

# Microstructure and Performance of Mg-substituted $\beta$ -TCP Porous Ceramics

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**Abstract**-- $\beta$ -tricalcium phosphate( $\beta$ -TCP) is an important biomaterial with good biocompatibility. The study was concentrated on the microstructure and performance of Mg-substituted  $\beta$ -TCP porous ceramics. The 6mol.% Mg-doped powders were fabricated by the method of gel-sol combustion with raw materials of  $\text{Ca}(\text{NO}_3)_2$ , PBTC and  $\text{Mg}(\text{NO}_3)_2$ . Mg-substituted  $\beta$ -TCP porous ceramics were obtained by molded-pressing with the foaming agent and the binder before calcined at 1000°C. The mechanical properties, microstructure, immersion performance had been evaluated by means of mechanical testing machine, X-ray diffraction, scanning electron microscopy with EDS and immersion test. The compressive test showed that the compressive strength of Mg-doped porous ceramics increased 10.5% from 5.92MPa to 6.54MPa compared with the pure porous scaffolds. The SEM Images demonstrated that the porosity of ceramic was about 65%, the size of interconnect holes were ranging from 50 to 200 $\mu\text{m}$ .

**Immersion test indicated that the Mg-substituted improved the performance of degradation apparently.**

**Keywords**-- $\beta$ -TCP; Mg-substituted; porosity; Microstructure; Immersion

## I. INTRODUCTION

Calcium Phosphate ( $\text{Ca}_3(\text{PO}_4)_2$ ) ceramics have been identified as important materials for bone reconstruction, such as beta-tricalcium phosphate ( $\beta$ -TCP) and hydroxyapatite (HAp)[1,2]. In particular, the  $\beta$ -tricalcium phosphate is one of the most attractive biomaterials due to the biological properties mainly biocompatibility, bioactivity, biodegradability[3,4]. The inorganic composition of  $\beta$ -TCP is similar to that of bone tissue, after implanted  $\beta$ -TCP shows an excellent biodegradability. The dissolved calcium and phosphate ions can be used for the formation of new bone tissues. The  $\beta$ -TCP porous bioceramics provide support for the growth of new bone indicated the material with good osteoconductivity.

In recent investigates, porous ceramics which should have features such as high porosity along with

micro-macropores and interconnected pore structures. But the porous scaffolds show poor mechanical properties especially in bending strength and toughness[5]. How to improve the mechanical properties of  $\beta$ -TCP porous ceramics rised the attention of scholars. Some authors investigated that the substitution of ions found in natural bones showed positive functions in improving the biocompatibility and mechanical properties of  $\beta$ -TCP[6]. Yoshida et al. suggested that the sinterability of  $\beta$ -TCP is enhanced by the substitution of mono-and divalent metal ions[7]. Mg is the fourth major cation in human body and the second most prevalent intracellular cation, approximately 50-60% of the total amount of Mg is in bone tissue and only 1.0% is in the extracellular fluid[8,9]. It has been demonstrated that the mechanical properties has been improved effectively with the substitution of Mg[7-12].

The purpose of the study was to investigate the influence of Mg-instituted  $\beta$ -TCP porous ceramics crystal structure and in vitro degradation in SBF and the compressive strength. In this study, pure and Mg-substituted  $\beta$ -TCP powders would be synthesised by the the gel-sol combustion method. Then the  $\beta$ -TCP porous bioceramics would be sintered at 1000°C with the pore-foaming agent and high temperature adhesive bondings added in.

## II. MATERIALS AND METHODS

### A. Materials Preparation

The precursors of  $\beta$ -tricalcium phosphate and Mg-substituted  $\beta$ -tricalcium phosphate had been made in fuming cupboard at 80°C under magnetic stirring. It has been reported that magnesium ions might substitute calcium site in the tricalcium phosphate lattice. The raw materials used for making precursors of  $\beta$ -TCP were calcium nitrate tetrahydrate (reagent grade, Chemical reagent Ltd, Co, Beijing) and 2-phosphonobutane -1,2,4-tricarboxylic acid (PBTC, 50wt%, Taihe Water Treatment Ltd. Co, Shandong). Weighing the reactants according to the atomic ratio of calcium and phosphorus 1.5, putting the reactants into a beaker and adding some deionized water. Then the reaction would go on under magnetic stirring with the reaction temperature controlled between 80°C and 100°C for 3 hours in fuming cupboard.

