

Preparation and properties of β -tricalcium phosphate porous bioceramic^①

ZHANG Shi-hua(张士华), XIONG Dang-sheng(熊党生), CUI Chong(崔崇)

(Department of Materials Science and Engineering, Nanjing University of Science and Technology, Nanjing 210094, China)

Abstract: Porous β -tricalcium phosphate bioceramic (PTCP) has important roles in surgical implants because of good biocompatibility. But the low compressive strength of the ceramic limits its application. The preparation of PTCP was improved with the adjustment of the constituents and the sintering process. A new type of PTCP material with high compressive strength was made. The compositions, microstructure and properties of PTCP were analyzed by TG-DSC, XRD, TEM, SEM and so on. The result indicates that stearic acid burns sufficiently and gives out carbon dioxide and water vapor when slowly heated between 200 °C and 400 °C so that the porous structure like coral in β -TCP bioceramic is formed. Through crystallization at 470 °C and 570 °C, more $\text{CaO-P}_2\text{O}_5$ glass-cement is converted into crystallite-glass, which is beneficial for improving the compressive strength of β -TCP bioceramic. PTCP can form a support action in bone imperfect section with good solubility.

Key words: β -TCP(β -tricalcium phosphate); porous bioceramic; biocompatibility; biodegradation

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1 INTRODUCTION

The ceramic materials based on calcium phosphates, have been studied since 1980 which included tricalcium phosphate (β -TCP) and hydroxyapatite (HA). There is a wide range of potential applications for bone substitutes in the form of dense or porous parts. Low biodegradability of HA hinders bone ingrowth and results in chemical bonding only at the interface between the bones and HA implant. Compared with HA, β -TCP is generally considered a resorbable bioceramic with good biodegradation^[1, 2]. The dissolved Ca^{2+} and P^{5-} can penetrate the tissue fluid to form new tissue progressively. Finally the implant PTCP disappears and the new living tissue comes into being. However, poor compressive strength have limited the applications of the PTCP material^[3]. This study is aimed at improving the preparation technology with the adjustment of the constituents and the sintering process and providing a new type of PTCP with high compressive strength.

2 EXPERIMENTAL

2.1 β -TCP powder synthesis

Powder was prepared by high-temperature solid-state reactions of brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, high purity) with calcium carbonate (CaCO_3 , high purity). The reaction equation is as follows^[3]:



To exclude any impurity, a mixing and forming process was carried out in a clean room. A 2:1 molar ratio of brushite to calcium carbonate was obtained by ball milling in polyethylene bottles with low wearable zirconia balls for 60 h at the speed of 60 r/min, using distilled water as the medium. Then the mixture was calcined at 850 °C for 2 h.

2.2 Glass-cement preparation

$\text{CaO-P}_2\text{O}_5\text{-Na}_2\text{O-MgO-Al}_2\text{O}_3$ material is a new bioactive glass. It has low melting point and high strength. It can be connected with living bones for good biocompatibility^[4]. Its composition is according to source shown in Table 1.

Table 1 Glass composition and its source

| Composition | Source | Mass fraction/ % |
|-------------------------|-------------------------------|------------------|
| P_2O_5 | $(\text{NH}_4)_2\text{HPO}_4$ | 80 - 65 |
| CaO | CaCO_3 | 18 - 10 |
| Na_2O | Na_2CO_3 | 15 - 10 |
| MgO | MgCO_3 | 5 - 1 |
| Al_2O_3 | Al_2O_3 | 3 - 0 |

Glass powder was prepared by high-temperature melting^[5]. Weigh the raw materials precisely as shown in Table 1, mix them in porcelain mortar and ball mill at the speed of 60 r/min for 20 h, then the

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Correspondence: ZHANG Shi-hua; E-mail: shzhang@mail.njust.edu.cn

mixed powder was calcined at 850 °C for 0.5 h and cooled rapidly. The acquisition was ground to fine powder and filtered through a particle size analyzer.

2.3 PTCP preparation

β -TCP powder, CaO-P₂O₅ glass cement powder and porous agent material were mixed in porcelain mortar. Their mass fractions are shown in Table 2. The mixture was isostatically pressed to pellet at 10–20 MPa for 5–15 s. The dried pellets were sintered which included crystallization and non-crystallization comparison experiment.

