Characterization and thermal decomposition of synthetic carbonate apatite powders prepared using different alkali metal salts

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Two types of synthetic carbonate apatite [potassium-containing carbonate apatite (CAK) and sodium-containing carbonate apatite (CANa)] were prepared and characterized by thermogravimetric analysis, X-ray diffraction analysis (XRD) and Fourier transform infrared spectroscopy. The chemical formulas of carbonate apatite were determined to be Ca$_{9.36}$K$_{0.12}$(PO$_4$)$_{5.12}$(CO$_3$)$_{0.88}$(OH)$_{1.73}$ and Ca$_{8.72}$Na$_{1.32}$(PO$_4$)$_{4.96}$(CO$_3$)$_{1.04}$(OH)$_{1.80}$, respectively. Thermogravimetric analysis showed that the final weight loss at 1,200°C reached about 11.2% for CAK and 13.9% for CANa. Carbonate loss gradually occurred above 150°C and continued to 1,200°C. The crystallinity of the apatite phase was found to be much improved between 800 and 850°C for CAK and 750 and 800°C for CANa, where rapid carbonate loss occurred. A small amount of CaO formed above 900°C. For CANa, NaCaPO$_4$ also formed above 700°C in both apatites. Although the lattice parameters of the carbonate apatites varied with temperature, the final a and c lattice parameters attained constant values of 0.9421 and 0.6881 nm.

Keywords: Carbonate apatite, Sintering, Thermal properties, Carbonate content

INTRODUCTION

Carbone apatite is a good candidate as a resorbable bone substitute for the deficit area in bone caused by bone tumors or accident. Granular or block-type carbonate apatite is suitable as a bone substitute and it is usually produced by sintering synthetic carbonate apatite powder. However, carbonate apatite decomposes during heating. High-temperature causes carbonate loss and converts carbonate apatite to CaO and other types of calcium phosphates, such as hydroxyapatite, tricalcium phosphate, and tetracalcium phosphate, depending on the Ca/P ratio. This process probably affects the bioreabsorbability of carbonate apatite, which is one of the most important biological properties. The carbonate content affects cell attachment and proliferation. Decomposition of synthetic carbonate apatite by heating has been reported by several researchers. However, most of the carbonate apatites used in these studies were synthesized by precipitation in calcium salt-ammonium phosphate solution in the presence of carbonate ions. The substitution mechanism in carbonate apatite varies with co-existing cations, such as alkali metal ions, which can substitute Ca lattice sites. Although carbonate ions substitute PO$_4^{3-}$ (B-type) and/or OH$^-$ sites (A-type) in carbonate apatite, the difference in charge of the ions makes the process of maintaining overall charge balance complicated. Several substitution mechanisms in B-type, A-type, and mixed A–B-type carbonate apatite have been reported and they depend on the synthetic conditions and the composition, which affect the decomposition process. Because alkali metal salts are a raw material for fabrication of carbonate apatite powder, the effect of co-existing alkali metal ions on the fabrication of carbonate apatite needs to be investigated.

In the present study, we synthesized carbonate apatite containing Na$^+$ ions [sodium-containing carbonate apatite (CANa)] and K$^+$ ions [potassium-containing carbonate apatite (CAK)] by different methods. This study aims to understand the decomposition process of carbonate apatite synthesized by two different routes by thermogravimetric (TG) analysis, X-ray diffraction (XRD) analysis, and Fourier transform infrared (FT-IR) spectroscopy of CANa and CAK.

MATERIALS AND METHODS

Preparation of carbonate apatite

Two types of carbonate apatite (CAK and CANa) were prepared by different methods.

1. CAK
Reagent grade K$_2$HPO$_4$, K$_2$CO$_3$, and KOH (Wako Pure Chemicals, Osaka, Japan) were dissolved in distilled water to prepare 0.1 mol/L solutions. The solutions were mixed at a ratio of 120 mL of K$_2$HPO$_4$, 55 mL of K$_2$CO$_3$, and 120 mL of KOH in a 500 mL beaker. Reagent grade calcium bis-acetate monohydrate (Wako Pure Chemicals) was also dissolved in distilled water to prepare a 1 mol/L solution. The calcium solution (20 mL) was added to the phosphate–carbonate mixed solution in the beaker at 90°C. The reaction was continued for 16 h at about pH 10 under stirring. After completion of the reaction, the precipitate was immediately suction filtrated and then washed with distilled water several times. The precipitate was dried at 60°C overnight and then subjected to TG analysis.

