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RESEARCH ARTICLE

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Synthesis of *β*-tricalcium phosphate using sol-gel self-propagating combustion method

Abstract *β*-tricalcium phosphate (*β*-TCP) is a key component of natural bone like hydroxyapatite. Pure and uniformly nanosized *β*-tricalcium phosphate powders were synthesized using a sol-gel self-propagating combustion method by using citric acid as a reductant and using fuel and nitrate as the oxidant. The thermal decomposition of nitrate-citrate xero-gel was studied by thermogravimetric-differential thermal analysis (TG/DTA) and the process mechanism of self-propagating combustion were discussed. The resulting powders calcined at 1023, 1173 and 1273 K were characterized by Ca/P ratio analysis, X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). It was found that the as-prepared powders were pure *β*-tricalcium phosphate having regular porous surface very similar to coral.

Keywords sol-gel preparation, self-propagating combustion, *β*-tricalcium phosphate, sintering, porosity

1 Introduction

Calcium phosphates, i.e., hydroxyapatite (HA) and *β*-tricalcium phosphate (*β*-TCP), are predominant inorganic components in human hard tissues. In recent years, the investigation of calcium phosphate-based bioceramics has attracted worldwide attention due to their excellent biocompatibility, bioactivity and, if porous, osteo-conductivity [1,2]. In comparison with the extensively and intensively investigated HA, the study of *β*-TCP seems very few, probably owing to its relatively minor proportion in natural bone. However, the porous *β*-TCP scaffold has been proven to have high resorption rate and biodegradability [3,4] *in vivo*. It is the biodegradability of *β*-TCP that makes it a potential material for bone reconstruction [5].

β-TCP can be conventionally prepared by solid-state methods [6] and wet-chemical processes [7]. Both methods have drawbacks such as high synthesizing temperature and low product purity. Therefore, developing more feasible synthesizing methods for *β*-TCP is of significance.

Sol-gel self-propagating combustion synthesis (SGSPC), based on sol-gel and self-propagating combustion principles, has been employed to prepare some inorganic compounds [8,9]. Due to molecular-level mixing of reactants and excellent chemical homogeneity as well as in-situ oxidation and spontaneous combustion of precursors [10,11], the SGSPC method is capable of reducing synthesis temperature and shortening reaction time [12]. In this work, the SGSPC was used to synthesize nano-sized *β*-TCP. The calcination process, phase evolution and morphology of *β*-TCP were investigated.

2 Experiments

All chemicals were analytical grade. A typical procedure was as follows: 0.0926 mol $Ca(NO_3)_2 \cdot 4H_2O$, 0.0926 mol $C_6H_8O_7 \cdot H_2O$ and 0.0617 mol $(NH_4)_2HPO_4$ were dissolved in 100 mL water in sequence and stirred for 30 min. The pH value of the mixture was adjusted to around 2 by adding 65% HNO_3 dropwise. The resulting clear solution was slowly vaporized at 353 K until a transparent gel appeared. Then, the translucent xero-gel was obtained by raising temperature to 373 K and sequentially vaporizing the remaining water. After heating it (in a platinum crucible) in a muffle furnace at 473 K for about 0.5 h to 1 h, the xero-gel spontaneously ignited and self-propagated rapidly with a remarkable volume expansion and plenty of gas release. When the self-combustion reaction was over, white precursors were found. Finally, the precursor was calcined at different temperatures for 1 h. Coral-like and fleecy *β*-TCP powders were obtained.

The thermal behavior of the xero-gel was studied by thermo-gravimetric/differential thermal analysis (TG/

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DTA). The phase composition of the as-synthesized β-TCP sample was determined by X-ray diffraction (XRD) (Rigaku D/max, Japan) and its morphology was observed by scanning electron microscopy (SEM) (JSM5610LV, Japan).The grain size was evaluated by transmission electron microscopy (TEM) (Hitachi H-800, Japan).

3 Results and discussion

3.1 Thermal analysis

Figure 1 shows the TG-DSC curves of the xero-gel. It can be seen that there is a very sharp and narrow exothermic peak along with a drastic weight loss at 473 K, which corresponds to auto-combustion reaction of the xerogel. The exothermic peaks and weight loss in the temperature region 573–1223 K could be attributed to the burning of the residual organic components and the peak at 1273 K implies the crystallization of β-TCP.

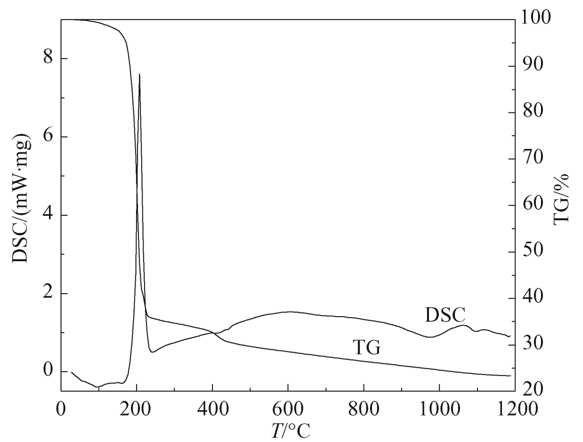

Fig. 1 TG-DSC curves of the xero-gel

3.2 Analysis of self-propagating combustion mechanism

The complexation reaction, as shown in Eq.(1), takes place between calcium ion and citric acid (a strong complexation agent) during the gelation [13] followed by formation of a stable calcium citrate complex.