Table 2 Composition of PTCP
(mass fraction, %)

| β -TCP | Cement | Porous agent |
|--------------|--------|--------------|
| 80–60 | 30–20 | 20–10 |

2.4 Structure and performance testing

The thermogravimetric measurement (TG-DSC) was carried out on German NETZSCH STA 449C device for the solid-state reaction materials and the PTCP pressed flans, which was performed in air up to 900 °C at a heating rate of 2 K/min with a Al₂O₃ pan. The phases of β -TCP powder, glass cement powder and PTCP pellets were analyzed by X-ray diffraction (XRD). The shape and size of β -TCP powder were observed by TEM. The infrared spectrum of glass cement was also recorded on America Nicolet 60SXB device. The microstructure of PTCP sample was observed by means of SEM. The pore ratio and volume density were tested by the way of static balance in liquid. The maximum and average diameters of pore canal were measured by the method of bubble test^[6]. With the ceramic test devices the compressive strength of PTCP samples was measured and with the spectrophotometer its solubility in simulative body fluid, which is a water solution of 0.03% KCl, 0.6% NaCl, 0.02% CaCl₂ and 0.31% lactonatrium, was measured.

3 RESULTS AND DISCUSSION

3.1 Solid-state reaction and β -TCP powder

Fig. 1 shows the TG-DSC curves of the solid-state reaction process. It shows that the reaction process includes two mass-loss processes, five endothermic reactions and one exothermic reaction. The details are recorded in Table 3 which shows that the solid-state reaction temperature should be 850 °C^[7]. In the course of reaction, γ -Ca₂P₂O₇ and β -Ca₂P₂O₇ are produced in turn and CaCO₃ decomposes to CaO, which maybe affects the purity of the production. In order to fully complete the reaction, heat preservation at some temperature stages is necessary^[8].

Table 3 Solid-state reaction process

| Temperature/ °C | Reaction equations |
|-----------------|--|
| 160–210 | $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{CaHPO}_4 + 2\text{H}_2\text{O} \uparrow$ |
| 477 | $2\text{CaHPO}_4 \rightarrow \gamma\text{-Ca}_2\text{P}_2\text{O}_7 + \text{H}_2\text{O} \uparrow$ |
| 580 | $\gamma\text{-Ca}_2\text{P}_2\text{O}_7 \rightarrow \beta\text{-Ca}_2\text{P}_2\text{O}_7$ |
| 717 | $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \uparrow$ |
| 850 | $\beta\text{-Ca}_2\text{P}_2\text{O}_7 + \text{CaO} \rightarrow \beta\text{-Ca}_3(\text{PO}_4)_2$ |

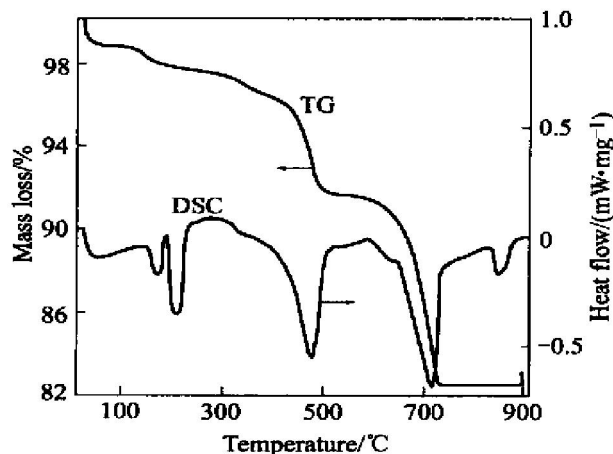


Fig. 1 TG-DSC curves of solid-state reaction process

Fig. 2 shows the X-ray diffraction pattern of the β -TCP powder. It shows that the crystal peak is very sharp and the main crystal phase of the powder is β -TCP. Hence, relatively high purity β -TCP powder can be prepared to meet experimental condition. Fig. 3 shows the TEM images of the β -TCP powder. It can be seen that the shape of the grains is similar to sphere and the geometry diameter is about 0.2 μm .

