

Fabrication and densification mechanism of MgO/Graphene composites with LiF as additive

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ABSTRACT

MgO/Graphene composites were prepared by combustion synthesis (CS) followed with spark plasma sintering (SPS) using LiF as sintering additive. The densification mechanism of MgO/Graphene composites doped with LiF was systematically investigated. With incorporating small amount of graphene into MgO, the spectral absorptivity of the composite was improved, whereas the density, hardness and average grain size were decreased. The densification of submicron sized MgO/Graphene ceramics was realized by the balance between sintering promoted by LiF and grain refinement of graphene.

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Graphene, a two-dimensional allotrope of carbon, is described to have a large number of extraordinary properties [1–3]. In virtue of the distinct 2D structure and prominent electrical, thermal and mechanical properties of graphene, incorporating graphene into ceramics to produce reinforced ceramic composites has great potential. The quality of the graphene dispersion in a ceramic material remarkably affects the final properties of the composite [4]. A considerable amount of work has been done with graphene to produce well dispersed ceramic composites [4–6]. There is a lot scope for further research to investigate scalable, energy-saving and environmentally friendly processing routes for preparing well dispersed graphene/ceramic composites [4,7]. Chakrabati et al. reported an innovative route for producing few-layer graphene by burning magnesium metal in a greenhouse CO₂ environment [8]. Combustion synthesis (CS) has been demonstrated to be a very promising method to synthesize high-quality graphene [9,10]. From the view of the green process, it is obviously unreasonable to remove a large amount of MgO with acid solution. MgO is not only a significant ceramic material with a lot of excellent physicochemical properties such as: high melting point, superior thermal stability and good mechanical properties, but also an excellent substrate for the homogenous dispersion of in situ formed graphene [7,11,12]. Therefore, it is a scientific and reasonable countermeasure to make full use of this combustion reaction [7].

However, the pinning effect of the homogeneously distributed graphene inhibits grain growth and hinders the movement of boundary, resulting in a refinement of microstructure and limited densification [13]. Usually, the densification of the single phase MgO ceramic is carried out by the pressure-less sintering or pressure aided sintering techniques, such as hot pressing, hot isostatic pressing and spark plasma sintering (SPS) [14–17]. Chen et al. reported that highly dense MgO/Graphene composites could be obtained by hot-pressing at 1700 °C for 1 h under the pressure of 30 MPa in a flowing Ar atmosphere [18]. Obviously, the conventional methods for the fabrication of dense MgO/Graphene composites need high sintering temperature. Thus, relatively novel consolidation techniques or additives are necessary to the fast densification of MgO/Graphene composites. LiF is commonly used as sintering additive in the fabrication of ceramics, which can enhance the densification due to the formation of grain boundary liquid phase [19–21]. Considering the fast densification of MgO/Graphene composites, it is reasonable to employ SPS technique with LiF additive.

In this study, MgO/Graphene composites were prepared by combustion synthesis followed with spark plasma sintering using LiF as sintering additive. The densification mechanism of MgO/Graphene with LiF was investigated. This method provides a fast route to fabricate the dense and well-dispersed ceramics/graphene composites.

MgO/Graphene mixture powders were obtained by the combustion reaction between Mg powders (20 μm, purify>99.7%) and CO₂ gas (>99.99%) according to the formula:



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Table 1
Physical and mechanical properties of SPSed MgO ceramics with different graphene contents.

G% (wt %)	Density (g/cm ³)	Relative density (%)	Hardness (GPa)	Average grain size (μm)
0	3.54	98.74	8.0 ± 0.6	1.84 ± 1.15
0.5	3.37	94.23	4.8 ± 0.6	1.59 ± 0.79
1.0	3.49	97.84	5.2 ± 0.7	1.36 ± 0.53
1.5	3.45	96.93	5.1 ± 0.4	0.99 ± 0.34
1.84	3.43	96.44	5.5 ± 0.3	0.34 ± 0.10

MgO powders (50 nm, Wuxi Zehui Chemical Co., Ltd.), which act as a diluent, were mixed into the reactant Mg powders in the mass ratio of 9:1. The mixture powders were put into a stainless-steel vessel and then placed in a sealed chamber filled with 1 MPa CO₂ gas. The reaction was initiated by passing an electric current through a tungsten coil immersed in mixture powders. After the reaction, the product powders were collected and were calcined at 800 °C in air to remove graphene for measuring the graphene content. The actual graphene content of the combustion synthesis product is 1.84%, and it is lower than the theoretical value of 2.29%, which may be caused by the impurity of Mg powders. Samples with different graphene contents (0.5%wt, 1.0%wt, 1.5%wt) were obtained by tailoring MgO into the combustion product. All the samples with 1%wt LiF addition (99.9%, Aladdin Industrial Corporation) were mixed by rolling mill for 1 h. The sample obtained by direct mixing the combustion synthesis product with 1%wt LiF is denoted as CS-9.