2. CANa
Ca(OH)$_2$ (75 g, Wako Pure Chemicals) was suspended in 300 mL of distilled water. Carbon dioxide (CO$_2$) gas was bubbled through the suspension solution to convert
Ca(OH)$_2$ to calcite. The reaction was performed at room temperature for 4 days under CO$_2$ gas flow at a flow rate of 20 L/h. The suspension was filtrated and washed with distilled water. After drying, 50 g of the residue was dispersed in 1 L of 1 mol/L Na$_2$HPO$_4$ (Wako Pure Chemicals) solution at 60°C and stirred at 250 rpm using a magnetic stirrer. The reaction was performed for 132 h. The solid residue was filtered, washed several times with distilled water, washed with ethanol, and then dried at 60°C.

The compositions of the two carbonate apatites were determined by atomic absorption spectroscopy (AAnalyst 200, Perkin Elmer, Waltham, MA, USA) for Ca, Na and K, and by spectrophotometry for P. The results are given in Table 1.

### Table 1 Composition of the synthesized carbonate apatites (wt%)

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Ca</th>
<th>K</th>
<th>Na</th>
<th>PO$_4$</th>
<th>Ca/P*</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAK</td>
<td>36.9</td>
<td>0.47</td>
<td>—</td>
<td>47.8</td>
<td>1.83</td>
</tr>
<tr>
<td>CANa</td>
<td>33.3</td>
<td>—</td>
<td>2.9</td>
<td>44.9</td>
<td>1.76</td>
</tr>
<tr>
<td>HAP$_b$</td>
<td>39.9</td>
<td>—</td>
<td>—</td>
<td>56.7</td>
<td>1.67</td>
</tr>
</tbody>
</table>

*Molar ratio, *Stoichiometric hydroxyapatite Ca$_{10}$(PO$_4$)$_6$(OH)$_2$.

**TG analysis of carbonate apatite**

About 15 mg of the carbonate apatite and HAP (HAP 200, Taihei Chemical Industrial, Nara, Japan) powders were used for TG analysis. TG analysis was performed at a heating rate of 10°C/min to 1,200°C in a static air atmosphere using a thermal analyzer (TG/DTA6300, SII NanoTech, Tokyo, Japan). TG analysis was also performed to various temperatures between 150 and 1,200°C, where a weight decrease was observed. The specimens after the analysis were subjected to XRD and FT-IR spectroscopy.

**XRD and FT-IR spectroscopy**

The specimens after TG analysis were ground into fine powders and characterized by powder XRD and FT-IR spectroscopy. The XRD patterns of the specimens were recorded with a vertically mounted diffractometer system (RINT 2500V, Rigaku, Tokyo, Japan) using counter-monochromatized CuK$_\alpha$ radiation generated at 40 kV and 100 mA. The specimens were scanned from 2θ = 20° to 40° in continuous mode at a scanning rate of 2°/min. The lattice parameter of the 5 samples of each was measured by using the integrated software package, PXDL (Rigaku, Version 1.8.1.). The FT-IR spectra were measured by the KBr disc method using a FT-IR spectrometer (Spectrum 2000XL, Perkin Elmer). The spectra were recorded with 100 scans at a resolution of 4 cm$^{-1}$.

**RESULTS**

Figure 1 shows the TG curves of CAK and CANa powders recorded from 25 to 1,200°C at a heating rate of 10°C/min in static air. Both of the carbonate apatites show rapid weight loss (about 2.5% for CAK and about 4% for CANa) immediately after the start of heating to 100°C, corresponding to release of adsorbed water. Gradual weight loss then occurs with rapid weight loss at around 800–850°C for CAK and 750–800°C for CANa. The rapid weight loss for CANa seems to proceed in two steps from the peaks observed in the derivative of the TG curve. The small rapid weight loss is caused by CO$_2$ release and corresponds to remarkable improvement in the crystallinity of apatite phase, which will be discussed later. The final weight loss at 1,200°C is about 11.2% for CAK and 13.9% for CANa. These values are comparable with other reported values$^5$, although the difference in carbon content should be taken into account.