3.2 Features of CaO-P₂O₅ glass cement

Fig. 4 shows the XRD pattern of the CaO-P₂O₅

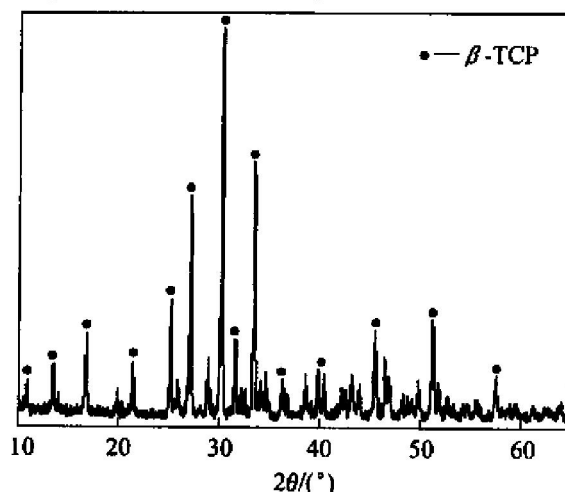


Fig. 2 X-ray diffraction pattern of β -TCP powder

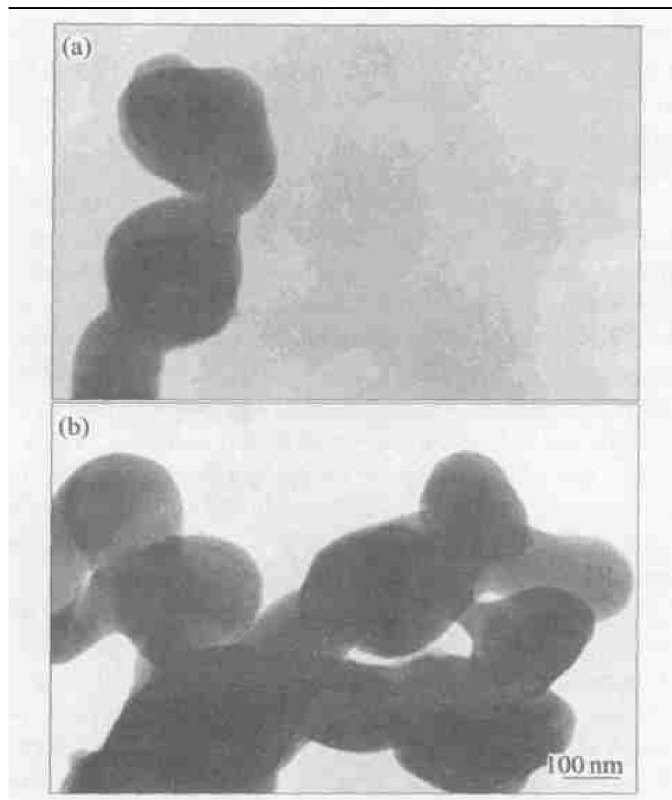


Fig. 3 TEM images of β -TCP powder

glass-cement. It can be seen that the main phase is noncrystal^[9]. Fig. 5 shows the infrared spectrum of the CaO-P₂O₅ glass-cement. All of infrared vibrancy modes are recorded in Table 4, comparing with those of the pure P₂O₅ glass^[8]. We can see that the infrared vibrancy modes of them are similar, so the basic structure of the CaO-P₂O₅ glass-cement is the same as that of the pure P₂O₅, which is made up of the PO₄ 3D-net structure^[10]. The center of this structure is the atom P and the framework is the chain structure of the —P—O—P—. At the same time, a few of cations make the chains break to a certain extent^[5].

Table 4 Infrared vibrancy modes of CaO-P₂O₅ glass and pure P₂O₅ glass

| Pure P ₂ O ₅ glass | CaO-P ₂ O ₅ glass | Vibrancy mold |
|--|---|----------------|
| 500(S) | 470 - 550(S) | δ OPO |
| 750(M) | 738 - 775(M) | ν_s POP |
| 1 100(S) | 1 104 - 920(S) | ν_{as} POP |
| 1 290(S) | 1 279(S) | ν_{as} OPO |

S—strong; M—middle; δ —bend vibrancy;
 ν_{as} —dissymmetry flex vibrancy;
 ν_s —symmetry flex vibrancy

