Control of hydroxyapatite crystallinity by mechanical grinding method

T. NAKANO, A. TOKUMURA, Y. UMAKOSHI*
Department of Materials Science and Engineering, Graduate School of Engineering, Osaka University, 2-1, Yamada-oka, Suita, Osaka 565-0871, Japan

S. IMAZATO, A. EHARA, S. EBISU
Department of Conservative Dentistry, Faculty of Dentistry, Osaka University, 1-8, Yamada-oka, Suita, Osaka 565-0871, Japan
E-mail: umakoshi@mat.eng.osaka-u.ac.jp

Crystallinity of hydroxyapatite reflecting crystal size and crystal elastic strain was controlled by the mechanical grinding (MG) technique using a set of container and balls made of SUS304 stainless steel or agate. Variation in the crystallinity through MG was monitored by the XRD method and represented by the broadening of the diffraction peak. Effect of changes in crystallite size and strain on the crystallinity was also examined using the Hall-plot method.

Crystallinity rapidly decreased with milling time. Significant crystallographic diffraction peaks disappeared and a broad diffraction around $2\theta = 32^\circ$ was observed after MG for 72 h. The broadening was dominantly due to an increase in crystal strain in addition to fine crystallite size. Contamination from the container and balls during MG was more suppressed using agate than SUS304 stainless steel.

The recovery process of crystallinity during heating between 300 °C and 1200 °C was examined focusing on the decrease in residual elastic strain. Low crystallinity was maintained at annealing temperatures below 800 °C but lattice defects were recovered above 1000 °C.

1. Introduction

Since hydroxyapatite [HAp: $Ca_{10}(PO_4)_6(OH)_2$] is a principal component of dentin, bone and soft tissues, application of a bioactive material has been attempted to recover the damaged parts of hard tissues regardless of that synthetic hydroxyapatite ceramics do not have osteoinductive properties [1]. Mechanical and biochemical properties of biological apatites are significantly different from those of synthetic apatite ceramics composed of pure HAp [2]. Human enamel apatites, for example, contain a very low concentration of two minor but important elements of carbonate and magnesium [2–4]. Biological apatites of dentin or bone differ in crystallite size with enamel having the largest apatite crystallites [1, 3, 4]. Crystallinity reflects crystal size and/or strain or perfection.

In this study, control of crysltallinity in pure HAp was attempted using the MG method which is useful for creating non-equilibrium phase and/or introducing a large amount of lattice defects. The effect of heating temperature on crystallinity was also examined.

2. Experimental procedure

Hydroxyapatite powder with high crystallinity (HAP-200) was provided by Taihei Chemical Industrial Co., Ltd. It was synthesized by mixing slurries of calcium hydrogen phosphate anhydrate ($CaHPO_4$) and calcium carbonate ($CaCO_3$) at 90 °C and subsequent drying. The details can be found in the paper [6].

The as received HAp powder was mechanically ground under high purity argon gas flow using a high-energy ball mill (Nisshingiken NEV-MA8) with a SUS304 stainless steel or agate container (volume 92 cm^3) which was cooled by flowing water. About 5 g HAp powder was charged in the container accompanied by 25 balls of SUS304 stainless steel or agate with 12 mm in diameter. The balls were rotated in the container at 680 rpm for an appropriate period, 72 h being at the longest time.

XRD analysis was performed by an X-ray diffractometer (Shimadzu XD-5A) with monochromatic CuK_α radiation at 40 kV to monitor changes of crystallinity of HAp during MG. Chemical analysis of the original

*Corresponding author.

powder and the MG powder was performed by a SEM-EDS method to examine the contamination from the container and balls. Powder morphology was observed in scanning electron microscope and transmission electron microscope. The MG powder was annealed at each temperature up to 1200 °C for 1 h in high purity argon gas to determine the effect of heating temperature on crystallinity.

3. Results and discussion

The original HAp powder was composed of columnar crystals extending along the *c*-axis with approximately 2 μm in length and 0.2 μm in diameter as shown in Fig. 5(a). It showed high crystallinity with many sharp X-ray diffraction peaks (see Fig. 2).

A color change from white to gray was observed when HAp powder was subjected to mechanical grinding using the SUS304 stainless steel: the color shade became deeper with milling time. No significant color change in the HAp was observed when agate container and balls were used for milling.

