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A Study of Hydroxyapatite Production from Waste Oyster Used Mechanochemical Treatment

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Dry grinding of a mixture of $CaCO_3$ and $Ca(H_2PO_4)_2 \cdot H_2O$ was conducted using a planetary ball mill in order to investigate solid state reaction for a synthesis of hydroxyapatite($Ca_{10}(PO_4)_6(OH)_2$, HAp) through mechanochemical treatment method. The raw materials, which are composed of waste oyster and calcium biphosphate($Ca(H_2PO_4)_2 \cdot H_2O$), were mixed and then treated mechanochemically. The synthesis of hydroxyapatite($Ca_{10}(PO_4)_6(OH)_2$, HAp) from the mixture was almost completed by about 60 minute grinding. The formation of HAp monophase in the ground mixture was characterized through X-ray diffraction (XRD) analysis. Moreover, the formation of HAp monophase depending on the grinding time was improved by increasing the grinding time.
Keywords: Waste Oyster, Mechanochemical Treatment, Planetary Ball Mill, Dry Grinding

Introduction

In recent years, a large quantity of waste oyster dumped from oyster farms has been one of the critical problems causing seaside pollution as waste oyster is filed up on the open and reclaimed foreshore. Therefore, in order to prevent the environmental problem, a number of studies for recycling of waste oyster have been conducted for the purpose of water treatment in the environmental field and concrete hardening in the architectural industry for a few decades. Waste oyster is made up of $CaCO_3$ as main composition and a small quantity of various impurities. It can also be used as raw material for fertilizer, provender, filler, paper coating, pigment, cosmetics and medicines.
In this work, the hydroxyapatite was synthesized with $CaCO_3$ from waste oyster and calcium biphosphate $Ca(H_2PO_4)_2 \cdot H_2O$) using mechanochemical treatment method. XRD analysis for phase characteristics and DTA analysis for thermal properties of the powder prepared by mechanochemical treatment method were performed in order to investigate the mechanism of solid state reaction for the synthesis of the hydroxyapatite. Additionally, the effect of pH value on suspension behavior of the powder in the ground and mixed solution was also considered for evaluation of the solid state reaction for the synthesis.

Experiment

Materials

Calcium carbonate was obtained using wet-physical treatment from waste oyster. Waste oyster was cleaned several times and immersed into the diluted acid solution for a short time to remove the salinity, and dried in the air. The dried oyster was crushed using Hammer Mill (Mitanuna Riken, Japan) and separated with 100 mesh sieve. In this study, inner part of waste oyster was selected as starting materials.
As shown on Figure 1, the XRD pattern of the separated inner part of waste oyster is correspondent to that of the commercial $CaCO_3$ material. And, reagent calcium biphosphate ($Ca(H_2PO_4)_2 \cdot H_2O$, CBP) was obtained commercially.

Mechanochemical treatment method

First of all, the each raw material was precisely weighed to coincide with a stoichiometry of HAp (Ca/P:1.67) with keeping away from absorbing excess moisture in air. The mole ratio of these materials for mixing is as follows :

$$CaCO_3 : Ca(H_2PO_4)_2 \cdot H_2O = 7 : 3$$

The chemical equation for the formation of HAp from the mixture of raw materials is represented as follows:

$$3Ca(H_2PO_4)_2 \cdot H_2O + 7CaCO_3 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 8H_2O + 7CO_2 \uparrow$$