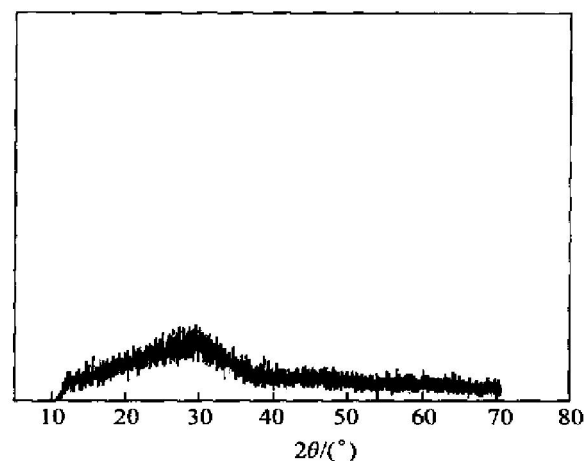


Fig. 4 XRD pattern of CaO-P₂O₅ glass-cement

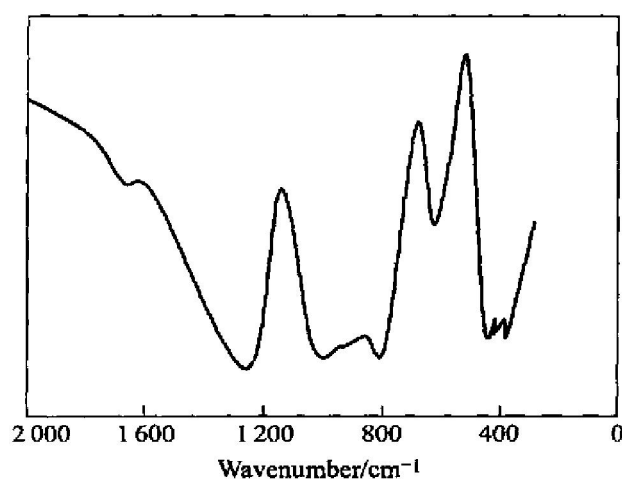


Fig. 5 Infrared spectrum of CaO-P₂O₅ glass-cement

3.3 Improvement of sintering process of PTCP

Fig. 6 shows the TG-DSC curves of the β -TCP flan. Firstly, it can be seen that there is an endothermal apex on the DSC curve at 70 °C because of stearic acid melting. Between 200 °C and 400 °C, the TG curve descends rapidly. The mass loss is approximate

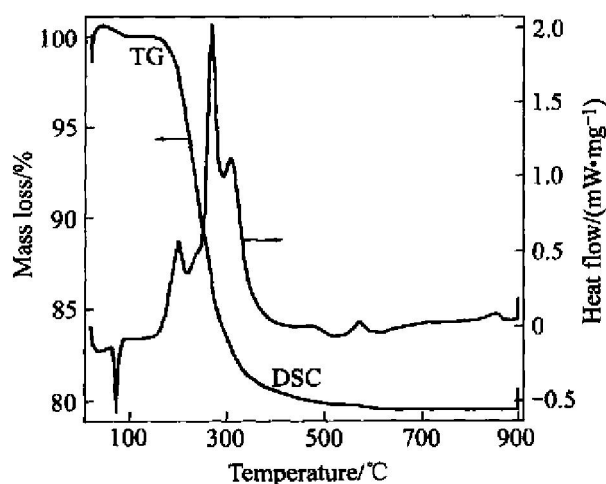


Fig. 6 TG-DSC curves of β -TCP flan

ly close to 20%, which is equal to the percentage of stearic acid in the β -TCP flake. Secondly, there are three exothermic peaks at the temperature of 210 °C, 290 °C and 310 °C on the DSC curve. It is concluded that stearic acid burns sufficiently and gives out carbon dioxide and water vapor at this stage, which results in porous-structure like coral in PTCP sample^[11]. Therefore, the temperature should be increased slowly in order to let gas completely volatilize and to form pores. These pores can provide passages for the body fluid pervading into PTCP material, which accelerates the β -TCP biodegradation. In addition, the glass-cement in the flake has crystallization in the temperature range of 450 ~ 600 °C. Because the free energy of crystal is lower than that of noncrystal, the reaction performs an exothermic process^[12]. 470 °C corresponds to the CaO-P₂O₅ glass core-forming temperature and 570 °C is its crystallization point. Therefore, the sintering-process of the β -TCP should be improved in two ways. On one hand, the temperature should be increased slowly at the stage of gas volatilization (200 ~ 400 °C); on the other hand, the temperature should be kept for a period of time at the temperature of core-forming (470 °C) and crystallization (570 °C) stages.

3.4 Microstructure and performance of PTCP

The PTCP samples are white block. The pore ratio is 45% ~ 50% and volume density is about 1.44 g/cm³. The average pore diameter is about 220 μ m and the maximum diameter is 400 μ m. The appropriate pore, which is convenient for living tissue to grow in, is between 150 μ m and 500 μ m^[13], so the PTCP we got is up to the mustard. Fig. 7 shows the X-ray diffraction patterns of crystallization sample and noncrystallization one. Their compositions are the same as shown in Table 2 and they are isostatically pressed to pellet at 10 ~ 20 MPa for 5 ~ 15 s, but one

is sintered which includes crystallization and another no crystallization. We can see their main phases are β -TCP. In crystallization sample, the amount of the glass phases is less, but the diffraction peak of the β -TCP crystal is much stronger.