As for precursors of Mg-substituted  $\beta$ -tricalcium phosphate (Mg content~ the atomic ratio should be [Mg/Ca+Mg=6mol.%]), magnesium nitrate hexahydrate (reagent grade, Beijing) was added into the reaction, also the atomic ratio should be maintained at (Ca+Mg/P=1.5). Then drying the precursors at 160°C in oven for 4 hours. Finally the precursors would be calcined at 1000°C to get the Mg-substituted  $\beta$ -tricalcium phosphate powders for further used.

In order to obtain Mg-substituted  $\beta$ -TCP porous ceramics, the stearic acid[13] was used as pore-foaming agent and the polyvinyl alcohol (PVA) was chose as the binders. Mix the raw materials into the mold homogeneously and mold pressing at 80MPa with a press machine. Then the samples were further thermal treated at 1000°C in the furnace.

### B. Particle Size Measurement

The particle size of Mg-substituted  $\beta$ -TCP powder was measured by BT-9300 type laser particle size distribution.

### C. Porosity Measurement

The porosity of Mg-substituted  $\beta$ -TCP porous ceramic was measured by the liquid discharge method. At first, the porous scaffold was weighed as M after dried to constant weight in the oven. Put some ethanol for the volume of  $V_1$  into the measuring cylinder, then the Mg-substituted  $\beta$ -TCP porous ceramic was submerged into the alcohol for 15 minutes, the volume would be maintained of  $V_2$  until there exist no bubble. Finally, take the sample out carefully and the volume of the ethanol remained in the cylinder was  $V_3$ . The porosity was calculated according to the formula below:

$$e = \frac{V_1 - V_3}{V_2 - V_3} \times 100\% \quad (1)$$

Where  $e$  is the porosity, the volume of sample is V ( $V = V_2 - V_3$ ); Three parallel samples were taken for every porous ceramics. Finally, the porosity value was achieved.

### D. Microstructure Characterization

X-ray diffraction analysis was used to identify the crystalline phases of Mg-substituted  $\beta$ -TCP powder over a  $2\theta$  range of 10°-70° at a speed of 10° per minute in the X-ray diffractometer. SEM was employed to observe the microstructural features and the pore size of Mg-substituted  $\beta$ -TCP porous ceramic.

### E. Compression Test

The compression test was conducted on a QT-1186 type tensile and compression testing machine with the limit load as 1000N. The test went on at the speed of 1mm per minute and the samples were prepared with the size of  $\phi 10\text{mm} \times 20\text{mm}$ . Three identical samples were used for the compressive test.

### F. Immersion Test

The immersion test was carried out in simulated body solution (SBF)[14] at the temperature of 36.8°C. The SBF was prepared by dissolving a reagent-grade NaCl, KCl,  $\text{NaHCO}_3$ ,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CaCl}_2$ ,  $\text{KH}_2\text{PO}_4$  into deionized water and buffered at pH 7.4. The samples were prepared with the size of  $\phi 20\text{mm} \times 10\text{mm}$ . After 28 days immersion, the samples were removed out of the solution, slightly washed with deionized water and dried in the oven for overnight. Then scanning electron microscopy (SEM) equipped with energy disperse spectrometer (EDS) was employed for the microstructure identification of the precipitate formation on the surfaces of the porous ceramics after soaking in SBF.

## III. RESULTS AND DISCUSSION

### A. Particle Size of Mg-substituted $\beta$ -TCP Powder

Particle size of the Mg-substituted  $\beta$ -TCP powders was shown in table 1. The median diameter was 11.17 $\mu\text{m}$  proved that the Mg-doped powder was micron grade. The table 1 clearly showed that D75 was 22.99 $\mu\text{m}$  meant that the diameter of most powders were less than 50 $\mu\text{m}$ . Also the Fig 1 showed that the size of more than 96 percent powders were less than 35 $\mu\text{m}$  meet the requirement for

further used. The phenomenon of Mg-substituted has not change the particle size of  $\beta$ -TCP powders.

