Journal of Chemistry, Vol. 48 (5), P. 591 - 596, 2010

STUDY OF THE FORMATION OF POROUS HYDROXYAPATITE CERAMICS FROM CORALS VIA HYDROTHERMAL PROCESS

Received 4 February 2010

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ABSTRACT

The hydrothermal method was used for preparation porous hydroxyapatite (HA) ceramic from coral scaffold, in two ways: synthesized directly from coral skeleton and synthesized from CaO, which was product of coral thermal decomposition. The obtained samples were characterized by techniques including X-ray diffraction (XRD), Scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). The analytical results confirmed that HA ceramic was formed by the indirect synthesis from fresh obtained CaO from coral aragonite. Determined reaction conditions were at 180^{o}C and 14 atm pressure for 36 hours.

Keywords: *porous hydroxyapatite, scaffold, coral, hydrothermal, XRD, SEM, FTIR.*

I - INTRODUCTION

Biomaterials including biometals, biopolymers, bioceramics… were increasingly used in biomedical applications, especially in orthopedic surgery.

Bioceramics have become one of the important fields of biomaterials, are specially developed for use as medical and dental implants. Among bioceramics, hydroxyapatite which is similar in composition and crystal structure to natural bone is found to be ideal bone graft substitute. This material has high biocompatibility and ability to bond directly to human bone without the elimination. HA ceramics have been used as bone graft substitute and reconstruction of bone defects, artificial eyes, repair of teeth defects, bioelectrode and biosensor, drug carrier…[1, 2]. Several studies have shown that in biologic implantations HA evokes no local or systemic toxicity and no inflammatory or foreign-body reactions [3, 4, 5]. The finding of valuable properties as well as the effective applications of HA ceramic in medicine, particularly in orthopedic surgery were considered as a great achievement of material science [6, 7].

HA ceramics, obtained from natural scaffold of mollusca in general, particularly from coral scaffold, have more higher biocompatibility compared to that of HA ceramics made by other sources.

Studies on the synthesis of HA ceramics started in the early 1970’s [8]. Several methods were used to prepare HA ceramics such as pressing and sintering method, solid phase reaction… The hydrothermal method for hydroxyapatite formation directly from corals was first used by Roy and Linnehan in 1974. They reported that complete replacement of aragonite by phosphates was achieved at 270°C and 103 MPa [9].

In our country, the research on manufacturing porous HA with similar structure to natural scaffold of mollusca has not been reported. This paper presents the first results of synthesis of porous HA via hydrothermal process from natural skeleton of Vietnam coral.

II - EXPERIMENT

The formation on HA was carried out in two ways: synthesized directly from coral skeleton and synthesized from CaO, which was product of coral thermal decomposition.

Coral skeleton was cut into small pieces (about 5x5x5 mm), boiled several times in water and alcohol to remove mechanical and organic impurities and then dried at 100°C.

For the direct synthesis from coral, the treated coral pieces and $(NH_4)_2HPO_4$ saturated solution were put into stainless steel pressure vessel. The amount of reagents was calculated with the molar ratio Ca/P = 1.7, a little NH_4OH was added to ensure pH 9 - 10. Hydrothermal process was carried out at 180 - 200°C in nitrogen atmosphere with various pressures from 8 to 14 atm for various time from 24 - 128 hours. The obtained product was washed with distilled water and dried.

For the second way, treated coral was calcined at 800°C for 1 hour in order to convert completely $CaCO_3$ to CaO. Hydrothermal process was performed immediately after that to maintain porous structure of CaO.

The samples obtained were then sintered at 1000°C for 1 hour to produce HA ceramic.

The obtained material was characterized using X - ray diffraction (XRD) with Cu Kα radiation, Siemens D5000 instrument; Field emission scanning electron microscopy (FE - SEM), Hitachi S4800 microscope; Fourier transform infrared spectroscopy (FTIR), IMPACT 410-Nicolet (USA).

III - RESULTS AND DISCUSSION

1. Characterization of coral skeleton

The main constituent of coral is aragonite $CaCO_3$ with 95 - 99 wt%, the rest is organics. Porosity volume is about 50% with pore size distribution in the range of 100 - 160 μm [8].

