Some Properties of Carbonate-Containing Hydroxyapatite Powder Prepared by Spray-Pyrolysis Technique Using Urea as a Foaming Agent

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The effect of urea addition on the formation of hydroxyapatite (HAp) through the spray-pyrolysis technique was examined. The crystalline phases of the powders prepared from the spraying solution without urea were HAp and a small amount of $\beta$-tricalcium phosphate; however, only carbonate-containing HAp was formed from the solutions with urea concentrations of 1.00 mol dm$^{-3}$ or higher. The SEM observations showed that the particle size of the as-prepared powder decreased with increasing urea concentration in the spraying solution. This reduction of the particle size may be due to the foaming action of CO$_2$ generated by the decomposition of urea. The relative density of the sintered body which originated from the solution with an urea concentration of 5.00 mol dm$^{-3}$ was comparable to that from the calcined and crushed powder which was obtained by spray-pyrolysing the solution without urea. The calcining and crushing operations before the fabrication of the sintered body may be omitted when the powders are prepared from starting solutions containing some urea.

Key-words: Spray-pyrolysis technique, Carbonate-containing hydroxyapatite, Urea, Foaming agent, Sinterability

1. Introduction

Spray-pyrolysis technique$^{1,2}$ is one of the powder-preparing techniques for ceramics. The stoichiometric and homogeneous compounds are prepared instantaneously by spraying solutions with the desired amounts of cations into the hot zone of an electric furnace. Since this technique is effective for the preparation of the multicomponent powders, several types of compounds have already been prepared by researchers: MgAl$_2$O$_4$, $\text{Y}_2\text{O}_3$-stabilized ZrO$_2$, Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$, YBa$_2$Cu$_3$O$_{7-\delta}$, Bi$_2$Ca Sr$_2$Cu$_4$O$_{10}$ and hydroxyapatite (Ca$_{10}$(PO$_4$)$_6$(OH)$_2$; HAp). The present authors also reported that calcium phosphates with various Ca/P molar ratios, such as HAp,$^{9,10}$ $\beta$-tricalcium phosphate ($\beta$-Ca$_3$(PO$_4$)$_2$; $\beta$-TCP),$^{10,11}$ calcium diphosphate (Ca$_5$P$_2$O$_9$),$^{10,12}$ and calcium metaphosphate (Ca$_3$(PO$_4$)$_2$),$^{10,12}$ can be prepared by the spray-pyrolysis technique.

When the starting solutions with inorganic metal salts are spray-pyrolysed using a two-fluid nozzle, the resulting powders tend to be composed of hollow and spherical agglomerates. The presence of these agglomerates may be detrimental to the densification of the compressed powders during the sintering.$^2$ Thus some milling of the resulting powders is required for fabricating dense bodies; moreover, the formation of some by-products is likely when a multicomponent powder is prepared by this technique.

In order to avoid forming these hollow agglomerates, some techniques have been proposed: (i) the formation of the solid secondary particles with the closely packed primary particles by the spray-pyrolysis of the partially polymerized metal alkoxide solution$^{13}$ and (ii) the reduction of the droplet sizes by the ultrasonic spray-pyrolysis.$^{14}$ On the other hand, urea is hydrolyzed to generate CO$_2$ and NH$_3$ at 70°C or higher. When the starting solutions containing urea are spray-pyrolysised, the droplet sizes are expected to be reduced by the foaming of the droplets during the generation of CO$_2$. Moreover, the presence of NH$_3$ may be effective for the preparation of HAp, because the pH in the droplets during spray-pyrolysis increases as more NH$_3$ is formed.

The purposes of this investigation were to prepare the agglomerate-free fine HAp powders by the spray-pyrolysis technique, using the solutions with urea as a foaming agent, and to examine some properties of the resulting powders. We propose that this technique be known as an urea-foaming spray-pyrolysis technique (UFSP technique). This investigation also provides some information which may be applicable to the fields of biomaterials,$^{15}$ ion exchangers,$^{16}$ adsorbents for chromatography$^{17}$ and catalysts.$^{18}$

2. Experimental

2.1 Preparation of powders by UFSP technique

As reported previously,$^{10,12}$ the spray-pyrolysis apparatus was composed of an atomizer (two-fluid nozzle with orifice diameter of 0.5 mm), a heating zone (fused silica tube: i.d. 8 cm and height 1.5 m;
electric furnace: i.d. 10 cm and height 1 m) and a powder collecting zone (test-tube type filter).