TABLE 1. PARTICLE SIZE OF PHYSICAL PARAMETERS ABOUT Mg-SUBSTITUTED  $\beta$ -TCP POEDER

median diameter:11.17 $\mu$ m	volume mean diameter:15.11 $\mu$ m	surface mean diameter:4.55 $\mu$ m	shading coefficient:20.67	
specific surface area:0.48m <sup>2</sup> /g	material refractive index:1.520+0.100i	medium refractive index:1.333	span:2.92	
D3:0.94 $\mu$ m	D6:1.36 $\mu$ m	D10:1.93 $\mu$ m	D16:2.79 $\mu$ m	D25:4.3 $\mu$ m
D75:22.99 $\mu$ m	D84:29.1 $\mu$ m	D90:34.61 $\mu$ m	D97:45.54 $\mu$ m	D98:48.67 $\mu$ m

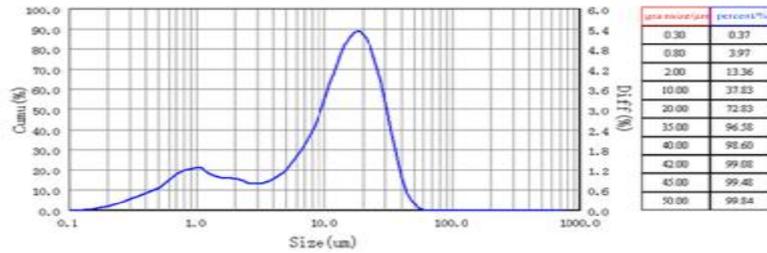


Figure 1. Particle size of powder distribution curve

### B. Microstructure of Mg-substituted $\beta$ -TCP porous ceramics

XRD analysis of Mg-substituted  $\beta$ -TCP porous ceramics were showed in Fig 2, the (a) showed that after calcined at 1000 °C there existed no impurities among the porous scaffolds, the characteristic peaks were obviously and no differences in the patterns were detected. However, the pattern (b) showed that compared with pure  $\beta$ -TCP porous ceramics the characteristic peaks of Mg-substituted scaffolds shifted to the right significantly. It should be that the radius of magnesium was 0.078nm and also the radius of calcium was 0.106nm. The process of Mg-substituted should be magnesium replaced the cite of calcium in the crystal lattice causing the lattice distortion. From the Bragg formula:

$$l = 2d \sin q \quad (2)$$

Where  $l$  is the wavelength of incident X-rays which is known;  $q$  is the angle of XRD diffraction peaks to be measured;  $d$  is the interplanar crystal spacing. In the formula  $l$  is constant, Fig 2(b) showed the  $q$  of Mg-substituted scaffolds became larger than pure  $\beta$ -TCP porous ceramics, so  $d$  would be smaller demonstrated that magnesium partly replaced the position of calcium in the lattice.

From the SEM microphotographs in Fig 3, it was evident that micro and mesopore structure were found in the surface of porous Mg-substituted  $\beta$ -TCP scaffolds. However, from Fig 3(b) hollow structure and fully interconnected geometry were successfully achieved

since the foaming agent as stearic acid led to the formation of the porous scaffolds with open porosity and macropores ranging from 50 to 200 $\mu$ m. The interconnected network structure were necessary for the circulation of body fluid and the bone tissue ingrowth and vascularization. The porosity of the Mg-substituted porous ceramics was nearly 65% and the size of holes would be controlled by the size of stearic acid. The large porosity would increase the surface area and the connection of the porous ceramics with the host bone. The gradient of the hole size was obtained by molded pressing, the gradient structure was in favour of the mechanical properties.

