reduced GO/alumina composite powders; (b) SPS behavior of reduced GO/alumina composite powders; (c) SEM image of fabricated sintered 3 vol.% reduced GO/alumina composite (low magnification) and enlarged SEM image of red box of (c). (A colour version of this figure can be viewed online.)
The SPS can minimize structural damage to the reduced GOs contained in the alumina matrix due to its fast densification rate. As shown in Fig. 2(a), shrinkage of the composite powders is calculated from the change of displacement between the upper and lower punches in the graphite mold. A plot of displacement, determined during the sintering process, was converted into values for the shrinkage of samples; this gives information on the in situ phase transformation (amorphous → γ → α) and simultaneously, the sintering behavior of the reduced GO/alumina composite powders, as shown in Fig. 2(b). The inset of Fig. 2(b) provides XRD patterns, obtained at stages I, II, and III, shown with temperature during the SPS process. The change of shrinkage at the initial stage (600–800 °C) is related to the removal of water and gases from the composite powders. A large shrinkage of the composite powders is observed as the temperature increases from 800 to 1050 °C (Stage II), which means that necking and densification have occurred; it also means that the amorphous phase has been transformed into the γ alumina phase. The small shrinkage at stage III indicates that grain growth and the final crystal structure-change to α alumina, also confirmed by the inset XRD patterns obtained at stage III, occurred in the samples at the same time.

As can be seen in the SEM images shown in Fig. 2(c), the sintered reduced GO/alumina composite has reduced GOs on the surface of the alumina matrix and there is no severe porosity. Red arrows indicate reduced GOs dispersed in the alumina matrix grain. The enlarged SEM image in the red-box region of Fig. 2(c) shows that the thickness of the observed reduced GOs is under 100 nm; the reduced GOs seem to be implanted in the alumina matrix.

Raman spectroscopy results, shown in Fig. 3(a), show two characteristic peaks at ~1350 cm\(^{-1}\), known as the defect band, and at ~1590 cm\(^{-1}\), known as the G peak; these two peaks represent the sp\(^2\) bonded planar carbon structures [35]. D and G peaks are also confirmed after the sintering process (the red line in Fig. 3(a)); this proves that the reduced GOs remain even after the SPS sintering process at 1400 °C. Interestingly, it was found that the G peak of the sintered sample was somewhat down-shifted compared to that of the composite powders. We believe that the down-shift of the G peak means that the reduced GOs are under tensile strain [35,36]; this strain stems from residual stress between the reduced GO and the matrix, generated during the sintering process, influencing the position of the G band [36–38]. That is, the reduced GOs withstand stress by sharing a portion of the load from the alumina matrix. In addition, the \(I_D/I_G\) ratio of the reduced GO/alumina composite decreased after sintering; this implies that the defects of the reduced GOs decreased under high-temperature regime [35].

Fig. 3(b) provides a TEM image of the interface between alumina and reduced GO in the reduced GO/alumina composite. There are three regions in the TEM image (Fig. 3(b)). The upper area corresponds to the alumina matrix (া), as confirmed by EDS analysis. The bright and lower area indicated by (ഒ) in Fig. 3(b) is a carbon region that is assumed to be reduced GO. The (ഓ) region consists of aluminum, oxygen, and carbon. It could be that the Al–O–C bond, known to exist because of the 1100 cm\(^{-1}\) peak in the FT-IR analysis (Fig. 1(f)), is present in this interfacial region. From this evidence, we believe that our composite exhibits strong bonding between reduced GO and the alumina matrix, which results in the homogeneous dispersion of reduced GOs.

### 3.3. Mechanical properties of reduced GO/alumina composites

The mechanical properties of the fabricated reduced GO/alumina composites are shown in Fig. 4(a) and (b). Fig. 4(a) shows the Vickers hardness (red line) and 3-point flexural strength (blue line) of the reduced GO/alumina composites as a function of the volume fraction of reduced GO. As the volume fraction of reduced GO increases from 0 to 3 vol.%, the hardness also increases, from 2008 to 2294 Hv. The plot also shows an increase in flexural strength, from 350 to 425 MPa, with increasing reduced GO content. The increase of strength produced by adding reduced GOs is related to the load bearing of reduced GO in the alumina matrix: strongly bonded reduced GOs help the composite to endure external strain.

Fig. 4(b) shows the indentation fracture toughness of the reduced GO/alumina composites, which was simply calculated from the equation proposed by Evans and Charles (\(K_C = 0.0824\sqrt{\frac{E}{\rho}}\)) [27]. The results show that the fracture
toughness of the reduced GO/alumina composite significantly increases with increasing volume fraction of reduced GOs. The fracture toughness of the composite displays its maximum value, 10.5 MPa m^{0.5}, when 2 vol.% reduced GOs are added. However, as the reduced GO content is increased up to 3 vol.%, fracture toughness is slightly reduced due to the agglomeration of reduced GOs.