Fig. 1 shows variation in concentration of impurity elements except the constituent elements of pure HAp powder during MG using the SUS304 stainless steel or agate container. Iron, chromium and nickel atoms were identified and their concentration increased with milling time in the powder ground with the SUS304 stainless steel container; only a slight amount of silicon was present in the powder mixed in the agate container. The color change may be due to the contamination of those three elements in the HAp powder from the walls of the container and balls. The color change is known to occur as a result of the absorption of visual light at a certain wavelength range, depending on the band structure, Fermi surface and density of state curves. Substitution of the Ca-ion site in pure HAp by Fe-ion may change the electronic structure and the absorption wavelength resulting in a darkening of the color [7]. In contrast, contamination was suppressed to a lower extent in the agate container. Trace silicon was also reported to promote bone remodeling without harmful effect on the human body [8]. Thus, agate is concluded to be a more suitable material as a set of MG container and balls for HAp.

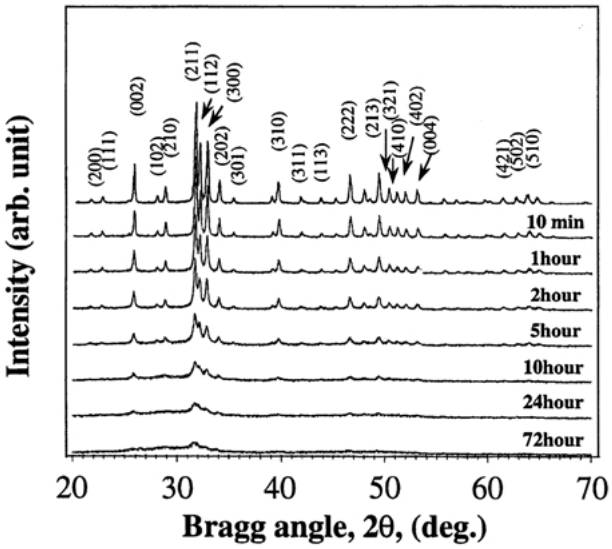

Figure 2 Change in XRD profiles of HAp powder during MG in the agate container.

Fig. 2 shows variation in XRD profiles of HAp powder during MG in the agate container. Diffraction peaks have broadened rapidly and the integrated peak width $(\beta_{1/2})$ at all the peaks increases with milling time. After 72 h of MG, a certain diffraction peak based on crystallographic planes is diminished and a broad maximum around $2\theta = 32°$ similar to amorphous state appeared. This remarkable change corresponds to a decrease in crystallinity.

Crystallinity is expressed as the reciprocal of the line broadening, $(\beta_{1/2})^{-1}$, at the (002) and (300) diffraction peaks (Fig. 3). The crystallinity rapidly decreases in the early stage of MG in 5 h and then is saturated at 24 h. The crystallinity of hydroxyapatites synthesized at various temperatures was reported to vary depending on reflection peak, such as (0 0 2) and (3 0 0) because the crystallinity is influenced by the crystallite shape and size [9]. In contrast the change in $(\beta_{1/2})^{-1}$ with milling time is independent of the reflection as shown in Fig. 3.

Crystallinity is predominantly determined by the two important factors of crystal size and residual elastic strain [10]. The cause of the broadening reflection peak can be derived by Hall-plot using the following equation:

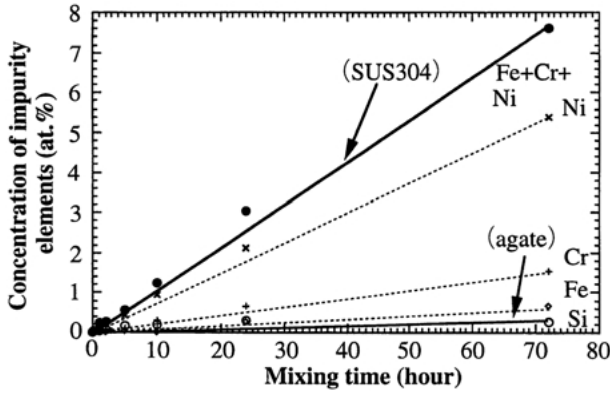

Figure 1 Variation in concentration of impurity elements in HAp powder during MG using the SUS 304 stainless steel or agate container.

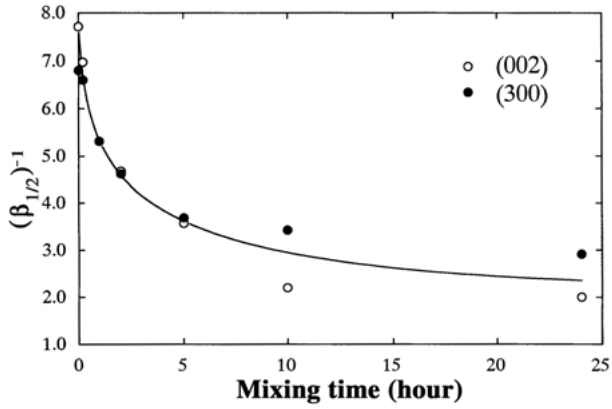

Figure 3 Change in $(\beta_{1/2})^{-1}$ at the (0 0 2) and (3 0 0) reflections of HAp powder during MG in the agate container.