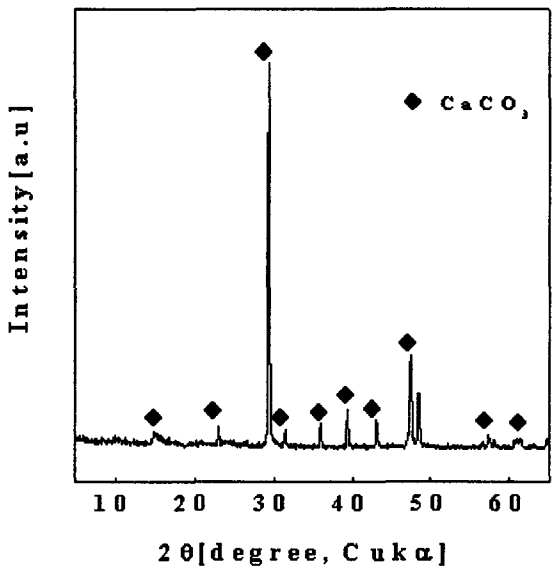

Figure 1. XRD pattern of $CaCO_3$ obtained from waste oyster

The raw materials were mixed vigorously using an agate mortar with a pestle prior to grinding. The mixture prepared prior to grinding is called "unground mixture" in this work. A planetary ball mill with a pair of zirconia pots($50cm^3$) containing 7 zirconia balls(Φ:15mm) as medium was used for grinding of the mixture. The mixture(3.5g) was put in the mill pots and then ground at the rotational speed of 690rpm varying only grinding time from 5 to 120 minutes. The grinding was paused for 10min by every 5 or 10min grinding time to prevent excess temperature increase inside the mill pots.

Characterization

XRD analysis was carried out using Cu-kα radiation to identify the phase and crystallinity of powders obtained. DTA was used to evaluate the thermal property of powders simultaneously in air at a heating rate of 10℃/min.

Results and discussion

Mechanochemical synthesis of HAp

Figure 2 shows the XRD patterns of the mixtures obtained by different grinding times. After 15 minute grinding, the peak intensity of $CaCO_3$ was reduced markedly and the most starting materials were converted into amorphous phases. Simultaneously, the very weak peaks of HAp were observed in the ground mixture, which means that the mechanochemical solid-state reaction proceeds when the interface of solid substances is closely contacted and sheared by grinding. After 30 minutes, the solid state reaction for HAp synthesis was enhanced noticeably. Although the marginal increment of them is observed at the prolonged grinding up to 120min in the profiles, the solid state reaction for HAp synthesis from the mixture seems to be completed in 30 minute grinding.

pH of the ground mixtures

Figure 3 illustrates the pH value of powder suspension of the mixtures was changed as a function of time after starting of grinding. The 0.5g of ground mixture was removed from the mill pot and dispersed into distilled water (150ml) with stirring vigorously using magnetic bar. The unground mixture varies at wide range over the measuring time. The acid indication of initial pH value of the mixture can be related to the dissolution of the little amount of H_2PO_4 generated before grinding. With an increase of measuring time, the pH value increased to the weak alkaline range and kept constant at around 8.5 mainly due to the dissolution of $Ca(OH)_2$. In the ground mixtures, however, the pH value was changed slightly, and the equilibrium pH value decreased as grinding progresses. Accordingly, the equilibrium pH value of the powder suspension of the mixture ground for 30min was measured as the neutral value and no noticeable changes were observed in the suspensions of the mixtures ground for further grinding time. This also confirms that the solid state reaction for HAp synthesis from the mixture of raw materials is almost completed through 30 minute grinding process.

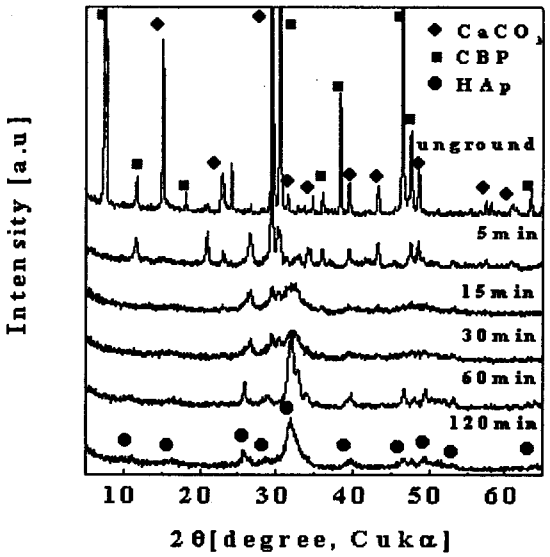

Figure 2. XRD patterns of $CaCO_3$-$Ca_3(H_2PO_4)_2 \cdot H_2O$ mixtures ground for different periods of time.

