

Low temperature synthesis of hydroxyapatite from $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}(\text{OH})_2$ based on effect of the spark plasma system (SPS)

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Abstract

A mixture of 6 mol of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and 4 mol of $\text{Ca}(\text{OH})_2$ was reacted to produce hydroxyapatite (HA) by spark plasma system (SPS). The reaction was carried out at 300–1200 °C under pressure of 20–670 MPa for 10 min in a vacuum. HA formation started at 300 °C at 600 MPa and was completed at 500 °C at 670 MPa, the same product being obtained at 1200 °C in air using a furnace. The temperature of the HA formation increased with decreasing pressure and was 1150 °C under 20 MPa. There was a linear relationship between the reaction temperature and pressure. The crystal size of the HA prepared at 500 °C at 670 MPa and that at 600 °C at 600 MPa by SPS were less than 1 and 2 μm, respectively.

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1. Introduction

Powder sintering has been based on sintering at atmospheric pressure or sintering under high pressure. Although these techniques have enabled the manufacture of various kinds of useful products from metal and ceramics, their limited effectiveness for the production of advanced materials has recently become apparent. The spark plasma system (SPS) was developed for sintering metal and ceramic powders in plasma as well as in an electric field [1]. SPS is characterized by a pulsed direct electric current, which is similar to that of an electric discharge machine. Unique products which cannot be made by ordinary methods have been created from ceramics, metals and polymers by SPS [2]. The formation of these products is based on the effect of the pulsed electric field, where spark plasma is generated between powders and a skin current can run on particle

surface. The spark plasma activates some chemical bonds, and crystal growth is enhanced by the skin current [2]. The mobility of dislocations is accelerated in the pulsed direct electric field [3].

Hydroxyapatite (HA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) is one of the most bioactive ceramics [4]. The chemical composition of HA consists of OH groups which are eliminated at high temperature. The stability of HA depends on the partial pressure of H_2O [5]. The HA powder can be stably sintered at 1300 °C in air using a furnace [6]. On the other hand, HA is stable below 1050 °C in a vacuum [7]. The decomposition temperature of HA is lowered till 800 °C by the catalytic action of Ti [8,9]. The majority of HA syntheses are carried out under the influence of water as follows: (1) precipitation method [10,11]; (2) hydrolysis method [12]; (3) hydrothermal method [13,14]; and (4) hydrothermal hot-pressing method [15]. HA is synthesized from 6 mol of CaHPO_4 (DCP) and 4 mol of $\text{Ca}(\text{OH})_2$ (CHO) without water by solid state reaction [4], although the synthetic condition has not been clarified.

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In this study, 6 mol of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (DCPD) and 4 mol of CHO were reacted to produce hydroxyapatite by SPS. The reaction was carried out at 300–1200 °C under pressure of 20–670 MPa. The HA formation was investigated by X-ray diffractometry, and the grain size of the prepared HA was observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

2. Experimental

2.1. Materials and reaction

The starting powders were DCPD and CHO (Wako Pure Chemical Ind., Japan, reagent grade), 6 mol of DCPD and 4 mol of CHO being mixed with an agate mortar and pestled for 20 min. These two materials were reacted by SPS (Sumitomo Coal Mining Co. Ltd., Japan, SPS1050). The mixed powder was put in a graphite die or a hard metal die and heated from 300 to 1200 °C at 20–670 MPa in a vacuum. The heating rate was controlled toward the goal temperature of 1000 °C as follows: from 20 to 900 °C at 100 °C/min, from 900 to 980 °C at 20 °C/min and from 980 to 1000 °C at 5 °C/min. The holding time at the goal temperatures was 10 min. For comparison with the SPS sample, the mixed powder was reacted from 500 to 1200 °C in air in a furnace without using SPS.