Fig. 8 shows the SEM images of the fracture section. It can be seen that there are lots of pores inside and pores are communicative, which is similar to the structure of loose coral. This structure is beneficial to the pervasion of the body fluid and the degradation of material itself. Fig. 9(b) shows that there are many glass phases surrounding the crystal phases in the non-crystallization samples. However, the glass phases are mostly converted into tiny crystals in the crystallization samples in Fig. 9(a). More tiny crystals are connected into porous network by remnant glass phases.

Table 5 lists the compressive strength of the crystallization and non-crystallization samples. The result indicates that the compressive strength of the crystallization sample is higher, which is more close to the strength of loose-bone. Therefore, it has certain supportable function at the place where the bone is missing^[14]. The crystallization changes most glass phases into tiny crystals, which is beneficial to improving the compressive strength^[15, 16].

Fig. 10 shows the solubility curves of crystallization sample and non-crystallization one. It can be

Table 5 Compressive strength of crystallization and non-crystallization samples (MPa)

| Samples | Non-crystallization | Crystallization | Loose bone |
|---------|---------------------|-----------------|------------|
| 1 | 15.6 | 19.8 | — |
| 2 | 14.8 | 22.7 | — |
| 3 | 14.5 | 21.4 | — |
| Average | 15.0 | 21.3 | 40 |

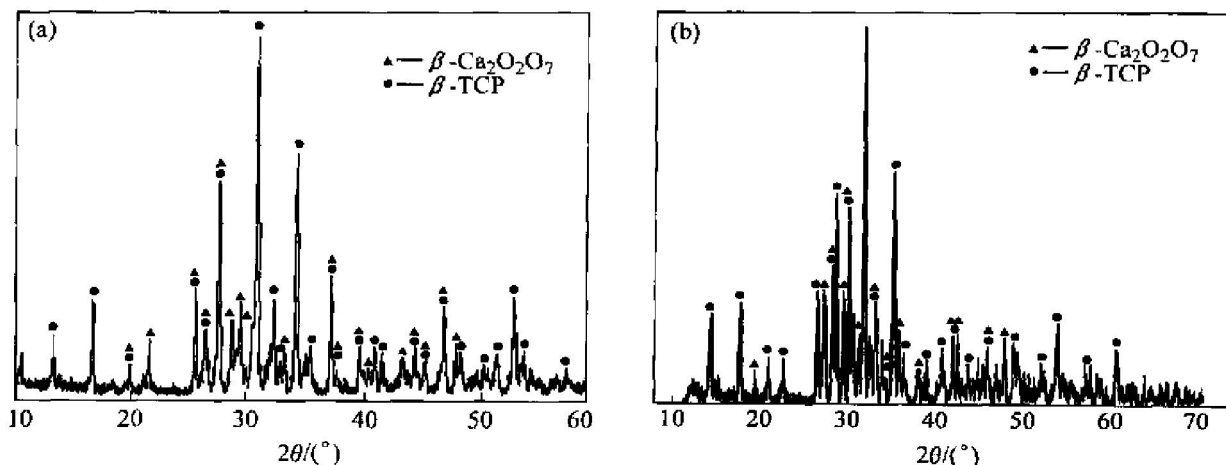


Fig. 7 X-ray diffraction patterns of crystallization(a) and non-crystallization(b) samples

