

# Ultrasonically Homogenized Precipitation for the Preparation of Functional Ceramic Powders

Y. Iida, K. Yasui, T. Tuziuti, and T. Kozuka

National Institute of Advanced Industrial Science and Technology (AIST)

2266-98 Shimoshidami, Moriyama-ku, Nagoya 463-8560, JAPAN

Fax: 81-52-736-7224, e-mail: y.iida@aist.go.jp

A new flow-through type sonochemical reactor consists of ultrasonic mixer and reaction coil has been designed to separate the nucleation process and the following crystal growth process to increase the controllability of sonochemical reaction. Its usefulness has been demonstrated in the preparation of hydroxyapatite particles. The irradiation of intense ultrasound at the very beginning stage of precipitation made the mixed solution into homogeneous state and the precipitate into amorphous. The regenerative operation of the reactor has been proved to be effective for the preparation of sub-micron apatite powders from an aqueous solution at 80°C.

Key words: ultrasound, sonochemistry, precipitation, apatite

## 1. INTRODUCTION

Ultrasound has proved extremely useful in the synthesis of a wide range of nanostructured materials, including nanoporous catalysts, and nanostructured oxide powders [1]. Usually, sonochemical experiments have been carried out using a simple set up, as illustrated in Fig. 1(a), where ultrasonic horn is immersed in a reaction solution contained in a round flask. The ultrasonic energy is directly transferred from the horn to the chemicals. The energy transfer is direct and effective and many stunning materials have been created with this setup. However, the reactor is so simple that the processes involved in the sonochemical reaction remained as a magical black box. Also, operation in a batch mode will not be suitable for industrial scale-up. In this paper, a new flow-through type reactor consisting of an ultrasonic mixer and a reaction coil is presented. The reactor is shown in Fig. 1(b) and it is abbreviated as RUSH, Reactor with UltraSonic Homogenization. The special features of RUSH are as follows; a) separation of nucleation from crystal growth, temporally and spatially. b) the homogeneity of reactants attained instantaneously by ultrasound and the degree of supersaturation can be controlled by the concentration and the providing speed of the reactants. c) easy and separate control of experimental parameters, such as reaction temperature, and reaction duration by changing the flow rates or the volume of reaction coil. d) rich varieties in operation mode, such as a flow-through one-pass operation or a regenerative operation.

The effectiveness of RUSH is experimentally demonstrated in the preparation of hydroxyapatite (HAP) powders. It is a compound of great interest in the industry of pharmaceutical products and preparation of biocompatible materials, mostly because it is the main inorganic component in calcified hard tissues of vertebrates [2].

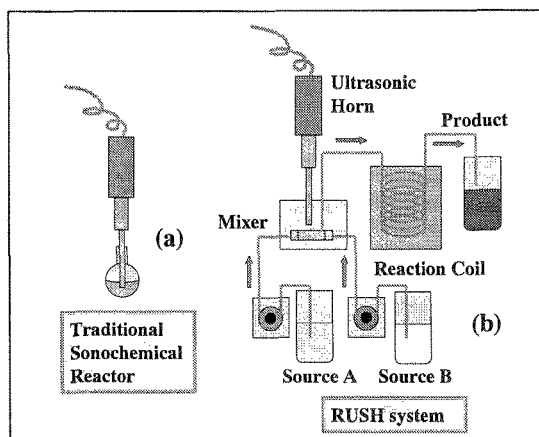


Fig.1 Reactor for sonochemistry. (a) traditional, (b) RUSH setup, consists of flow-through ultrasonic mixer and reaction coil.

## 2. EXPERIMENTAL PROCEDURE

The experimental setup of RUSH is schematically illustrated in Fig.1(b). The reactants were provided by peristaltic pumps into the mixing chamber (20mm diameter and 10mm height) which located 5mm below the top of ultrasonic horn (Branson S-250D) operated at 20kHz and 50-100W output. The body of mixing chamber were made from titanium metal and the windows of Pyrex glass (2mm thickness) were attached both at the top and the bottom sides. Extremely powerful mixing of reactants was performed by ultrasound. Then, the completely mixed solution flew into the reaction coil made of Teflon tubing (i.d.2mm x o.d.3mm, length 20m). The coil was heated in an oil bath, temperature controlled at 80°C. The flow rate is an important experimental parameter, which determines the residence

time. At the typical flow rate of 2mL/min, the reaction solution stays in the mixing chamber for 1.5 minutes and in the reaction coil for 30 minutes.

The chemical procedure for the formation of HAP followed the literature by Ioku, Yoshimura and Somiya [3]. The solution of  $0.167 \text{ mol}\cdot\text{dm}^{-3} \text{ Ca}(\text{NO}_3)_2$  and  $0.100 \text{ mol}\cdot\text{dm}^{-3} (\text{NH}_4)_2\text{HPO}_4$ , both were pH controlled at 10.0-10.5, were used as Ca and  $\text{PO}_4$  sources, respectively.