$$C_6H_8O_7 + Ca^{2+} = C_6H_6O_7Ca + 2H^+ \quad (1)$$

Subsequently, the citrate (a strong reductant) reacts with nitrate (a strong oxidant), causing a release of plenty of gas and reaction heat. The reaction is a rapid redox reaction as shown in Eq. (2).

$$5C_6H_6O_7Ca + 18NO_3^- + 18H^+ = 30CO_2 + 9N_2 + 24H_2O + 5CaO \quad (2)$$

During the self-propagating combustion process, the following probable reaction mechanism was proposed in the stagnant atmosphere based on thermodynamic deduction [14]:

$$2(NH_4)_2HPO_4 = 4NH_3 + P_2O_5 + 3H_2O \quad (3)$$

$$2CaO + P_2O_5 = \beta\text{-}Ca_2P_2O_7 \quad (4)$$

$$\beta - Ca_2P_2O_7 \rightarrow \gamma\text{-}Ca_2P_2O_7 \quad (5)$$

$$2\gamma - Ca_2P_2O_7 + 2C_6H_6O_7Ca = CaH_2P_2O_7 + 4C_2Ca + 4CO_2 + 4H_2O + O_2 \quad (6)$$

$$2C_2Ca + 5O_2 = 2CaCO_3 + 2CO_2 \quad (7)$$

$$CaCO_3 = CaO + CO_2 \quad (8)$$

$$2CaO + CaH_2P_2O_7 = \beta\text{-}Ca_3(PO_4)_2 + H_2O \quad (9)$$

3.3 Ca/P molar ratio determination

The contents of Ca and P in the product were precisely measured using the improved EDTA complex titration [15] and phosphormolybdate-quinoline precipitation method, respectively. The molar ratio (Ca/P) obtained is 1.50, which is quite close to theoretical value of β-TCP.

3.4 XRD analysis

Figure 2 shows the XRD patterns of as-prepared β-TCP samples treated at 1023, 1173 and 1273 K for 1 h. It can be clearly seen from Fig. 2a that there are large numbers of HA diffraction peaks when the sample is calcined at 1023 K. Figure 2b shows that the major phase is already β-TCP at 1173 K but there still exist some impurity phases such as HA and $Ca_2P_2O_7$. However, almost no other phases except β-TCP were found in Fig. 2c when the calcination temperature was kept at 1273 K. The three strongest peaks (2θ: 31.0°, 34.4° and 27.8°) correspond to the (0210), (220) and (214) crystal faces of β-TCP, respectively. Moreover, the narrow and sharp diffraction peaks suggest good crystallinity of the samples.

3.5 SEM and TEM observation

The SEM image in Fig. 3 clearly exhibits the surface morphology of the resulting noncompact powders calcined at 1273 K. A large number of uniform and nearly regular micropores with average pore diameter of 5μm distribute on the whole surface. This is probably caused by a series of decomposition reactions. The size and morphology of these micropores are very similar to coral. At the same

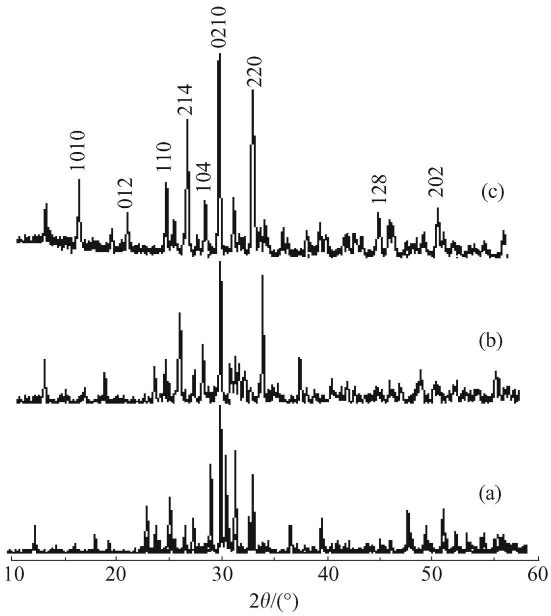

Fig. 2 XRD patterns of the β-TCP samples obtained at different temperatures
a – 750°C, b – 900°C, c – 1000°C

time, TEM observation gave the evaluated size of 100 nm for the β–TCP powders.

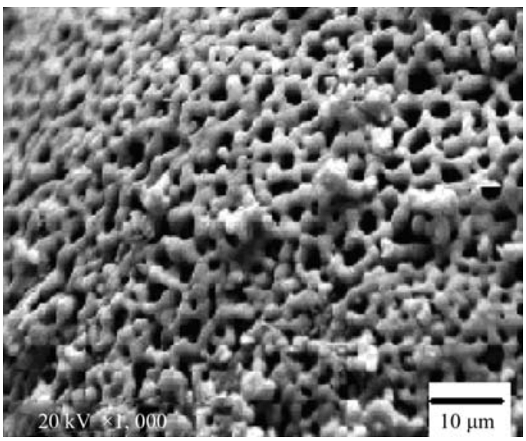

Fig. 3 SEM image of the surface microstructure of the resulting incompact powders calcined at 1273 K

4 Conclusions

β-TCP nanoparticles with high purity and good crystallinity have been synthesized by a sol-gel self-propagating combustion method. The grain size of the β-TCP powder is about 100 nm. Regular and coral-like micropores distributed on the surface of the sintered powders were observed.

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