Journal of Alloys and Compounds 696 (2017) 560–565

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Characterization of magnesium phosphate cement fabricated using pre-reacted magnesium oxide

Ai-juan Wang*, Na Song, Xiao-jie Fan, Jun-ming Li, Li-jing Bai, Yang Song, Rui He

School of Materials Science and Engineering, Xi'an University of Technology, Xi'an 710048, China

ARTICLE INFO

Article history:
Received 21 January 2016
Received in revised form
28 October 2016
Accepted 19 November 2016
Available online 21 November 2016

Keywords:
Ceramics
Chemical synthesis
Microstructure
Curing behavior

ABSTRACT

Magnesium phosphate cement (MPC) has the potential to be used as biomaterials but the high level of heat being generated during this exothermic reaction limits its use. It is very important to control the curing behavior of MPC. MPC was fabricated using pre-reacted magnesium oxide as raw materials in this paper. Pre-reacted magnesium oxide was fabricated according to the hydrated reaction mechanism of MPC. Curing behavior, phase compositions and microstructure of MPC were characterized, as well as the chemical activity of pre-reacted magnesium oxide. The results indicated that pre-reacted magnesium oxide was composed of residual magnesium oxide and hydrated products. The mean particles size increased as the hydrated products united magnesium oxide together to form bigger clusters; meanwhile the chemical activity decreased. The setting time and peak temperature of MPC was adjusted successfully, and the phase compositions are still same with those of MPC obtained by pure magnesium oxide. The phase compositions of MPC fabricated with different pre-reacted magnesium oxide particles were all composed of hydrated products and residual magnesium oxide. No observable impurity ensures the purity of MPC. The whole synthesis process of MPC in this work is composed of two stages. The first stage is to obtain pre-reacted magnesium oxide, and the second is to fabricate MPC using magnesium oxide obtained in the first stage. Both stages are designed according to the hydrated reaction mechanism of MPC, and thus ensure the purity of MPC. In conclusion, the curing behavior was successfully controlled, producing a same phase compositions to that of the MPC whilst causing the changes in the setting time and peak temperature.

1. Introduction

Magnesium phosphate cement (magnesium phosphate chemically bonded ceramic, MPC) attracted much attention in the field of road repairing [1,2] and immobilizing environmental threat element [3,4] as cement because of its very fast setting time, good mechanical properties and low temperature stabilization. Until the last ten years, its good biocompatibility caused much more attention in biomedical field [5–10]. Previously, MPC was combined with calcium phosphate cement (CPC) to develop novel calcium-magnesium phosphate cement (CMPC) [8,10], and showed its degradation rate occurred significantly faster than that of pure CPC in simulated body fluid (SBF) solution. The antibacterial activity of Na-containing MPC against Streptococcus sanguinis was also evaluated, and further studies on early compressive strengths showed it is substantially higher than that of CPC [7]. Both passive and active in vitro resorption of MPC by osteoclastic cells have also been tested and indicated the biodegradability [9]. Besides, Gene mutation assay, chromosome aberration assay, and DNA damage assay indicated its excellent biocompatibility [6]. It can be concluded that MPC might have the potential to be applied in orthopedic, endodontic treatments, reconstructive and maxillofacial surgery.

MPC is formed by acid-base reaction between magnesium oxide and phosphate accompanied by the release of heat [11], shown in Eq. (1).

$$MgO + KH_2PO_4 + 5H_2O \rightarrow KMgPO_4 \cdot 6H_2O \quad (1)$$

$$\Delta Hf \quad -602 \quad -1568 \quad -286 \quad -3724\ (kJ/mol)$$

Studies indicated that thermal necrosis will occur in bone tissue exposed to temperatures in excess of 50 °C for more than 1 min [12], 55 °C for 30 s and 60 °C for 5 s [13]; less than 1 s is enough to

* Corresponding author.
E-mail address: ajwmxl@163.com (A.-j. Wang).

http://dx.doi.org/10.1016/j.jallcom.2016.11.278
0925-8388/

cause the transepidermal necrosis at 70 °C [14]. Lundskog [15] also pointed that bone tissue heated at 50 °C for 1 min or 47 °C for 5 min will not remain as the functioning bone but will be resorbed and replaced with fat cells. In conclusion, the higher the temperature is, the shorter the exposure duration before thermal bone necrosis occurs is. Considering that MPC fabricated using 3 g raw materials generate temperatures above 70 °C [11], we hypothesized that temperature generated by MPC curing should be sufficiently high to cause thermal necrosis of cell. The high level of heat being generated during this exothermic reaction limited its use as biomaterials because the exposure of bone tissue to high temperature lead to the incidences of bone necrosis and tissue damage, ultimately resulting in the failure [7,16,17].

Fortunately, the kinetics and exothermic temperature of the hydrated reaction can be adjusted by the properties of raw materials or adding additives. Previous studies indicated the reaction rate could be reduced using mono-potassium phosphate because of its smaller dissociation constant and lower molar solubility [11,18]. Boron compounds could also be used to control the kinetics and exothermic peak temperature of MPC by limiting the contact each other between magnesium oxide and phosphate [19]. Effect of liquid-to-solid ratios on the setting time, temperature variation of MPC have also been studied in our laboratory [20], which again indicated the feasibility of adjusting its curing behavior. Although all the above methods could be used to control the curing behavior, other properties were possibly sacrificed, especially the phase purity.