**Fig. 5(a)** shows the Vickers hardness values of reduced GO/alumina (red points), which values are compared to those of pure alumina samples with various grain sizes. This result is clearly described by the hardening of alumina according to the Hall–Petch relation \(H_m = H_0 + k(d_m)^{1/2}\), where \(H_m\) is the hardness of the matrix, \(H_0\) is the frictional hardness, \(k\) is a constant, and \(d_m\) is the mean grain size of the alumina matrix. The results indicate that the reduced GO/alumina composites show a higher hardness than that of pure alumina samples of the same grain size. Apparently, the hardening of the matrix by grain refinement causes additional hardening of the composite, as shown in **Fig. 5(a)**, because we used reduced GOs of the same process and size in order to confirm the effect on the matrix. **Fig. 5(b)** more clearly elucidates the effect of grain refinement and reduced GO addition for reduced GO/alumina composites. The 3 vol.% reduced GO/alumina composite with fine matrix is additionally hardened by the reduced GOs from the fine grained pure alumina matrix. Thus, we can conclude that there is a synergetic hardening of the composite arising from matrix-grain refinement and the addition of reduced GOs bonded with the alumina matrix.

As previously suggested in the analysis of the yield strength of the CNT/metal composites [24], the hardness of ceramic materials can be expressed with the following equation, generalized from theoretical models using the load transfer concept, when a perfect interface is assumed:

\[
H_c = H_m + H_f V_f R
\]

where \(R\) is the hardening efficiency of the reinforcement, \(V_f\) is the volume fraction of reinforcement, and \(H_m\) is the hardness of the matrix. Hardening of a composite by reinforcements is limited by their volume fraction and the \(R\) value, which is related to shape; the aspect ratio of the reinforcement; and the hardness value of the matrix, which can be changed by microstructural factors such as grain size.

**Fig. 5(c)** clearly demonstrates a “bridge” of reduced GOs in the crack of the composite. White arrows indicate reduced GOs, and direct evidence that reduced GOs are bridging the cracks can be seen. **Fig. 5(d)** schematically illustrates a crack in the alumina matrix bridged by reduced GOs in the reduced GO/alumina composite. The increase in toughness is related to the strong bond between the reduced GO and alumina matrix, which forms a “bridge” across the crack; these bridges prevent crack propagation by dissipating the energy. Reduced GOs are considered to play a role in absorbing the load transferred from the alumina matrix.

The SEM micrographs show that in pure alumina samples (Fig. 5(a)), crack propagation was relatively straight without deflection; however, cracks in the reduced GO/alumina sample show deflection in the branched crack structures (Fig. 5(b)). It seems that homogeneously dispersed reduced GOs disturb crack propagation and thus improve the fracture toughness of the composites. However, averaged total crack length of the 3 vol.% reduced GO/alumina composite was slightly decreased, even though crack deflection has been generated. It is observed that deflected crack is directed towards the grain boundary of alumina and propagated along the boundary which is the weak region in the materials. In particular, agglomerated reduced GO sheets usually locate at the grain boundary rather than in the grain of the matrix, and they accelerate crack propagation. Thus, once crack propagated along the agglomerated reduced GO surface, fracture can be easily occurred and then resulted in low toughness values. Actually, since agglomeration of reduced GO sheets is occasionally discovered at the 3 vol.% reduced GO/alumina in our molecular level mixing process, the toughness value is decreased at 3 vol.% while the peak value of fracture toughness is shown at 2 vol.%. Compared to toughness value, however, the hardness of the composite is continuously increased up to 3 vol.% reduced GO/alumina due to grain refinement and reinforcing effect. From these results, it could be confirmed that the homogeneous distribution of reduced
GOs within the alumina matrix and the formation of strong interfaces between reduced GO and alumina simultaneously enhance the mechanical properties of reduced GO/alumina composites.

4. Conclusion

A novel method for fabricating reduced GO/alumina composites, using a molecular level mixing process and spark plasma sintering, has been proposed. The produced reduced GO/alumina composites exhibit homogeneously distributed reduced GOs that are strongly bonded with the alumina matrix. Most interestingly, we observed Al–O–C bonding using FT-IR analysis and the interface area of the reduced GO and alumina matrix using TEM analysis; both showed strong evidence of the molecular level mixing process. Due to its characteristic microstructure, fabricated reduced GO/alumina composites show remarkably enhanced strength, hardness of 2300 Hv, and fracture toughness of 11 MPa m$^{0.5}$; all these values are superior to those of monolithic materials and the reduced GO/alumina composites that have been reported by other researchers [please see Supporting information Table S1]. The mechanisms that enhance the mechanical properties of these composites were found to be the strong bonding between reduced GOs and the alumina matrices, and the load sharing and crack bridging by reduced GOs in the alumina matrix.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2014.06.074.

REFERENCES