The resulting samples were put into a graphite mold with an inner diameter of 30 mm and sintered in vacuum at a sintering temperature of 1000 °C under the pressure of 30 MPa by SPS (SPS-625, FUJI Electronic). The heating rate of 100 °C/min and dwell time of 5 min were applied in the SPS process. The sintered samples were thermal etched at 800 °C for 2 h in air for average grain size characterization.

The microstructure of the SPSed samples was investigated by scanning electron microscopy (SEM; S-4800, Hitachi, Japan) and transmission electron microscopy (TEM; FEI Talos F200, American). The bulk density of the sintered samples was obtained by the Archimedes method and the hardness was tested by the Vickers indentation method (HV-10Z) with a load of 29.4 N and dwell time of 10s. Spectral

absorptivity was measured by ultraviolet-visible-near IR spectrophotometer (Cary 6000i, Agilent Technologies, American) equipped with an internal integrating sphere.

The density, relative density, hardness and average grain size of the sintered samples are exhibited in Table 1. The theoretical density of the MgO/G composites is calculated by the rule of mixtures, assuming densities of 3.58 g/cm³ and 2.20 g/cm³ for MgO and graphene, respectively [7]. As shown, the incorporation of graphene onto MgO leads to the decrease of density and hardness. The decrease of density can be accounted for the addition of graphene and the presence of porosity. While the decrease in hardness can be attributed to the weak van der Waals bonds between graphene layers. Besides, graphene often generates localized porosity, which can enable ceramic grains to be displaced as graphene is deformed, and facilitates the sliding of grains as sheets of graphene become sheared [22]. The hardness of all the graphene-added samples shows little obvious change with the change of graphene content. Moreover, the relative density of the sample with the graphene content of 0.5% reaches the minimum. That may be explained by the densification mechanism of the MgO/Graphene composites doped with LiF, which will be discussed later. The SEM micrographs of the thermal etched samples are shown in Fig. 1 for obtaining the average grain size from typical areas. It can be found that with increasing the graphene content, the average grain size was significantly decreased from 1.84 μm to 0.34 μm. Therefore, the grain growth and densification were obviously hindered by the addition of graphene.

Fig. 2 shows the microstructure of the CS-9 sample. It can be clearly seen that the grain size is about 300 nm and the graphene mainly distributed in the grain boundary, which wrap around MgO grains. Consequently, graphene inhibits grain growth and densification of MgO ceramics by hindering grain boundary diffusion. And Fig. 2(c) shows the combustion synthesized graphene is 5–6 layers.

The densification mechanism of MgO/Graphene composites doped with LiF can be inferred from the microstructure information, which is shown in Fig. 3. On the one hand, precious researchers have reported that LiF can form a transient liquid phase at the early stage of sintering to promote the rearrangement of grains and grain-boundary mobility [21,23,24]. On the other hand, a systematic study concludes that LiF reacts with C to form volatile CF_x (where x represents F stoichiometry). If LiF removes C through the formation of CF_x, then the remaining Li ions may