Figures 2a and b show the XRD patterns of CAK and CANa after TG measurements to various temperatures between 150 and 1,200°C, respectively. The XRD pattern for CAK at 150°C shows broad diffraction peaks similar to those before the measurement (data not shown), which is characteristic of conventional synthetic hydroxyapatite or carbonate apatite. Upon heating to 600°C, there is no remarkable change in the XRD pattern. However, for temperatures above 600°C,
the diffraction peaks became sharper and their intensity increases with increasing temperature, indicating that the crystallinity of the carbonate apatite increases. For 900°C, an additional small peak assigned to CaO appears at 2θ=37.3°, as indicated by the solid circle (●) in Fig. 2a, and it slightly increases in intensity at 1,200°C. The XRD pattern of CANa at 150°C also shows broad diffraction peaks corresponding to the apatite phase, although the crystallinity is lower than that for CAK from the ill-separated diffraction peaks between 30° and 35°. Similar to CAK, the XRD pattern shows no significant change below 600°C. However, the diffraction peaks become sharper and their intensity increases with temperature above 600°C. The same trend was also observed when dental enamel consisting of carbonate apatite was heated to 1,173 K (900°C)\(^{19}\). Above 700°C, additional small peaks appear at 2θ=23.3°, 32.5°, and 33.6°, as indicated by the open circles (○) for 1,200°C in Fig. 2b. The peaks are assigned to NaCaPO\(_4\) because CANa contains Na ions. It has been reported that NaCaPO\(_4\) also forms as a decomposition product of bone apatite in meat and bone meal at 500°C or higher\(^{20}\). For CANa, CaO also formed above 900°C and the amount seemed to be larger than that for CAK.

Figures 3a and b show the change in the \(a\) and \(c\) lattice parameters of the hexagonal apatite phase with temperature, respectively, for CAK and CANa. Both of the carbonate apatites show similar changes in the...
a lattice parameter, that is, the $a$ lattice parameter decreases with increasing temperature, reaches a minimum (400°C for CANa and 600°C for CAK), and then increases with increasing temperature. The $a$ lattice parameter comes close to a constant value of 0.9421 nm (shown by the dashed line in Fig. 3a) above 1,000°C in both cases, which is the $a$ lattice parameter of stoichiometric hydroxyapatite. The $c$ lattice parameters of CAK and CANa gradually increase and decrease with increasing temperature, respectively. CAK and CANa also have the almost same $c$ lattice parameter above 800°C (0.6881 nm, as shown by the dashed line in Fig. 3b), which is the $c$ lattice parameter of stoichiometric hydroxyapatite.21)

Figure 4 shows the FT-IR spectra of CAK and CANa before and after TG measurements to various temperatures between 150 and 1,200°C. The spectra for both of the carbonate apatites before the TG measurements show several absorption bands owing to the PO$_4^{3-}$ group (900–1,200 cm$^{-1}$ and 500–650 cm$^{-1}$) and the CO$_3^{2-}$ group (1,350–1,550 cm$^{-1}$ and about 870 cm$^{-1}$). The absorption band for CO$_3^{2-}$ with two maxima at 1,455 and 1,410 cm$^{-1}$ is characteristic of B-type carbonate apatite, in which CO$_3^{2-}$ ions substitute for PO$_4^{3-}$ ions. The FT-IR spectra do not change with heating to 600°C, except for a slight decrease in the intensity of the CO$_3^{2-}$ absorption band and appearance of a small shoulder around 630 cm$^{-1}$. The shoulder peak (•) is clearly observed at 700°C and it is assigned to the libration mode of OH$^-$ in the apatite structure. The presence of OH$^-$ ions is confirmed by a sharp small band at 3,570 cm$^{-1}$, which is the characteristic stretching vibration mode of the OH$^-$ group in hydroxyapatite. The absorption band for CO$_3^{2-}$ greatly decreases between 600 and 700°C and finally almost disappears at 1,200°C.

Figure 5 shows the change in the CO$_3^{2-}$ contents of the carbonate apatites with temperature. The carbonate content was calculated from an intensity ratio of the CO$_3^{2-}$ band at 1,410 cm$^{-1}$ to the PO$_4^{3-}$ band at 575 cm$^{-1}$ based on the method reported by Featherstone et al.22)

**DISCUSSION**

**Characterization CAK and CANa and their substitution mechanisms**

From the Ca, P, K, Na, and carbonate contents, the chemical formulas of the carbonate apatites were determined to be Ca$_{9.36}$K$_{0.12}$(PO$_4$)$_{5.12}$(CO$_3$)$_{0.88}$(OH)$_{1.73}$ for
CAK and Ca$_{8.72}$Na$_{1.33}$(PO$_4$)$_{4.96}$(CO$_3$)$_{1.04}$(OH)$_{1.80}$ for CANa.