### C. Mechanical property of Mg-substituted $\beta$ -TCP porous ceramics

Fig 4 showed the compressive curve of porous ceramic before and after Mg-substituted. From the formula the compressive strength could be calculated:

$$P = \frac{Fc}{S} \quad (3)$$

Where  $P$  was the compressive strength;  $F_c$  was the critical damage load;  $S$  was the force area of the sample. From fig 4 it could be seen clearly that the damage load rised from 465N before Mg-doped to 513N after Mg-doped. The force area was  $7.85 \times 10^{-5} \text{mm}^2$ , so the compressive improved 10.5 percent after Mg-doped from 5.92MPa to 6.54MPa. The result demonstrated that the Mg iron substituted improved the mechanical properties of porous ceramic obviously.

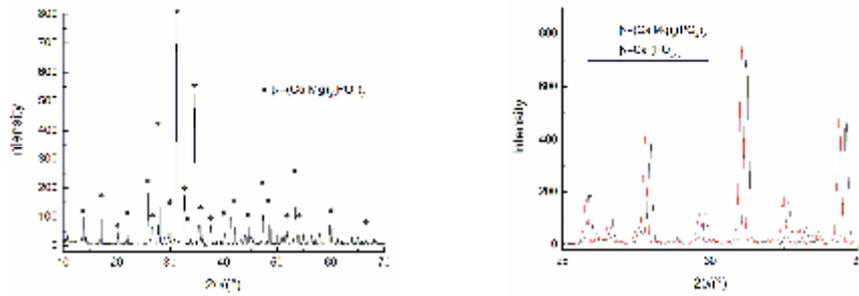


Figure 2. XRD patterns (a) Mg-substituted  $\beta$ -TCP porous ceramic (b) before and after Mg-substituted

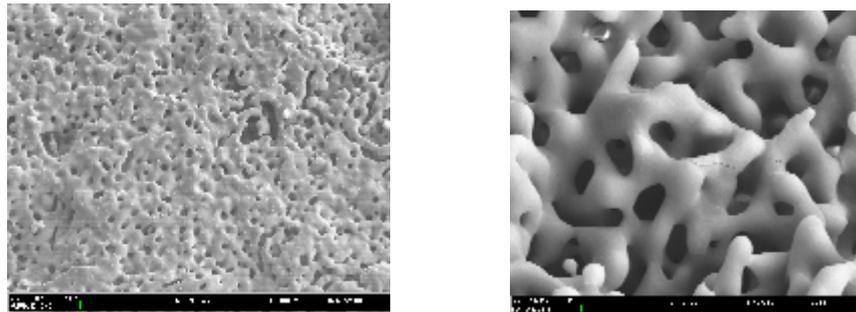


Figure 3. SEM Images (a) the surface of Mg-doped ceramic (b) the internal image of Mg-doped ceramic

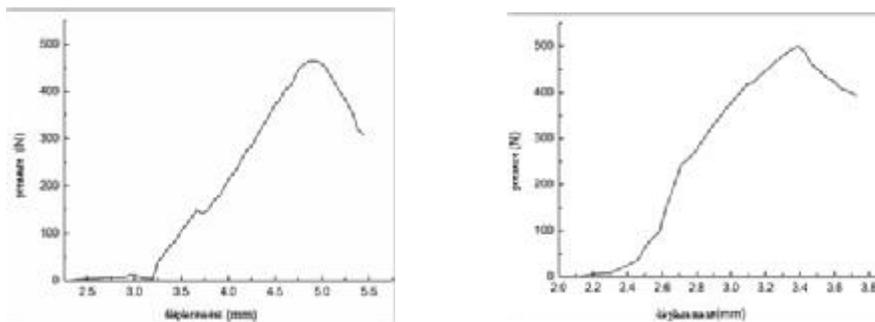


Figure 4. compression curve (a) before Mg-substituted porous ceramic (b) after Mg-substituted porous ceramic

#### D. Immersion property of Mg-substituted $\beta$ -TCP porous ceramics

Fig 4 showed the SEM Images of Mg-substituted  $\beta$ -TCP porous ceramics before and after 28 days immersion in SBF solution at 36.8°C. Fig 4 illustrated that some of the newly generated precipitate deposited on the surface of Mg-substituted  $\beta$ -TCP porous scaffolds. The porous scaffolds showed two different surfaces: a smooth surface before immersion and a surface with lots of small grain formed after immersion.