### 3. RESULTS AND DISCUSSION

The effects of ultrasonic irradiation at the mixing period, which corresponds to initial nucleation and the followed dynamic migration of chemical species between the precipitation and the solution, are illustrated as the differences of XRD patterns in Fig.2 All the peaks appeared in the patterns corresponds to those of HAP (ICPD 84-1998). The dramatic difference between the two patterns is the broad rise of background centered around  $2\theta = 30$  degree for the precipitate obtained with ultrasonic irradiation. This broad peak suggests the suppression of crystal growth by intense ultrasonic irradiation [4]. Because the solubility product of  $\text{Ca}^{2+}$  and  $\text{PO}_4^{3-}$  is very small,  $1 \times 10^{-115}$ , almost all the ions will instantaneously precipitate in the mixing chamber as amorphous precipitates. Without sonication, the precipitates somehow proceed to crystallize in the usual manner. On the other hand, with intense ultrasound, amorphous precipitates experience vigorous agitation in random direction, the structure should be disordered more. The highly amorphous and disordered structure remained even after the annealing process in the reaction coil. The particle size distribution determined by laser scattering method indicated the particles with mean diameter around  $10\mu\text{m}$ , both with and without sonication. However, as shown in Fig.3, no particles larger than  $1\mu\text{m}$  was found by the SEM observations. Therefore the

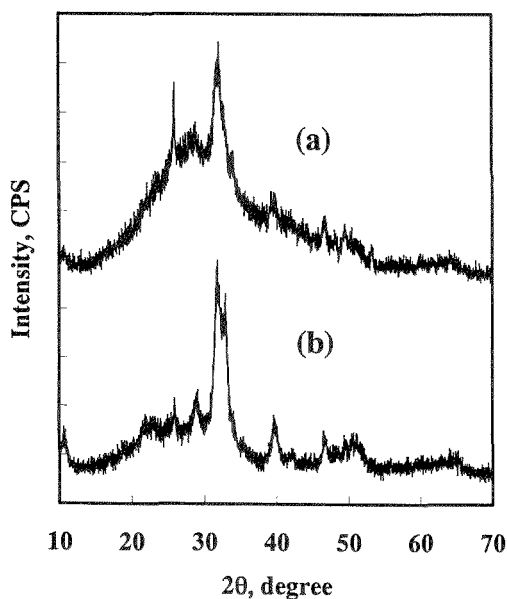


Fig.2 XRD patterns of hydroxyapatite precipitates; (a) with ultrasound, (b) without ultrasound.

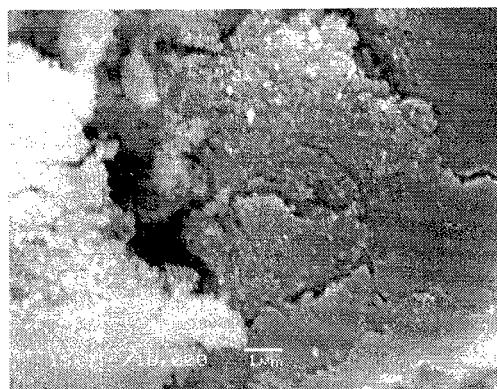


Fig.3 SEM image of the hydroxyapatite precipitates obtained by RUSH.

observed particle distribution reflected the size of the aggregates of the amorphous or the nano sized particles of HAP. The same trends were observed in the case of the diluted starting solutions, such as 1/5 or 1/20 concentration of the original solutions.

The RUSH system can be operated in a regenerative manner if the 'product' solution is directed into the source beaker, as shown in Fig. 4. Combination of the concentrations and the volume of the starting solutions can be the adjustable experimental parameters. For example, Ca rich starting mode was carried out as follows; 50mL of  $0.167 \text{ mol}\cdot\text{dm}^{-3} \text{ Ca}(\text{NO}_3)_2$  and 250mL of  $0.020 \text{ mol}\cdot\text{dm}^{-3} (\text{NH}_4)_2\text{HPO}_4$  were used as starting solutions and the products solution were fed into the Ca solution beaker. Because the two pumps were operated in the same speed, the initial product solution contained a small amount of HAP precipitate and the excess of Ca ions. With the progress of the reaction,  $\text{PO}_4^{3-}$  ions were successively added into the product solution till the stoichiometric end point. The ultrasound can interact with the solution/precipitates continuously in the mixing chamber to assist the homogeneous precipitation of HAP. The  $\text{PO}_4$  rich mode was operated in the same manner with 250mL of  $0.033 \text{ mol}\cdot\text{dm}^{-3} \text{ Ca}(\text{NO}_3)_2$  and 50mL of  $0.1 \text{ mol}\cdot\text{dm}^{-3} (\text{NH}_4)_2\text{HPO}_4$ . Figure 5 shows the XRD patterns of HAP precipitates obtained in the regenerative operation with the continuous ultrasonic irradiation of