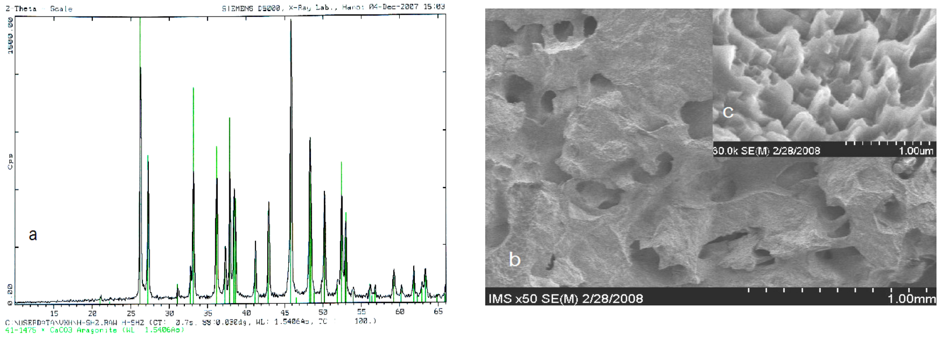

Figure 1: XRD pattern (a) and SEM images (b, c) of coral

XRD pattern of coral (Fig. 1a) showed the peaks characterized only for aragonite phase. In SEM image (Fig. 1b), it can be seen that large pores were linked up to each other with dimension of 120 - 160 μm. The porous framework was formed by aragonite crystals which compactly arrange in order (Fig. 1c), improving chemical and mechanical stability of coral framework. Hydrothermal process therefore takes place entirely at very high pressure.

2. Characterization of CaO, obtained from the coral decomposition

SEM images of coral after thermal decomposition were presented in figure 2.

It was noted that the structure was more porous, regular pore distribution and not in certain direction, pore dimension of 5 - 50 µm (Fig. 2a). $CaCO_3$ was converted to CaO in granular form. CaO particles were dispersed with clear boundary. Some smaller pores 0.1 - 0.5 µm were also observed in the image (Fig. b).

From CaO small particles with unstable bond, the formation of HA were expected to be performed more readily in comparison to the direct process from aragonite.

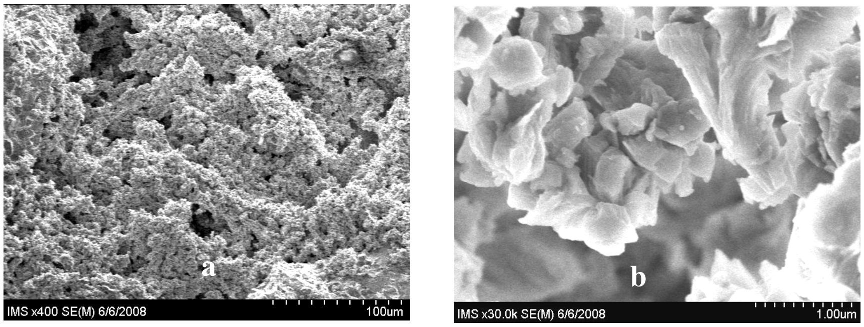

Figure 2: SEM images of coral after thermal decomposition at 800°C

3. Hydrothermal process

a) The direct synthesis from coral aragonite

Hydrothermal process took place according to the following reaction equation:

$$10CaCO_3 + 6\,(NH_4)_2HPO_4 + 2H_2O \rightarrow$$

$$Ca_{10}(PO_4)_6(OH)_2 + 6(NH_4)_2CO_3 + 4H_2CO_3 \quad (1)$$

The product was characterized by XRD (Fig. 3), which demonstrated that main phase was $CaCO_3$. A small part of HA was formed, as evidenced by characteristic peaks at 2θ: 26.88°, 31.77° and 32.2° (JCPDS #24-0033). Reaction time was increased to 128 hours, the intensity of these peaks did not change proving that amount of HA in the product was not increased.