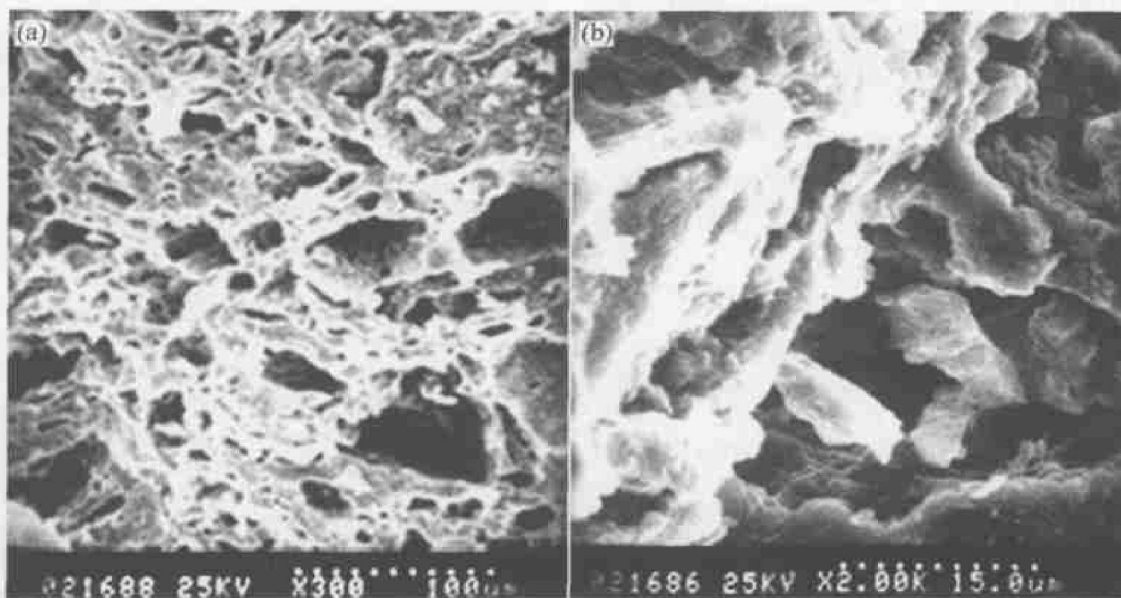


Fig. 8 SEM fractographs of samples

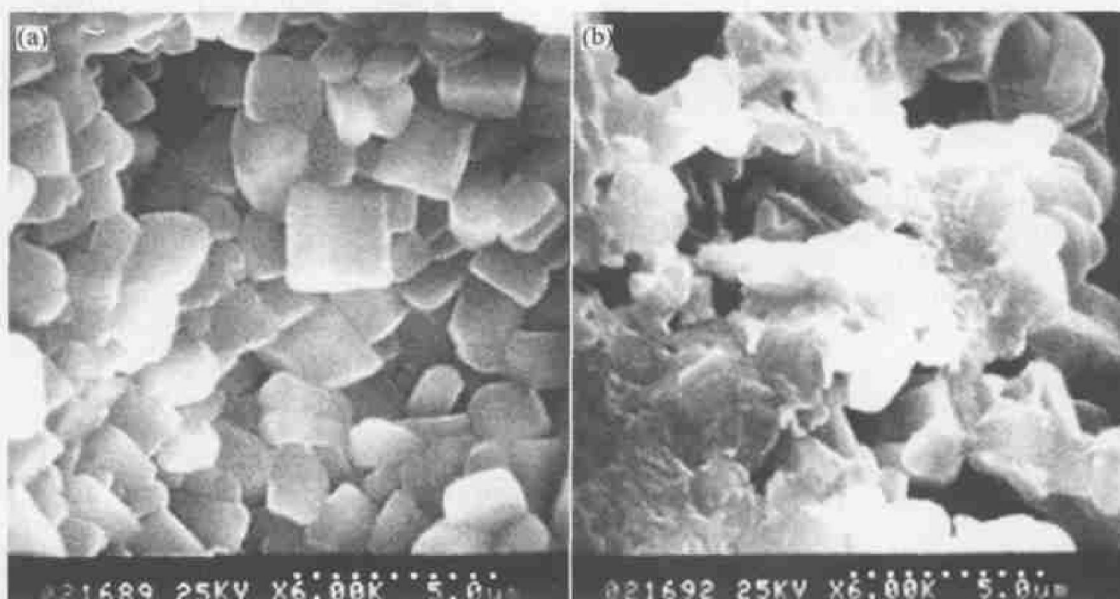


Fig. 9 SEM images of crystallization(a) and non-crystallization(b) samples

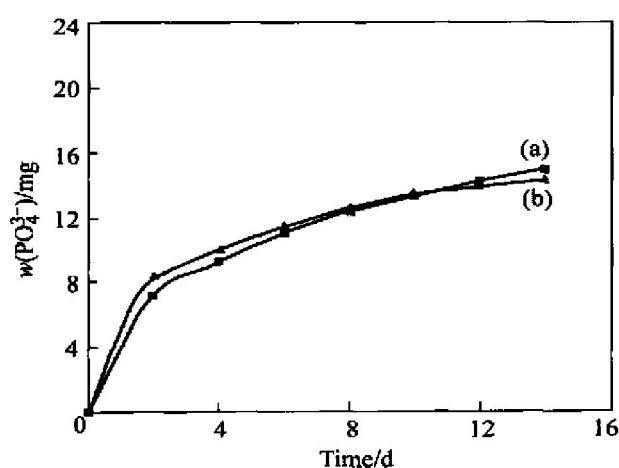


Fig. 10 Solubility curves of crystallization(a) and non-crystallization(b) samples

