Magnesium Phosphate Cements/GNPs Composites by Combustion Synthesis and Acid-Base Reaction

Nan Lu\textsuperscript{ab}, Jiaxi Liu\textsuperscript{ab}, Gang He\textsuperscript{a}, Jiangtao Li\textsuperscript{ab,\textdagger}

\textsuperscript{a} Key Laboratory of Cryogenics, Technical Institute of Physics and Chemistry, Chinese Academy of Science, Beijing 100190, China

\textsuperscript{b} Center of Materials Science and Optoelectronics Engineering, University of the Chinese Academy of Science, Beijing 100049, China

lijiangtao@mail.ipc.ac.cn

Abstract. Magnesium phosphate cements (MPC)/graphene nanoplatelets (GNPs) composites were fabricated by combustion synthesis and acid-base reaction. MgO/GNPs mixture powders were obtained by the combustion reaction between Mg powders and CO\textsubscript{2} gas. The composites were prepared by mixing MgO/GNPs mixture powders with potassium dihydrogen phosphate (KH\textsubscript{2}PO\textsubscript{4}) using borax as retarder. The effect of GNPs content on mechanical and functional properties of the prepared MPC/GNPs composites was investigated. The results show that this MPC/GNPs cements mainly consisted of MgO and KMgPO\textsubscript{4}•6H\textsubscript{2}O. Moreover, the crystallinity of KMgPO\textsubscript{4}•6H\textsubscript{2}O in lower surface is better than the upper surface due to the difference of temperature. With incorporating small amounts of GNPs into MPC, the spectral absorptivity of the composite was improved to 0.95 in most spectral regions. Nevertheless, the compression strength shows little change with changing the GNPs content, which may be attributed to use coarse MgO powder as reactant. In virtue of short processing time and homogeneous distribution of GNPs, the novel fabrication provides a new route for preparing GNPs-cement based composites.

1. Introduction
Magnesium phosphate cements (MPC), also known as a typical chemically bonded phosphate ceramic, are clinker-free, quick-setting, high early compressive strength, good volume stability and strong bonding strength, which can be obtained through acid-base reactions between magnesia and phosphate acid or soluble acid phosphates [1-4]. Therefore, MPC currently used as patch repair materials of damaged roads, bridges and runways [3,5], in maxillofacial surgery and endodontic treatments with antibacterial properties [6,7] and as an encapsulant for various nuclear wastes [8,9]. In order to improve the comprehensive properties of MPC, many researchers investigated the effects of different fillers on the properties of MPC, which mainly is focused on fly ash [10-13]. Nevertheless, there are few publications reported the effects of nanomaterials on the properties of MPC, such as graphene oxide (GO) and graphene nanoplatelets (GNPs) [14].

Graphene nanoplatelets (GNPs) have raised the interest as a promising filler in composites, which can be attributed to excellent physical, chemical and mechanical properties [15-17]. Zeyu Lu et al. [14] demonstrated that the effect of GO on the properties and microstructures of the magnesium potassium phosphate cement (MKPC). And with the addition of 0.05 wt.% GO, the compressive and flexural strength of MKPC can be improved to 6.8% and 8.3%, respectively.
In this work, MPC/GNPs composites were synthesized by combustion synthesis and acid-base reaction. First, MgO/GNPs mixture powders were prepared by the combustion reaction between Mg powders and CO$_2$ gas. Then the MPC/GNPs composites were obtained by mixing MgO/GNPs mixture powders with potassium dihydrogen phosphate (KH$_2$PO$_4$) using borax as retarder. The aim of this paper is to investigate the effects of GNPs content on the mechanical and functional properties of MPC/GNPs composites. This work achieved the homogenous dispersion of GNPs in MPC matrix and provided an original and fast method to fabricate the GNPs-cement based composites.