Seven kinds of starting solutions with the Ca/P ratio of 1.67 were prepared by mixing 0.50 mol·dm⁻³ Ca(NO₃)₂, 0.30 mol·dm⁻³ (NH₄)₂HPO₄, 0.4 mol·dm⁻³ HNO₃ and (NH₂)₂CO (urea). The concentrations of the urea were zero, 0.10, 0.50, 1.00, 3.00, 5.00 and 7.00 mol·dm⁻³; the solution containing urea of 0.10 mol·dm⁻³ is, for example, abbreviated as U₀.₁. The resulting solutions were sprayed into the heating zone (600°C) using a compressor at the air-flow rate of 10 dm³·min⁻¹.

2.2 Characterization of resulting powders

The crystalline phases of the obtained powders were identified using an X-ray powder diffractometer (XRD) with Ni-filtered Cu Kα radiation (40 kV, 25 mA) (RAD-IIA, Rigaku Corp.); the crystalline phases were checked with reference to the JCPDS cards. The crystallite sizes were calculated from Scherrer's formula using (002) and (300) reflections of HAp. The lattice constants were also calculated by the least-squares method on the basis of XRD data, using (002), (210), (300), (310), (222), (213), (410) and (400) reflections of HAp (50 kV, 240 mA; Rint-1500). The amounts of Ca and P in each powder were determined using an X-ray fluorescence spectrometer (40 kV, 70 mA; SXF-1200, Shimadzu). FT-IR measurements were carried out by the powder diffusion reflection method (Shimadzu 8200D; measurement range, 400-4000 cm⁻¹) using KBr. The particle shapes were observed using a scanning electron microscope (SEM: 5-430, Hitachi). The specific surface area (SSA) was measured by the BET method using N₂ as an adsorption gas. The primary particle size (GBET) was calculated by assuming the primary particles to be spherical:

\[ GBET = \frac{6}{\rho \cdot s} \]

where \( \rho \) is the theoretical density of HAp (3.16 g·cm⁻³).

2.3 Sinterability of resulting powders

The shrinkage of the compressed powders was measured using a thermomechanical analyser (TMA: high-temperature type, Rigaku Denki, Tokyo) at the heating rate of 10°C·min⁻¹: the as-prepared powder was pressed at 140 MPa to form a cylindrical compact with a diameter of 5 mm and a thickness of ~3 mm.

After ~0.3 g of the two kinds of powder, i.e., (i) as-prepared powder and (ii) the calcined (600°C, 1 h) and crushed powder, were uniaxially pressed at 100 MPa and then cold-isostatically pressed at 150 MPa to form the cylindrical compacts with diameters of 10 mm and heights of ~3 mm, the compacts were fired at 1150°C for 5 h: the heating rate from room temperature up to 1150°C was 10°C·min⁻¹. The relative density was calculated by dividing the bulk density of the sintered body by the theoretical density of HAp (3.16 g·cm⁻³). The grain sizes of the sintered body were calculated by the intersect method using SEM micrographs.

3. Results and discussion

3.1 Properties of resulting powders

Figure 1 shows the crystalline phases of the powders obtained by spraying the solutions with various concentrations of urea. Although HAp and β-TCP were present in the powder obtained by the spray-pyrolysis of U₀, the amount of β-TCP was reduced with an increase of the urea concentration of 0.10 to 0.50 mol·dm⁻³; only HAp was present in the powders derived from U₁ and U₃. When U₅ and U₇ were sprayed, not only HAp but also urea was present; the X-ray intensities of the urea derived from U₇ were higher than those derived from U₅.