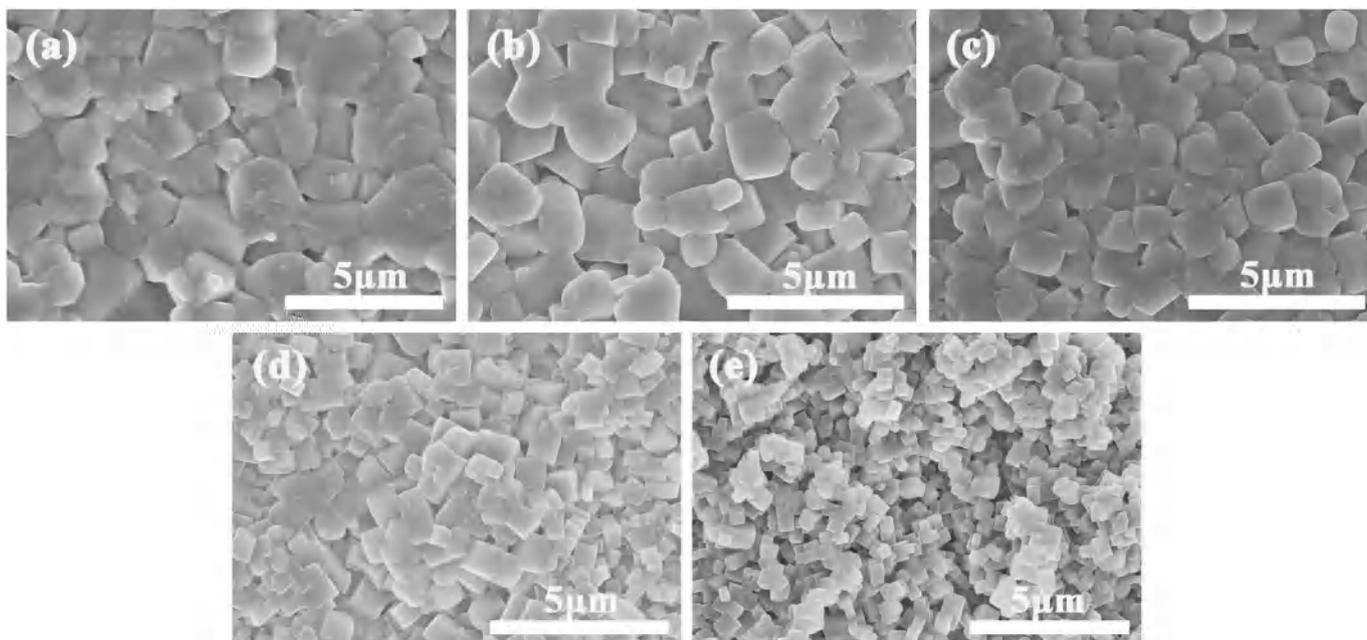


Fig. 1. The SEM images of the thermal-etched samples with different graphene contents: (a) 0%; (b) 0.5%; (c) 1.0%; (d) 1.5%; (e) 1.84%.

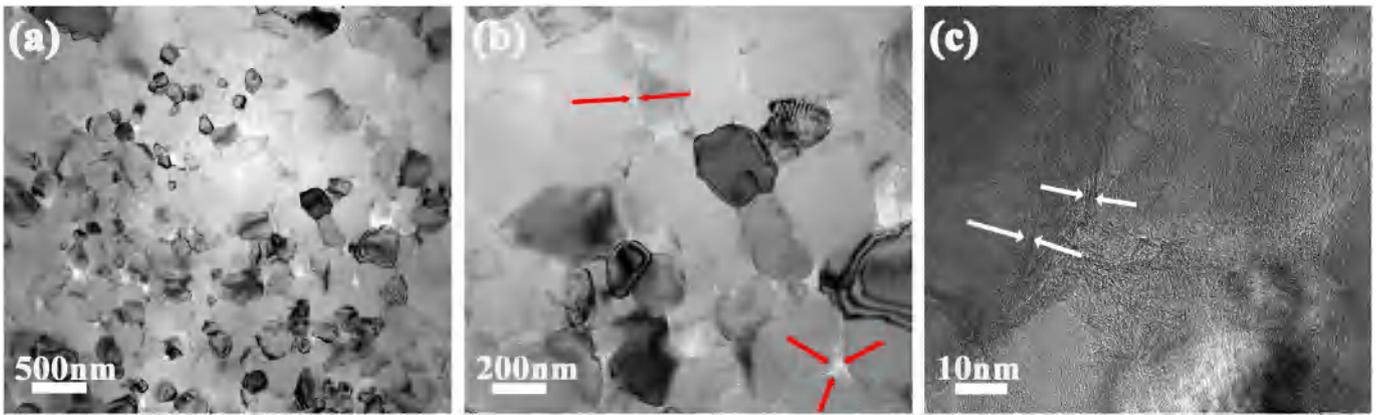


Fig. 2. The TEM images of the CS-9 sample.