2.2. Decomposition of materials and characterization of the reacted product

The decomposition temperature of DCPD was determined by differential scanning calorimetry at a heating rate of 0.67 °C/s in air (Seiko Instruments, Japan, SII DSC 6300). The reacted products were subjected to X-ray diffraction (XRD) by an X-ray diffractometer (Rigaku, Japan, Rotaflex, RU-200B) using the $\text{Cu K}\alpha$ line. The surface of the reacted product was polished to make a mirror surface and was etched at 1000 °C for 30 min in air. The etched surface of the sintered product was observed by a scanning electron microscope (SEM) (JEOL, Japan, JXA-8621MX, and Hitachi, Japan, S-800). The microstructure was analyzed by a transmission electron microscope (TEM) (JEOL, Japan, JT-007).

3. Results

3.1. Reaction in furnace

The results of the DSC measurement indicated that DCPD lost water and was transformed into DCP at 149 °C. DCP was decomposed at 460 °C. It was confirmed by X-ray diffractometry that CHO was stable until 900 °C and then decomposed into CaO over 1000 °C. The mixture of 6 mol of DCP and 4 mol of CHO was reacted in air in a furnace, not

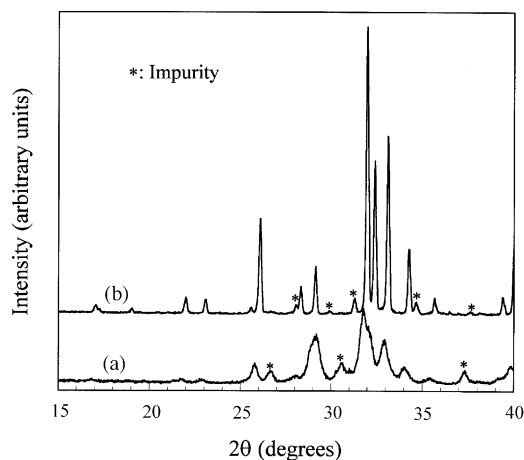


Fig. 1. XRD patterns of the products reacted in furnace for 1 h in air: (a) at 600 °C and (b) at 1200 °C.

using SPS. The reaction of DCPD and CHO did not occur at 500 °C, but started near 600 °C. Fig. 1a shows that HA with impurities was formed at 600 °C for 1 h. The diffraction peaks of the product was not sharp and exhibited the formation of a small crystallite, i.e. nucleus. This nucleus was unstable at this temperature and disappeared after heating at 600 °C for 10 h. The nucleus did not grow to stable size at 600 °C in the furnace.

The formation of HA from DCP and CHO was indistinct below 1000 °C, but was distinguishable at 1200 °C. The reacted product consisted of HA and a small amount of the impurity which was not identified, as shown in Fig. 1b. It was clear that preparation of HA was possible in air by solid state reaction. Judging from the half-value width of the diffraction peaks, the crystal of the product which prepared at 1200 °C was not a nucleus. The HA crystal was stable and did not decompose after the reaction at 1200 °C for 10 h in air. The impurity neither decreased nor increased after the long reaction.

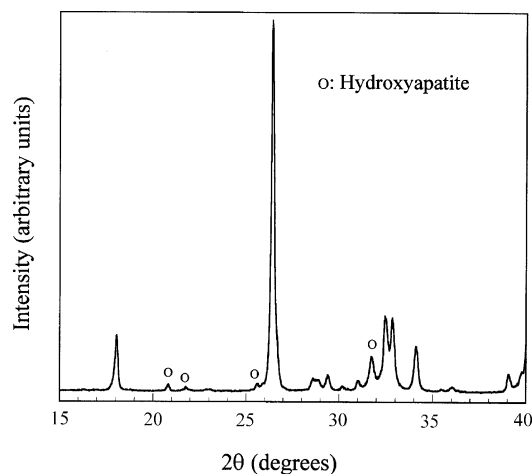


Fig. 2. XRD pattern of the product reacted at 300 °C at 600 MPa for 10 min by SPS.

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