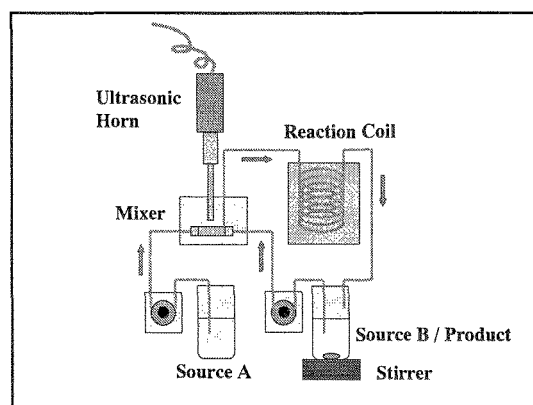


Fig.4 RUSH system in regenerative mode

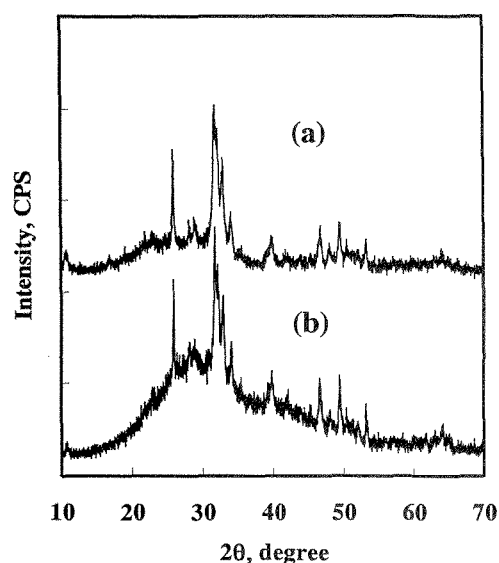


Fig.5 XRD patterns of hydroxyapatite precipitates; (a) Ca rich mode, (b) PO<sub>4</sub> rich mode.

60W. Again, the characteristic broad rise of background centered around  $2\theta = 30$  degree were observed in the both modes, especially in PO<sub>4</sub> rich mode. However, the peaks are becoming narrower than those in Fig. 2 This means that the crystallization from amorphous state and the crystal growth have proceeded in the reaction coil during the regenerative operation. In addition, the differences in the rise of background in the two modes, higher rise in PO<sub>4</sub> mode, may indicate that the amorphous HAP particles formed in the presence of PO<sub>4</sub><sup>3-</sup> ions were more liable to aggregate than in the Ca<sup>2+</sup> rich condition. The reason is not clear at this stage, but the surface charge of nano precipitates seems to be responsible. The SEM image of HAP obtained by Ca rich mode is shown in Fig. 6. The rod like particles about 500μm × 100μm size could be found from the image. From the XRD pattern of the HAP powder shown in Fig.4, the elongation of crystal occurs in the direction of c-axis because the (002) diffraction peak at  $2\theta = 25.90$  degree is obviously narrower than the (300) peak at  $2\theta = 32.90$  degree.

It should be noted that there are some characteristic differences between the proposed RUSH and the well-known homogeneous precipitation method. In the latter, the precipitant is generated gradually and homogeneously throughout the solution. The level of supersaturation remains low and compact crystals with narrow particle size distribution can be obtained. The main disadvantage of the method is that the reagents to be used in the method are very specific and limited, such as urea for pH rise. In RUSH, the homogeneity of reactants attained instantaneously by the action of ultrasound and the degree of supersaturation can be widely controlled by the concentration and the providing speed of the reactants. Furthermore, the combination of precipitants will not be limited by their chemical nature.

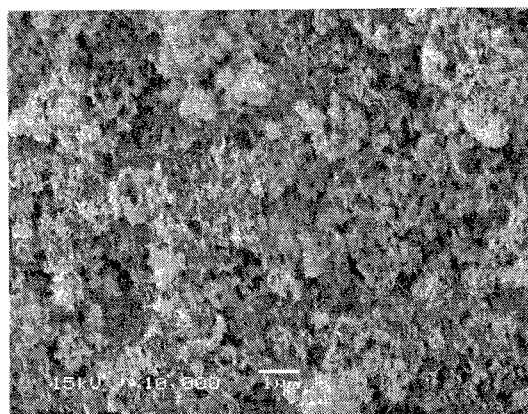


Fig.6 SEM image of the hydroxyapatite fine crystals synthesized by regenerative RUSH in Ca rich mode.

#### ACKNOWLEDGMENTS

This work was supported by Industrial Technology Research Grant Program in 2003 from New Energy and Industrial Technology Development Organization (NEDO) of Japan.

#### REFERENCES

- [1] K. S. Suslick and G. J. Price, *Annu. Rev. Mater. Sci.*, **29**, 295-326 (1999).
- [2] H. Monma, *Kogyo Zairyou* (in Japanese), **28**, 97-102 (1980). (Hydroxyapatite as fine ceramics)
- [3] K. Ioku, M. Yoshimura and S. Somiya, *Nippon Kagaku Kaishi* (in Japanese), **1988** 1565-1570 (1988). (Hydrothermal Synthesis of Ultrafine Hydroxyapatite Single Crystals)
- [4] A. Guinier, "X-Ray Diffraction in Crystals, imperfect Crystals, and Amorphous Bodies", Dover Publications, New York (1994).

(Received October 8, 2003; Accepted March 12, 2004)