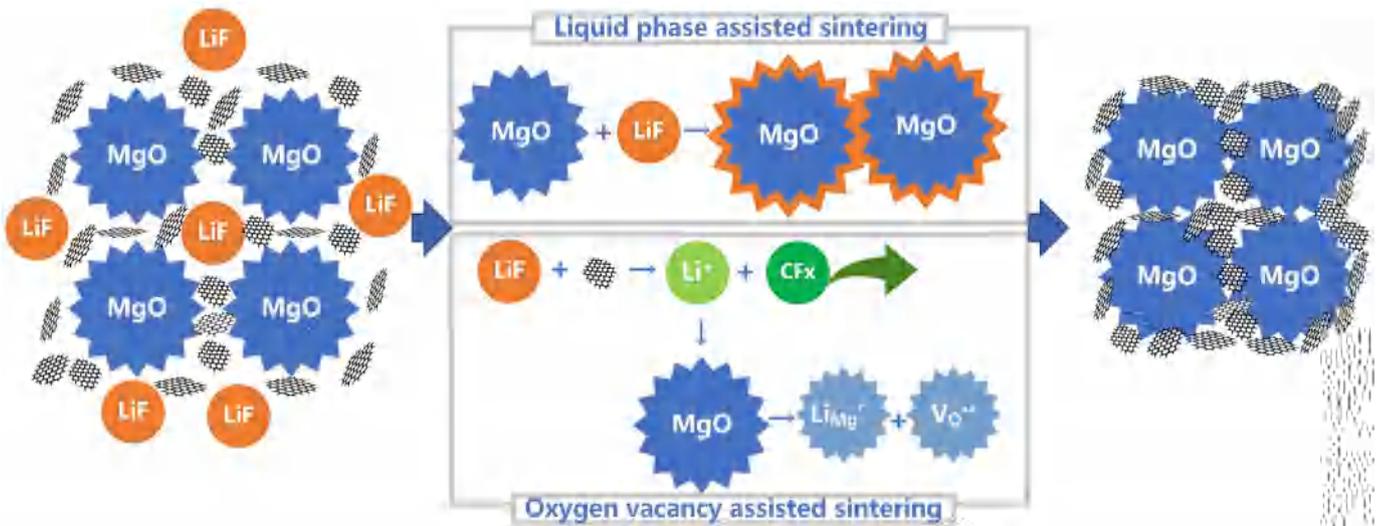


Fig. 3. The densification mechanism of MgO/Graphene ceramics doped with LiF.

diffuse through the MgO structure by substituting for Mg ions along with oxygen vacancies. It implies an increase in the oxygen vacancy concentration and hence an increase in either the densification rate, the grain-boundary mobility, or both [23,25,26]. Although Graphene inhibits sintering and densification by wrapping around grains and impeding grain boundary diffusion, LiF can ameliorate this problem by reacting with graphene [12]. The realization of sintering and densification of MgO/G composites doped with LiF is the result of the interaction of liquid phase assisted sintering and oxygen vacancy assisted sintering. The minimum relative density may be ascribed that a small amount of graphene reacts with LiF and the excess LiF evaporates.

Fig. 4 demonstrates the spectral absorptivity of the sintered MgO samples with different graphene content. In the wavelength interval of 200–2500 nm, the spectral absorptivity of samples with graphene added is obviously higher than the sample without graphene added. Due to the addition of graphene, MgO, an optically transparent material, is transformed into an optically absorptive material. Moreover, the absorptivity reaches maximum as the graphene content of 1.5%. The absorptivity of all the graphene-added samples has little change and exceeds 0.9 in most spectral regions. The above-mentioned results indicate that MgO/Graphene

composites become another optical ceramics, which have an excellent infrared radiation property [27,28].

In summary, MgO/Graphene composites were prepared by combustion synthesis followed with spark plasma sintering using LiF as sintering additive. The uniform wrapping of MgO by graphene deteriorates the densification of ceramics, but is beneficial to the refinement of microstructure. But LiF can ameliorate densification problem through the interaction of liquid phase assisted sintering and oxygen vacancy assisted sintering. Through process optimization based on the above-mentioned two densification mechanisms, this method not only realizes high densification, but also ensures grain refinement. The MgO/Graphene composite with the relative density of 96.44% and the grain size of about 300 nm was obtained at the sintering temperature of 1000 °C, which is 700 °C lower than that of hot pressing. The absorptivity of the MgO/Graphene composites exceeds 0.9 in most spectral regions, thus it is a typical infrared ceramic, which has potential applications in the field of radiation cooling.

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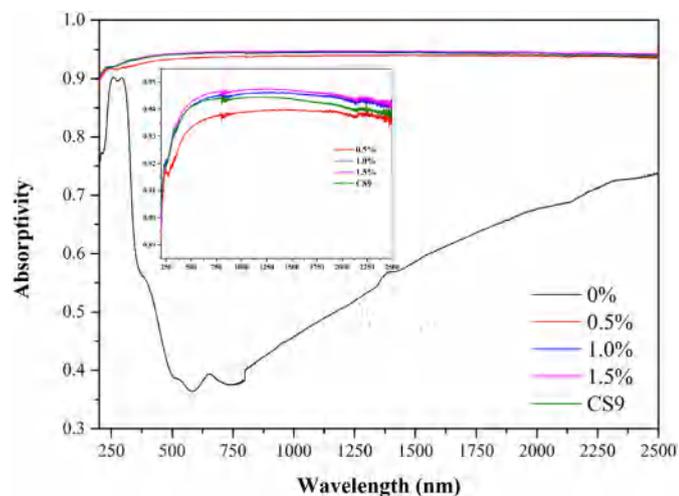


Fig. 4. The spectral absorptivity of the sintered samples with different graphene content.

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