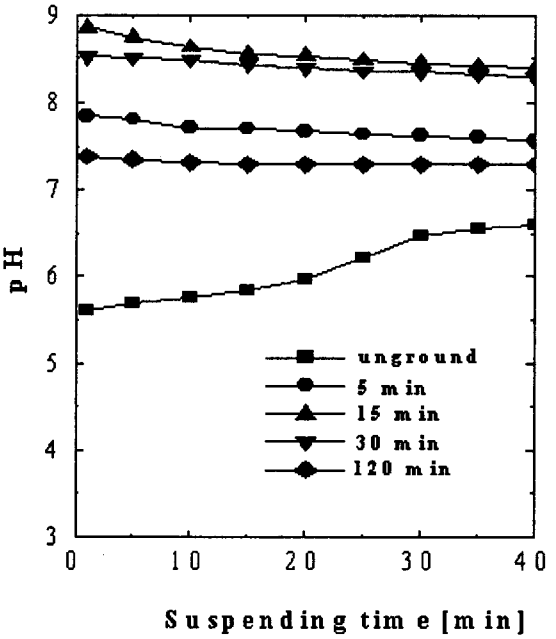

Figure 3. pH of the powder suspensions $CaCO_3$-$Ca_3(H_2PO_4)_2 \cdot H_2O$ mixtures as a function of time after grinding.

Thermal analysis of the ground mixtures

Figure 4 shows the DTA curves of the mixture after grinding for 60 minutes. In the case of the mixture, a main endothermic reaction corresponding to weight loss at the vicinity of the dehydration temperature of H_2O released from the solid state reaction for Hap synthesis is noticeable. It is also noted that no peaks with appreciable

thermal reactions of starting substances were detected at the temperature range studied in the work. In addition, the relatively weak exothermic reaction at approximately 890℃ may be attributed to the decomposition of HAp into tricalcium phosphate(β -TCP) by the following reaction.

$$Ca_{10}(PO_4)_6(OH)_2 \rightarrow 2Ca_3(PO_4)_2 + Ca_4P_2O_9 + H_2O$$

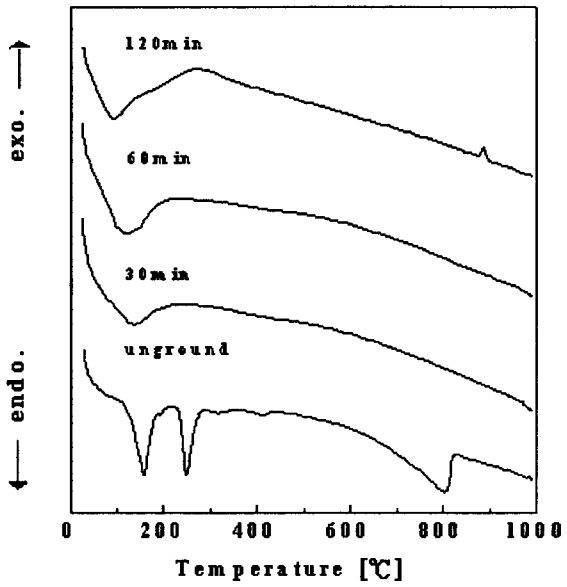

Figure 4. DTA curves of $CaCO_3$-$Ca_3(H_2PO_4)_2 \cdot H_2O$ mixtures after grinding for different periods of time

Conclusions

Mechanochemical synthesis of HAp from the mixture of waste oyster and calcium biphosphate with a Ca/P molar ratio of 1.67 was conducted by dry grinding using a planetary ball mill at room temperature. It is concluded that the formation of HAp depends significantly on the grinding time. All the starting mixtures are converted to HAp completely through 60 minute grinding and the equilibrium pH value of the powder suspension of ground mixtures is measured and considered as neutral value after completion of the reactions.

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