2. Experiment

2.1. Sample preparation

The MgO/GNPs mixture powders were obtained by the combustion reaction between Mg powders (20μm, > 99.7%) and CO$_2$ gas (> 99.99%) according to the following reaction:

$$CO_2 + 2Mg \rightarrow 2MgO + C(\text{Graphene})$$

MgO powders (D50=80μm, Hebei Meishen Technology Co., Ltd., 98%) were added to the reactant Mg powders in the mass ratio of 8:1. The above-mentioned powders were mixed and placed in a graphite boat. Then this boat was put into a vacuum reactor and preheated to 100°C. The reactor was subsequently filled with 1 MPa CO$_2$ and the reaction was initiated by an electric tungsten coil immersed in the reactant powders. The product powders were collected and 3g product powders were calcined in 800°C to measure the GNPs content.

The MPC/GNPs composites were synthesized by a through-solution chemical reaction between MgO (D50=80μm, Hebei Meishen Technology Co., Ltd., 98%) and KH$_2$PO$_4$ (Sinopharm Chemical Reagent Co., Ltd., ≥99.5%) with borax (Sinopharm Chemical Reagent Co., Ltd., ≥99.5%) as retarder:

$$KH_2PO_4 + MgO + 5H_2O \rightarrow MgKPO_4 \cdot 6H_2O$$

KH$_2$PO$_4$ was milled by ball mill (MSK-SFM-3, MTI Corporation) for 15min. MgO powders were added to obtain samples with different GNPs contents (based on MgO). MgO and KH$_2$PO$_4$ was mixed by Vacuum Rev-Rot Gravity Mixer (VM600A2) in the mole ratio of 3.8:1 with 1wt.% borax added. The water/cement ration is 0.18 ml/g and the addition of water into the mixture powders can initiate the acid-base reaction. All the samples were set in disposable paper cup. According to the difference of GNPs contents, the prepared samples are named as MG-0, MG-0.5, MG-1.0, MG-1.5, MG-2.0, MG-2.5 corresponding to GNPs contents of 0%, 0.5%, 1.0%, 1.5%, 2.0%, 2.5%, respectively.

2.2. Sample characterization

The phase composition of samples was accessed by X-ray diffraction (XRD, D8 Focus, Bruker) with a step of 0.02° and a scanning rate of 0.2°/sec. The microstructure was investigated by scanning electron microscopy (SEM, S-4300, Hitachi, Japan) coupled with energy dispersive spectroscopy (EDS, INCA, Oxford Instrument, UK). Raman spectroscopy (Raman, inVia Reflex, Renishaw, England) was performed with the laser wavelength of 532nm and ultraviolet-visible-near IR spectrophotometer (Cary 6000i, Agilent Technologies, American) equipped with an internal integrating sphere was used to measure the spectral absorptivity of the samples. Specimens with dimensions of 6 mm in diameter and 12mm in height were used for compressive test. The specimens were set in a lab at a temperature of 22 ± 1 °C and the compressive strength was measured at 1d using Microcomputer Control Electronic Universal Testing Machine (CMT4204) with a cross-head speed of 1mm/min. Five specimens of each GNPs content were tested to obtain the average compressive strength value.

3. Results and discussion

3.1. Combustion temperature profiles

The combustion temperature profile of reactant mixture powders at some point is shown in Figure 1.
The reactant mixture powders were preheated to 100 °C in order to achieve complete reaction of Mg powders. It is clear to be seen that reaction was within tens of seconds from starting to completion and the maximum combustion temperature is 1030.8 °C.