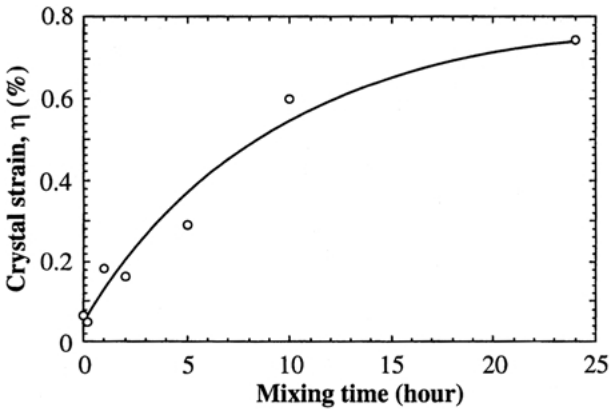

Figure 4 Change in the crystal strain in HAp powder during MG in the agate container.

$$\beta_{1/2} = \frac{k\lambda}{\varepsilon \cos\theta} + 2\eta \tan\theta \qquad (1)$$

where k is the constant, θ is the Bragg angle, λ is the wavelength of X-ray, ε is the crystallite size and η is the crystallite strain (residual elastic strain). In general, crystallite size in metals rapidly decreases with increase in milling time but only a slight change in crystallite size is observed in HAp powder during MG. The crystal strain in HAp powder rapidly increases with milling time and reaches about 0.75% after the MG for 24 h as shown in Fig. 4. The decrease in crystallinity is therefore due to crystal strain rather than to the refinement of crystal. The crystal strain shows no anisotropy along the *a*- and *c*-axes since there is no significant difference in changes of the inverse of $\beta_{1/2}$ for (3 0 0) and (0 0 2) reflections as shown in Fig. 3.

Fig. 5 shows scanning electron micrographs of HAp powder before and after MG for 72 h. The columnar crystals consisting of the second stage product coalesce and form particles after the MG as shown in Fig. 5(b). Individual crystals can be no longer distinguishable in the particles. A halo reflection like amorphous pattern was observed in the XRD profile of the MG powder of HAp. As shown in Fig. 6, electron diffraction analysis of the MG powder shows clear diffraction spots. Electron micrograph of each crystal shows a large number of black dots corresponding to a high density of lattice defects. These defects may contribute to the increase in stored crystal residual strain. Since the dissolution process of HAp after implantation is known to be very sensitive to the defect structure [11], control of the density and morphology of those lattice defects is important.

Control of the crystallinity of HAp powder is necessary for its biological application. Fig. 7 shows variation in the inverse of $\beta_{1/2}$ for (0 0 2) and (3 0 0) reflections in the powder heated at various temperatures after MG for 72 h. The crystallinity sharply increases above 800 °C and is strongly recovered at 1000 °C. Of course, heating the specimens to high temperature could also promote crystal growth and increase the reciprocal of the line broadening. If the appropriate annealing

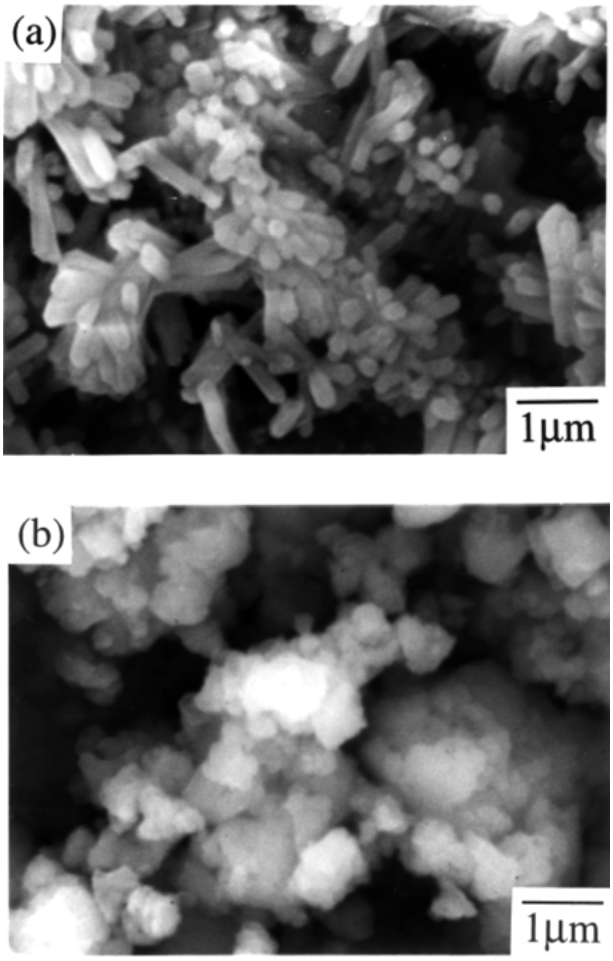

Figure 5 Scanning electron micrographs of HAp powders. (a) Before MG; (b) after MG for 72 h.