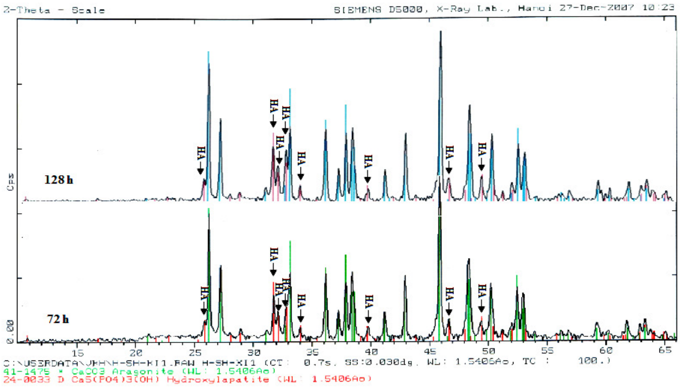

Figure 3: XRD pattern of the product of hydrothermal process

This is a heterogeneous between solid aragonite phase and liquid phase of $(NH_4)_2HPO_4$. Because aragonite crystalls arranged in dense block, it was difficult for $(NH_4)_2HPO_4$ molecule to diffuse inside. They were only adsorbed on the surface of aragonite, HA was therefore created a thin layer on the surface. The reaction conditions of temperature, pressure and time should be more severed to convert aragonite $CaCO_3$, which was inside solid phase, into other form. This confirmed that it is impossible to directly synthesize HA by hydrothermal process of coral aragonite with pressure equal or less than 14 atm.

b) Synthesis HA with immediate stage of converting $CaCO_3$ aragonite to CaO

The reaction between CaO and $(NH_4)_2HPO_4$ can take place as follows:

$$10CaO + 6(NH_4)_2HPO_4 + 4H_2O \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 12NH_4OH \qquad (2)$$

The role of H_2O was very important in this process, as both a reagent and a solvent accelerating diffusion of $(NH_4)_2HPO_4$ into the porous structure making the heterogenous reaction to take place entirely. The experiment results indicated that HA was not created without water.

XRD characterization of the product:

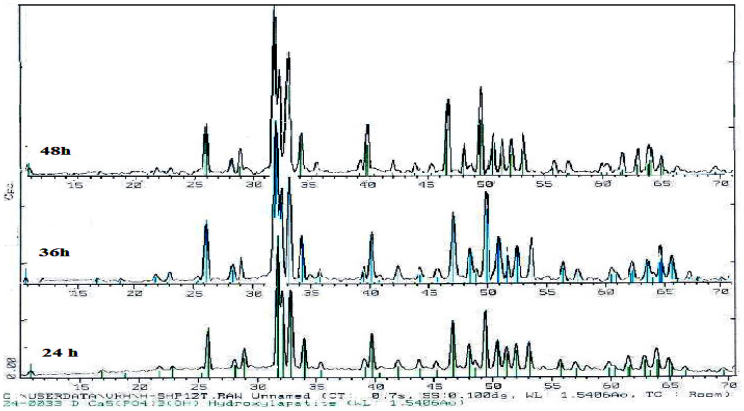

Figure 4: XRD pattern of porous HA after hydrothermal process

XRD pattern of the products was showed in figure 4. It is noticed that:

With the reaction time of 24 hours, XRD data indicated characterization peaks of HA, peaks for impurity phases were not appeared. The reaction time increased to 36 hours, XRD pattern exhibit the sharper peaks with intensity were nearly equivalent to that of standard HA. Two peaks, at $2\theta = 31.77^{o}$ and 32.20^{o} respectively, were distinguished clearly. This confirmed that with reaction time of 36 hours, single phase with high crystallinity of HA was formed.

XRD characterization of the product with reaction time of 48 hour was also similar.

SEM characterization of the product:

SEM image of HA sample (Fig. 5a) demonstrated that created HA particles was un-uniform with a size distribution of 0.5 - 0.8 μm. The particles were aggregated, however their boundaries was seen clearly, indicating that obtained sample was porous block but not porous ceramic.

This product then was sintered at1000°C for 1 hour.

SEM image of sintered HA (Fig. 5b) demonstrated that morphology of initial coral framework was still maintained. HA particles were aggregated into porous ceramic, their boundaries were disappeared. Pores were linked together in three directions with pore size about 0.2 - 0.5 μm.