seen that both of them are soluble and their solvency is approximate. So the crystallization does not weaken PTCP solvency while improving its strength.

4 CONCLUSIONS

The solid-state reaction method is simple and efficient. The β -TCP particles look like sphere and their average diameter is about 0.2 μm . The structure of the CaO-P₂O₅ glass-cement is similar to the pure P₂O₅ glass that is made up of the PO₄ 3D-net structure. The improved sintering process includes slowly increasing temperature at the stage of gas volatilization (200–400 °C) and keeping for a period at the stages of core-forming (470 °C) and crystallization (570 °C). In the PTCP crystallization sample, the main crystal is β -TCP. In addition, there are also

a few of β - $\text{Ca}_2\text{P}_2\text{O}_7$ crystals and glass-cement remnants. The glass phases can be mostly converted into tiny crystals, which largely improves the compressive strength of the PTCP with good solubility. The crystallization PTCP has a function of support at the place where the bone is missed.

REFERENCES

- [1] Rey C. Calcium phosphate biomaterials and bone mineral [J]. *Biomaterials*, 1990, 11: 13 - 19.
- [2] CUI Furzhai, FENG Qingling. *Biomaterial Science* [M]. Beijing: Science Press, 1996.
- [3] LIU Jianguo, XU Shengxiang. The development of studies on biodegradation material in orthopaedics during lately 30 years[J]. *China Hurt Magazine*, 1996, 12(1): 64 - 66.
- [4] CHEN Fang, CHEN Xiaoming, JI Guojin, et al. The structure and dissolve properties of cement in degradation ceramics[J]. *Journal of Wuhan University of Technology*, 1995, 17(4): 143 - 145.
- [5] GAN Furxi. *Glass Properties in Optics and Spectrum* [M]. Shanghai: Shanghai Science and Technology Press, 1992.
- [6] LIAO Jichang. *Powder Metallurgy Porous Material* [M]. Beijing: Metallurgical Industry Press, 1979.
- [7] LI Shipu, CHEN Fang, CHEN Xiaoming, et al. Preparation of β -tricalcium phosphate powder and its properties [J]. *Journal of Wuhan University of Technology*, 1995, 17(4): 146 - 148.
- [8] CHEN Fang, LI Shipu, JIANG Xin, et al. Study of preparation of biodegradable TCP-ceramics by foaming and its structure and properties[J]. *Journal of Wuhan University of Technology*, 1995, 17(4): 140 - 142.
- [9] Mark P W. *Crystallite Glass* [M]. Beijing: Architecture Industry Press of China, 1988.
- [10] Kokubo T. Bioactivity of Glass-ceramics[A]. *Proc of 15th International Congress on Glass* [C]. Leningrad, 1989. 114 - 119.
- [11] WU Fengqi, RUAN Shengping, LI Xiaoping. Synthesis, characterization and photocatalytic degradation properties of TiO_2 nanocrystal[J]. *Functional Material*, 2001, 32(1): 69 - 71.
- [12] ZUO Yansheng. *Analytical Methods of Material* [M]. Beijing: Beijing University of Technology Press, 2000.
- [13] WU Jiaofeng, XU Xiaohong. Study and preparation of a porous tricalcium phosphate bioceramic [J]. *Journal of Ceramics*, 1999, 20(2): 104 - 107.
- [14] LI Lihua, ZHEN Yuming, CHEN Zhuanghong. Research on bioactive materials for medical applications[J]. *Journal of Wuhan University of Technology*, 1993, 15(3): 32 - 37.
- [15] Hyun S R, Hyuk J Y, Kug S H. An improvement in sintering property of β -tricalcium phosphate by addition of calcium pyrophosphate[J]. *Biomaterials*, 2002, 23: 909 - 914.
- [16] LIU Guanghua. *Material Chemistry* [M]. Shanghai: Shanghai Science and Technology Press, 2000.

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