The aim of this study is to control the curing behavior of MPC using pre-reacted magnesium oxide, meanwhile ensures its phase purity. Pre-reacted magnesium oxide was fabricated according to hydrated reaction mechanism of MPC. According the reaction mechanism, hydrated products firstly appeared on the surface of magnesium oxide during fabricating MPC, which possibly lowered the continued hydrated reaction rate through preventing the further contact to each other between MgO and other ions. As a result, curing behavior could be adjusted when pre-reacted MgO was used as the raw materials to manufacture MPC. Its curing behavior as well as the microstructure and phase compositions was also evaluated.

2. Materials and methods

2.1. Materials

Medical grade magnesium oxide particles (MgO, medical grade, Zehui Chemical Industry Group, China) and chemically pure monopotassium phosphate particles (KHP, chemical reagent, Beijing Kang Pu Hui Wei Technology Co., Ltd, China) were used as the raw materials. Deionized water was used as the liquid phase.

2.2. Synthesis

Synthesis of pre-reacted MgO. MgO and KHP were mixed with the weight ratios (M/P) of 5:1, 15:1, 25:1, 35:1, 45:1 respectively using planetary ball mill (QM-3SP2, Nanjing University Instrument Plant) for 3 h. Weight ratio of solid powders (total weight of pre-reacted MgO and KHP) to liquid phase is 4:1. The powders were balanced 3 g each time. Reaction started after dropping deionized water into the solid powders slowly and kept hand mixing. After reaction finished, pre-reacted MgO was obtained by milling the reaction product for another 3 h, followed by being dried at 100 °C for 24 h.

Synthesis of MPC. Pre-reacted MgO and fresh KHP powders were milled with the weight ratio of 4:1 using planetary ball mill for 3 h. New mixed solid powders were balanced 3 g each time. Deionized water was added into mixture again under hand mixing. Weight ratio of solid powders (total weight of pre-reacted MgO and KHP) to liquid phase is still 4:1, which is the same ratio as that used to fabricate pre-reacted MgO. MPC was prepared after hydrated reaction finished, followed by further being incubated in 37 °C and a 100% humidity box for 7 days.

2.3. Characterizations

The kinetic analysis method was used to determine the releasing rate of Mg^{2+} ions to estimate the chemical activity of pre-reacted MgO prepared using different M/P ratios, because the measuring principle was similar with the reacting process of MPC [8,21]. Briefly, MgO was dispersed into deionized water and then OH^- ions appeared. The solution would turn to be red after the addition of phenothalin because of the appearance of OH^- ions. After that, citric acid solution (5 vol%) was added into the red color solution, and the color became achromatic color as the processing of neutralization reaction. Lastly, citric acid was continued to be added, and the color of the solution appeared red again because OH^- ions formed again. The time between the colors changed from achromatic color to red was recorded. The shorter time meant the faster appearing rate of $Mg(OH)_2$, and thus the high releasing rate of Mg^{2+}.

Surface temperature variation of MPC during hydrated reaction was recorded using an infrared radiation thermometer (IRT, Raytek, FLUKE-63). Setting time was determined according to ASTM C 191Method B with modification using an automatic Vicat apparatus (HA-XWB-300B). Phase compositions and microstructure of pre-reacted MgO and MPC were characterized by X-Ray Diffractometer (XRD, Shimadzu, 7000S) using Cu Kα radiation and Scanning Electron Microscopy (SEM, Japan Electron Optics Laboratory Co., Ltd, JSM-6700F) after sprayed Cu coating. The samples used for XRD and SEM were cured for 7 days.

3. Results

3.1. Pre-reacted MgO

The microstructure of MgO before and after pre-reacted was shown in Fig. 1. Compared with MgO before pre-reacted (Fig. 1 a,c), larger aggregates with the size about 20 μm of the pre-reacted MgO was obtained (pointed by the black arrow in Fig. 1 b). It should be noted that besides MgO, hydrated products seemed to be appeared and then linked MgO together from higher magnification (Fig. 1 d). Besides, new materials have the typical microstructure of hydrated products appeared (pointed out by the black arrow). The new formed hydrated products usually have rod-like structure, and can grow much larger in size [11,22,23], but MgO usually have nearly spherical structure. XRD results (Fig. 2) testified that only hydrated products characteristic diffraction peaks ($KMgPO_4 \cdot 6H_2O$, KMP) were observed besides the diffraction peaks of MgO, indicating that the material linking MgO particles together should be the hydrated products. Studies on the formation process hydrated products had been carried out by Z. Ding et al. [22]. Hydrated products accumulated more and more around MgO particles during the hydrated reaction, and further binded MgO together to form clusters. This is in accordance with the results shown in Fig. 1 d. Aggregates appeared because hydrated products linked MgO together.

Besides, it is very important that no matter what the M/P ratios are, all the pre-reacted MgO was composed of residual MgO and hydrated products. Biocompatibility evaluation on MPC is mainly focused on the compositions [5–9]. Obviously, there is only hydrated products and residual MgO, and no other materials existed using this method, indicating that using pre-reacted MgO as raw materials is feasible to fabricate MPC. Compositions of pre-reacted