![Figure 1](image)

**Figure 1.** The combustion temperature profiles of reactant mixture powders at some point.

### 3.2. Phase composition and microstructure

The XRD patterns of 7-day MPC specimens with different GNPs contents are exhibited in Figure 2. Figure 2 (a), (b) and (c) is corresponding to the XRD patterns of the lower surface, the upper surface and ground powders from cured specimens, respectively. It can be found from Figure 2(a)(c) that MPC specimens with different GNPs contents are mainly consist of MgO and KMgPO₄•6H₂O. GNPs phase cannot be detected in the MPC/GNPs specimens due to low content. On the other hand, compared Figure 2(a) with Figure 2(b), the crystallinity of all specimens in lower surface is better than that in upper surface as a result of the heat release difference. It illustrates that temperature plays a crucial role in the crystallinity of KMgPO₄•6H₂O. Moreover, the XRD patterns of the ground powders from cured specimens demonstrates that MPC specimens with different GNPs contents are mainly crystalline phase.

Figure 3 shows the microstructure of MG-0 and MG-2.0 because there are no significant differences in SEM micrographs between the MPC specimens with different GNPs contents. It can be seen from Figure 3 that the spherical particles are distributed in the matrix and many cracks exist in all specimens. According to the size and morphology of the raw MgO powders, it can be speculated that MgO might be the above-mentioned spherical particles and distributed in the KMgPO₄•6H₂O matrix. Furthermore, there are a large number of short fibers between the cracks, which may be attributed to the cracking of specimens during the curing process. The SEM-EDS mapping images are shown in Figure 4 to investigate the elemental distribution of samples. Consistent with the SEM results, MgO spherical particles are distributed in the KMgPO₄•6H₂O matrix. In addition, C signals show homogeneous distribution in the scanning zone, which demonstrates that GNPs realize a uniform distribution in the cement matrix through this route.
Figure 2. The XRD patterns of (a) the lower surface (b) the upper surface and (c) the ground powder from cured specimens.

Figure 3. The SEM micrographs of (a)(b) MG-0 and (c)(d) MG-2.0.
3.3. Spectral characteristics

Figure 5 presents the Raman spectra of MPC specimens with different GNP contents. All the MPC/GNP specimens have the characteristic peaks of graphene, namely D and G bands. 2D and D+G bands are not obvious for low GNP contents samples. The G band, belonging to the double-degenerate irreducible representation $E_{2g}$, appears near 1584 cm$^{-1}$ [18], and the disorder-induced D band emerges approximately 1350 cm$^{-1}$ [19]. Raman spectroscopic investigation confirms the presence of GNP in the MPC/GNP specimens.
Figure 6 demonstrates the spectral absorptivity of the prepared samples in the wavelength range of 250-2500nm. It illustrates that the spectral absorptivity of specimens can be remarkably improved by the addition of GNPs. Besides, absorptivity increases with the increasing of GNPs contents and shows little change in the above-mentioned wavelength range. When the GNPs content is 2.5%, the spectral absorptivity reaches the maximum and exceeds 0.95 in most spectral zone. The results indicate that MPC/GNPs specimens have an outstanding infrared radiation property.

3.4. Compressive strength
The compressive strength of MPC specimens with different GNPs contents is displayed in Figure 7. There is little change in the compressive strength of the samples with different GNPs contents, which may be attributed to the dimensions of the raw MgO powders. Therefore, the poor mechanical properties limit the use of MPC specimens to load-bearing application.
4. Conclusion
In this study, MPC/GNPs composites were prepared by combustion synthesis and acid-base reaction. The MgO/GNPs mixture powders were obtained by Mg powders combustion reaction in CO$_2$ atmosphere first, then MPC/GNPs specimens were fabricated through chemical reaction between MgO/GNPs and KH$_2$PO$_4$ with borax as retarder. The effect of GNP's content on mechanical and functional properties of the as-prepared MPC/GNPs composites was investigated. All the specimens consist of MgO and KMgPO$_4$•6H$_2$O and the crystallinity of KMgPO$_4$•6H$_2$O is closely related to the temperature. With incorporating small amounts of GNP's into MPC, the spectral absorptivity of the composite is remarkably improved and the absorptivity of one specimen exceeds 0.95 in most spectral regions. This work achieved the homogenous dispersion of GNP's in MPC matrix and provided a novel and fast method to fabricate the GNP's-cement based composites.

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