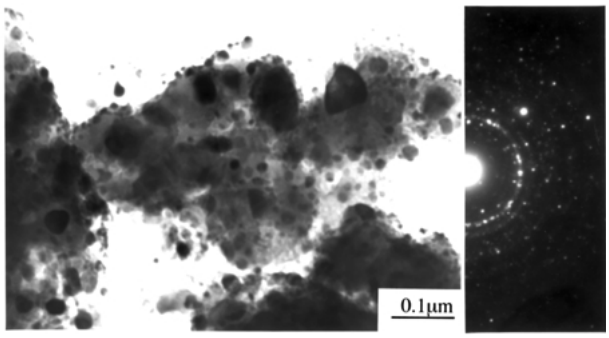

Figure 6 Electron micrograph and diffraction pattern of the MG HAp powder milled for 72 h.

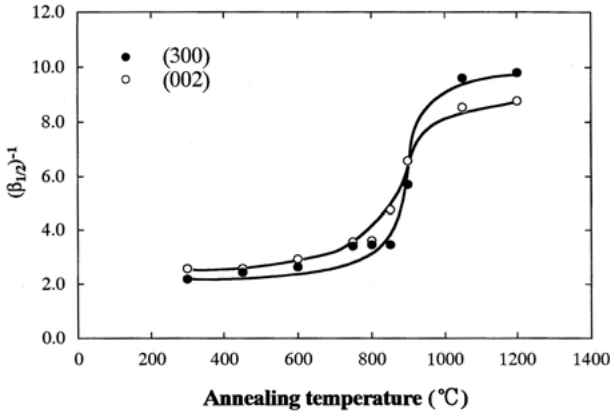

Figure 7 Change in $(\beta_{1/2})^{-1}$ for (0 0 2) and (3 0 0) reflections in the HAp powder heated at various temperatures after MG for 72 h.

process is selected, HAp ceramics with various crystallinities can be produced. Hot isostatic pressing to sinter synthetic HAp ceramics at low temperatures is now being developed to maintain the low crystallinity with stored crystal strain after consolidation.

4. Conclusions

The MG method and subsequent heat treatment were applied to control the crystallinity of HAp ceramics and the following conclusions were reached:

1. Low crystallinity of HAp powder can be produced by MG. If an agate container and balls are used, contamination of HAp powder is effectively suppressed although a slight amount of silicon is present in the powder. Low crystallinity is due to a large amount of crystal strain rather than refinement of crystallite.
2. Low crystallinity of HAp can be maintained during annealing below 800 °C, but lattice defects are recovered above 1000 °C. If an appropriate annealing process is selected after MG, HAp ceramic with various crystallinities can be obtained.

Acknowledgments

This work was supported by Research for the Future Program of the Japan Society for the Promotion of Science (JSPS) (Project: Biological Tissue Engineering) (JSPS-RFTF98I00201). Y. Umakoshi would like to thank Hosokawa Powder Technology Foundation for a financial support. The authors would like to thank Mr F. Kaji and Mr M. Ueda, Taihei Chemical Industrial Co., Ltd. for supply of HAp powder.

References

1. G. DSACULSI, J. M. BOULER and R. Z. LEGEROS, *International Review of Cytology* **172** (1997) 129.
2. R. Z. LEGEROS, R. KIJKOWSKA, C. BAUTISTA and J. P. LEGEROS, *Connective Tissue Research* **33** (l995) 203.
3. R. Z. LEGEROS, O. R. TRAUTZ, J. P. LEGEROS and E. KLEIN, *Science* **155** (l967) 1409.
4. R. Z. LEGEROS, *Prog. Crystal Growth Charact.* **4** (l981) 1.
5. J. S. BENJAMIN, *Met. Trans.* **1** (l970) 2943.
6. N. MATSUDA, F. KAJI and M. WATANABE, *Phosphorus Research Bulletin* **6** (l996) 345.
7. M. OKAZAKI, J. TAKAHASHI and H. KIMURA, *J. Osaka Univ. Sch.* **25** (l985) 17.
8. E. M. CARLISLE, *Science* **167** (l970) 279.
9. M. OKAZAKI, J. TAKAHASHII and H. KIMURA, *J. Osaka Univ. Sch.* **24** (l984) 13.
10. W. H. HALL, *J. Inst. Met.* **75** (1948–49) 1127.
11. G. DACULSI, J. P. LEGEROS and D. MITRE, *Calcif. Tissue Int.* **45** (l989) 95.

Received 10 August 1999
and accepted 25 October 2000