The disappearance of β-TCP with increasing urea concentration from 0 to 1.00 mol·dm⁻³ may be associated with the presence of NH₃ generated by the decomposition of urea. The formation of NH₃ raises the pH in the droplet and shortens the reaction time needed for the nucleation and nuclear growth of HAp. The presence of the urea in U₅ and U₇ suggests that NH₃ and CO₂ formed by the decomposition of urea during the spray-pyrolysis react with one another again to form urea.

The obtained powders were observed by SEM. Typical micrographs are shown in Fig. 2. The powder obtained by spraying U₀ was composed of both spherical agglomerates with the diameters of ~5 μm.
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The particles sizes of the obtained powders were reduced with increasing urea concentration. When U5 was sprayed, the fine particles with the sizes of <1 μm were observed, together with some fragments of the original spherical agglomerates. The spherical agglomerates may be formed via the following processes: (i) the removal of the solvent from the droplet surface, (ii) the formation of microcrystalline calcium phosphates and (iii) the crystal growth of calcium phosphates. The spherical agglomerate sizes are dependent on the droplet sizes of the starting solution. Since the urea is decomposed to generate CO₂ along with NH₃, the droplet sizes may be reduced with increasing amounts of urea, owing to the foaming action due to the CO₂ generation in the droplets. The presence of the fragments derived from U5 suggests that the rapid foaming of CO₂ gas in the spherical agglomerates may contribute to fracturing the agglomerates.

The compositions of the obtained powders are listed in Table 1. Although Ca and P contents of the stoichiometric HAp are 39.89 and 18.50 mass%, respectively, the Ca and P contents of HAp prepared in this study were slightly lower than those of the stoichiometric HAp; moreover, the Ca and P contents decreased with increasing the amount of urea. The Ca/P molar ratio increased from 1.66 to 1.74 with an increase in urea concentration of the starting solution.

The Ca and P contents are lowered with increasing the urea concentration. This decrease is attributed to the presence of some residual waters, the adsorbed CO₂ gas and the reprecipitated urea in the powders. An increase of the Ca/P ratio with increasing amount of urea indicates that the PO₄ group in HAp may be substituted by the CO₃²⁻ group which originates from the urea. The apatites obtained from the solutions with urea seem to be carbonate-containing HAp (CO₃HAp). In order to confirm the formation of CO₃HAp, FT-IR spectra and the lattice constants were measured.

Figure 3 shows the FT-IR spectra of the powders derived from U0 and U5. In both IR spectra, the absorptions assigned to the PO₄ group were detected at 1300–900, 600 and 570 cm⁻¹ and that assigned to the OH group at 3570 cm⁻¹. The absorptions in the ranges of 1600 to 1300 cm⁻¹ were assigned to the NO₃ group. Only in the case of U5 were some additional absorptions detected at 1542, 1455, 1415 and 883 cm⁻¹. These absorptions may be assigned to CO₃²⁻ groups. Monma and Takahashi reported that when the CO₃²⁻ group substitutes for the PO₄ in an HAp structure (Type B of CO₃HAp), the characteristic absorptions appear at 1455, 1430, 1415, 864 or 872 cm⁻¹ in the IR spectra and that when the CO₃²⁻ group substitutes for the OH (Type...
A), the absorptions appear at 1542 or 1546, 1465, 879 or 883 cm\(^{-1}\). The present absorptions indicate that the CO\(_3^{2-}\) group substitutes for both PO\(_4\) and OH in HAp structure, as presented in Fig. 3 (see arrow marks); thus this apatite is referred to as Type-AB of CO\(_3\)HAp. The absorptions at 2350 and 2200 cm\(^{-1}\) are assigned to the reverse symmetric-stretching vibrations of CO\(_2\) and the absorption at 2000 cm\(^{-1}\) to the CN group.