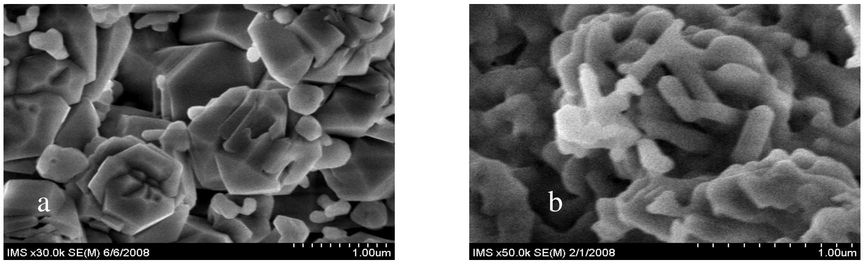

Figure 5: SEM images of HA sample before (a) and after (b) sintering at 1000^{o}C

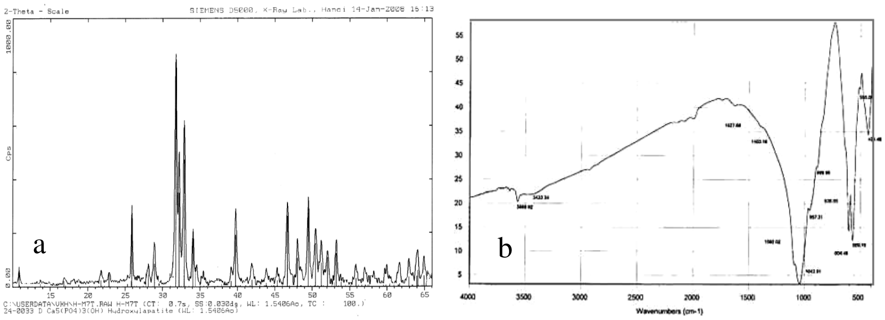

Figure 6: XRD pattern (6a) and FTIR spectrum (6b) of obtained HA ceramic

XRD pattern of obtained HA ceramic (Fig. 6a) showed only characterization peaks of HA.

In addition, in FTIR spectrum (Fig. 6b), it can be seen only adsorption bands at 1100, 1030, 960, 560 - 600, 470 cm^{-1} corresponding to PO_4^{3-} group and adsorption bands at 3570, 632 cm^{-1} corresponding to OH^- group. Adsorption band of free H_2O at was very weak.

XRD data combined with FTIR spectra confirmed that HA created from this hydrothermal was singe phase crystal with high crystalline and thermal stability up to 1000^{o}C.

XRD and FTIR characterization was consistent to NIST standard for HA [10].

Determination of stability and porous structure of HA ceramic is in progress.

IV - CONCLUSION

Porous HA was successfully synthesized from natural framework of coral by hydrothermal process of fresh obtained CaO from coral aragonite and $(NH_4)_2HPO_4$. Determined reaction condition was at 180^{o}C and 14 atm pressure for 36 hours.

Sintering at 1000^{o}C for 1 hour, obtained porous HA ceramic was preserved morphology of initial natural framework of coral.

XRD and FTIR characterization was consistent to NIST standard for HA.

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NGHIÊN CỨU SỰ TẠO THÀNH GỐM XỐP HYDROXYAPATITE TỪ SAN HÔ BẰNG PHẢN ỨNG THỦY NHIỆT

Tóm tắt: Phương pháp thủy nhiệt đã được sử dụng để nghiên cứu điều chế gốm xốp hydroxyapatite (HA) từ khung san hô theo hai con đường: tổng hợp trực tiếp từ khung xương san hô và tổng hợp gián tiếp qua CaO, là sản phẩm trung gian của quá trình phân hủy nhiệt san hô. Các mẫu tạo thành được đặc trưng bằng phương pháp nhiễu xạ tia X (XRD), hiển vi điện tử quét (SEM) và phương pháp hồng ngoại (FTIR). Từ các kết quả phân tích, khẳng định được rằng gốm HA có thể tổng hợp được từ san hô bằng phương pháp gián tiếp qua CaO mới được tạo thành từ sự phân hủy nhiệt CaCO3 dạng aragonite của san hô.