Fig 5 and Fig 6 showed the EDS patterns of Mg-substituted  $\beta$ -TCP porous ceramics before and after

immersion. From the data in the pattern, it could be seen clearly that the atomic ratio of calcium and phosphate was 1.497 (almost 1.5 the target value of  $\beta$ -TCP) before immersion. However, after immersion the atomic ratio had increased to 1.626 (nearly 1.67 the desired value of hydroxyapatite). The change from fig 5 to fig 6 demonstrated that during the immersion the Mg-substituted  $\beta$ -TCP porous ceramics had dissolved in the SBF solution partly, at the same time the bone-like hydroxyapatite generated on the porous scaffolds surface. The magnesium ion substituted did in favour of the in vitro immersion.

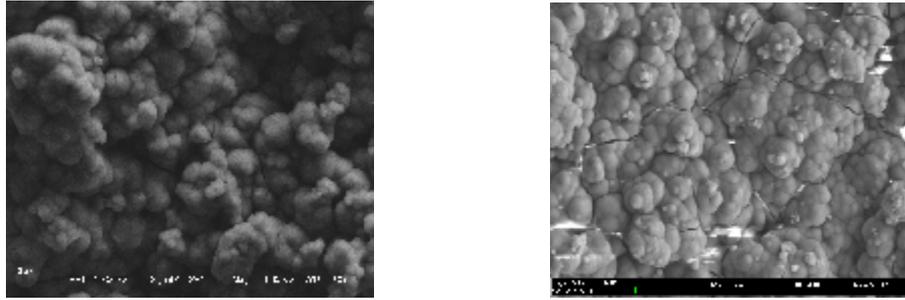


Figure 4. SEM Images for Mg-substituted  $\beta$ -TCP porous ceramics (a) before immersion (b) after immersion for 28 days

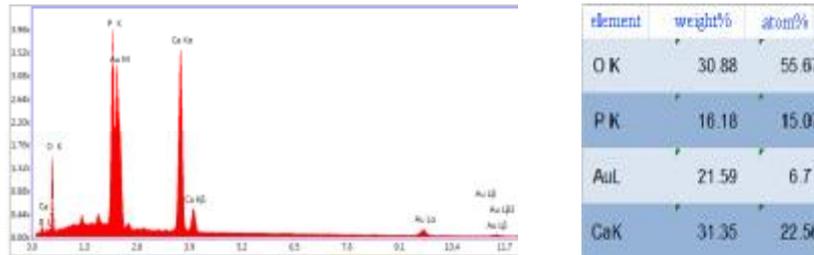


Figure 5. EDS patterns for Mg-substituted porous ceramics before immersion

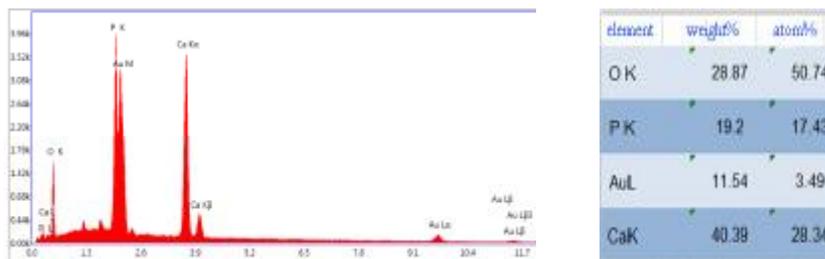


Figure 6. EDS patterns for Mg-substituted porous ceramics after immersion

#### IV. CONCLUSION

To study the properties of 6mol.% Mg-substituted of  $\beta$ -TCP porous ceramics, the gel-sol combustion method was employed to synthesis pure and Mg-doped powders. After calcined at 1000°C the size of Mg-doped  $\beta$ -TCP powders were at micro scale meet the requirement for further used. The compressive test indicated that after Mg-doped the compressive strength increased 10.5% compared to the pure  $\beta$ -TCP porous ceramics. During the in vitro immersion experiment the Mg-doped porous ceramics showed a good biodegradability, after partly dissolved in SBF solution there generated the bone-like hydroxyapatite. Mg ions substitution apparently improved the mechanical properties and degradation of  $\beta$ -TCP porous ceramics.

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