In order to examine the solid-solutions of CO\(_3^{2-}\) into HAp, we measured the lattice constants of the \(a\)- and \(c\)-axis. The experimental errors were within ±0.001 nm. Results are shown in Fig. 4. The lattice constant of \(a\)-axis was reduced with an increase of the urea concentration up to 0.50 mol·dm\(^{-3}\); however, the value increased with a further increase in the urea concentration. On the other hand, no changes in the lattice constants of the \(c\)-axis were appeared, regardless of an increase of the urea concentration. The lattice constant of the \(a\)-axis in HAp may be reduced by the substitution of a CO\(_3^{2-}\) group into the PO\(_4\) site, whereas it may be enhanced by the substitution of a CO\(_3^{2-}\) into the OH site. The above results suggest that the CO\(_3^{2-}\) group preferentially substitutes into the PO\(_4\) sites at lower urea concentrations than 0.50 mol·dm\(^{-3}\), whereas it may preferentially substitute into the OH sites at the higher concentrations.

Generally, Type A and Type B of CO\(_3\)HAp are prepared by solid state and liquid phase reactions, respectively. Thus the present CO\(_3\)HAp powders (Type B) seem to be formed via a process similar to the liquid phase reaction in the case of the urea concentration up to 0.50 mol·dm\(^{-3}\), whereas CO\(_3\)HAp powders (Type A) are formed via a process similar to the solid state reaction in the case of the urea concentrations above 0.50 mol·dm\(^{-3}\). The CO\(_3\)HAp (Type AB) may be formed as a result of the reactions of CO\(_3\)HAp (Type B) with CO\(_2\) gas in the CO\(_2\)-richer atmosphere during the spray-pyrolysis at the higher urea concentrations.

The specific surface areas of the as-prepared powders are shown in Fig. 5. The SSA increased with an increase of urea concentration; the SSA of the powder derived from U1 was the largest (~42 m\(^2\)·g\(^{-1}\)) among the values of the powders examined. Although these SSA values do not correspond to the particle sizes observed by SEM (Fig. 2), this discrepancy may be due to the presence of the micropores formed by the release of CO\(_2\) and NH\(_3\) during the spray-pyrolysis. Figure 6 shows the changes of primary particle size and crystallite sizes with urea concentration. The primary particle sizes were in the range of 40 to 125 nm (Fig. 6(a)). On the other hand, the crystallite size (002) increased with an increase of urea concentration (Fig. 6(b)); the crystallite size derived from U1 was the largest (22 nm) among the powders examined. With a further increase in urea concentration, the crystallite size was reduced and became constant at 17 nm. The crystallite size (300) decreased with an increase of urea concentration; the crystallite size derived from U1 was the smallest (23 nm) among those of the powders examined. The crystallite size increased with increas-
ing urea concentration up to 5.00 mol·dm⁻³; it became almost constant (34 nm) with a further increase in urea concentration.

The changes in crystallite sizes (002) and (300) indicate that the crystal growth of HAp along the direction of c-axis is restricted when the urea concentration is 1.00 mol·dm⁻³ or higher. This may be due to the difference in crystal growth rates among HAp, CO₂HAp (Type B) and CO₂HAp (Type AB); the rates will be also affected by the CO₃²⁻ contents in CO₂HAp. Assuming that the crystallite shape is rectangular, the primary particles of the powders derived from U1 and U5, for example, are composed of ~4 crystallites and ~5 crystallites, respectively.

3.2 Sinterability of resulting powder

In order to examine the densification behavior of as-prepared powders during the heating, the linear shrinkage of the compact was measured using TMA. The contraction of compacts derived from U0 and U5 initiated at ~700 and ~400°C, respectively; the shrinkage of each compact was ~12 and ~20% from room temperature up to 1200°C.

On the basis of the above findings and the previous paper, the sinterability of the resulting powders were examined by firing at 1150°C for 5h. In the case of the as-prepared powders (Fig. 7), the relative densities of the sintered bodies decreased with increasing urea concentration; they increased at and above 0.50 mol·dm⁻³. Although the relative densities attained ~92% at the urea concentrations of 3.00 and 5.00 mol·dm⁻³, they decreased again at 7.00 mol·dm⁻³.

The sinterability varies according to the kind of the HAp powder derived from the solutions with various urea concentrations. The reason may be explained in terms of the difference in introduction of CO₃²⁻ into the PO₄ site and/or OH site of HAp. Although the crystallite derived from U0 is HAp, CO₂HAp (Type B) is formed by the spray-pyrolyses of U0.1 and U0.5, whereas CO₂HAp (Type AB) is formed by those of U1, U3, U5 and U7. The solid-solution of CO₂²⁻ into HAp creates some vacancies to compensate for the charge balance. From the results of the lattice constant (a-axis) in Fig. 4, the amount of CO₂²⁻ present in the OH site of HAp increases with increasing the urea concentrations from 1.00 to 5.00 mol·dm⁻³. An introduction of CO₂²⁻ into the OH site creates some vacancies; the migration of those vacancies contributes to promoting the densification.

The relative densities of the sintered bodies derived from U0.1 and U0.5 are lower than those from U0.1, 1, 3, 5 and 7. This fact may be explained by assuming that the vacancies present in PO₄ sites of HAp migrate more slowly than those in OH sites. Additional vacancies will be formed by the release of CO₂ from CO₂HAp during the sintering, thus promoting the densification. In addition, an increase in relative density with increasing urea concentration from 0.50 to 5.00 mol·dm⁻³ may be attributed to the reduction of the particle sizes owing to the urea-foaming actions. The decrease of the relative density with a further increase in urea concentration may be ascribed to the creation of pores due to the release of CO₂ and NH₃, because the urea which is reprecipitated in the spray-pyrolysed powder must be decomposed during heating.

By calcining and crushing the powders, the relative densities of each sintered body changed with increasing urea concentration, similar to the case of the as-prepared powders. The relative density of the sintered body without urea addition was ~93%; this value was comparable to that fabricated by using the as-prepared powder derived from U5. This result indicates that for the powders formed from the solution containing urea one can omit the calcining and crushing operations needed for the fabrication of ceramics.

The crystalline phases of the sintered bodies were HAp and a trace of β-TCP. The FT-IR spectra did not contain any absorptions assigned to NO₃⁻, CO₃²⁻ and CN⁻; only the characteristic absorptions assigned to HAp were detected after firing at 1150°C for 5h.

Figure 8 shows the relationship between urea concentration and average grain size of the sintered body, together with the typical SEM micrographs of the polished surface derived from U5. The average grain size derived from the as-prepared powders was ~1.7 μm. In SEM micrographs, these grain sizes appeared to be uniform. In the case of the calcined and crushed powders, however, the average grain size decreased with increasing urea concentration from 0 up to 1.00 mol·dm⁻³ and then increased with a further increase in urea concentration. The microstructure of the sintered body appeared to be inhomogeneous, compared with those of the sintered bodies derived from the as-prepared powders.

The HAp powder has been prepared by various processes such as dry process, wet process and hydrothermal process. The dry process has the ad-
The obtained HAp powder shows poor sinterability. The wet process has the advantages for preparing the powder with the large SSA and the good sinterability; however, the Ca/P ratio of the obtained HAp powder tends to be lower than the stoichiometric value (=1.67). These two processes need the calcining and crushing operations prior to the ceramics fabrication. Although the hydrothermal process may prepare the fine HAp particles with the Ca/P ratio of 1.67,23) little information on continuous powder preparations by this process has been available so far.24) The present UFSP technique makes the continuous powder preparation possible; the calcining and crushing operations of the resulting powders may be omitted during the fabrication of the ceramics. Thus we consider that the UFSP technique is effective for preparing the starting powders for ceramics.

4. Conclusions

The following results were obtained from the investigation of carbonate-containing HAp powder prepared by UFSP technique.

(1) The crystalline phases of the powders prepared from the spraying solution without urea were HAp and a small amount of β-TCP; however, CO$_3$-HAp was formed from the solutions with urea. CO$_3$-HAp may be formed by NH$_3$ and CO$_2$ due to the decomposition of urea.

(2) The particle sizes of the as-prepared powder were reduced with increasing urea concentration of the spraying solution. This reduction of particle size may be attributed to the foaming actions of CO$_2$ generated by the decomposition of urea.

(3) The relative density of the sintered body derived from U5 was comparable to that derived from the calcined and crushed powder without urea addition. The calcining and crushing operations before fabrication of the sintered bodies may be omitted if one uses the powders prepared from the urea-containing solutions.

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References