In the determination, PO$_4^{3-}$ is only substituted by CO$_3^{2-}$ and no vacancies exist, that is, the total number of PO$_4^{3-}$+CO$_3^{2-}$ is always 6, as in stoichiometric hydroxyapatite, and the OH$^-$ content was calculated based on an electroneutrality condition. Comparing the formulas of the two carbonate apatites, although the carbonate contents are almost the same, more Ca ions are substituted by Na ions for CANa than by K ions for CAK. This difference is because of the difference in the ionic radii of Na$^+$ and K$^+$, that is, K$^+$ ion is too large to substitute for Ca$^{2+}$. However, the K$^+$ ion has a larger ionic radius than the Ca$^{2+}$ ion, which makes it difficult for K$^+$ to substitute Ca$^{2+}$. De Maeyer et al. reported the substitution mechanisms of Na$^+$ and K$^+$-containing carbonate apatite from hydrolysis of monetite$^{12}$. There are five substitution mechanisms of carbonate and/or alkali metal ions in B-type carbonate apatite. The following four equations are mainly involved for Na$^+$ and K$^+$-containing carbonate apatite:

\[
\begin{align*}
\text{Ca}^{2+} + \text{PO}_4^{3-} + \text{OH}^- & \leftrightarrow \text{V}^{4+} + \text{CO}_3^{2-} + \text{V}^{0+} \quad (1) \\
\text{Ca}^{2+} + 2\text{PO}_4^{3-} & \leftrightarrow \text{V}^{4+} + 2\text{CO}_3^{2-} \quad (2) \\
\text{Ca}^{2+} + \text{PO}_4^{3-} & \leftrightarrow \text{M}^+ + \text{CO}_3^{2-} \quad (3) \\
\text{Ca}^{2+} + \text{OH}^- & \leftrightarrow \text{M}^+ + \text{V}^{0+} \quad (4)
\end{align*}
\]

where M denotes the alkaline metal (Na or K) and V$^4$ is a vacancy at the lattice site expressed by the subscript. The predominant mechanisms are Eqs. (1) and (3) for carbonate and M$^+$ ion substitution. Equation (4) also occurs for Na-containing carbonate apatite and Eq. (2) occurs for K-containing carbonate apatite, although the extent of substitution varies with the synthetic conditions, such as the M$^+$ and carbonate ion concentrations and their molar ratio. We calculated each contribution to substitution in CAK and CANa based on the obtained compositions. For CAK, the contributions of Eqs. (1)–(3) are 43%, 38%, and 19%, respectively. There is no contribution from Eq. (4). In contrast, for CANa, the main contribution is from Eq. (3) (78%) and the remainder is from Eq. (4). This suggests that coupled substitution of (Ca$^{2+}$+PO$_4^{3-}$) by (Na$^+$+CO$_3^{2-}$) is predominant in Na-containing carbonate apatite$^{9}$, while this mechanism is not predominant in K-containing carbonate apatite. This result can be explained by the difference in the ionic radii of Na$^+$ and K$^+$, that is, K$^+$ ion is too large to substitute for Ca$^{2+}$.

Decomposition process of carbonate apatite

When both of the carbonate apatites were heated to 1,200°C at a heating rate of 10°C/min in a TG apparatus, they showed weight loss immediately after the start of heating, as shown in Fig. 1. CANa has a larger weight loss than CAK with heating to 100°C owing to loss of adsorbed or adsorbed water. The FT-IR spectra of CAK and CANa before heating show absorption bands of water at 1,600 and 3,500 cm$^{-1}$, indicating the presence of free water. Some water remains even after heating to about 700°C. This is probably not only adsorbed water but also structural water, although it is not clear how water exists in the apatite lattice. The FT-IR spectra also show a slight decrease in the intensity of the absorption band for CO$_3^{2-}$ at around 1,400–1,500 cm$^{-1}$ during heating to 700°C for CAK and 600°C for CANa. During heating, water and CO$_3^{2-}$ are released from carbonate apatite. However, the XRD pattern is unchanged except for the peak positions, reflecting a change in the lattice constants, as shown in Fig. 3. The XRD patterns become well resolved between 700 and 800°C for CAK and 600 and 700°C for CANa, indicating improvement in the crystallinity of the carbonate apatites. In these temperature ranges, liberation of CO$_3^{2-}$ rapidly proceeds and seems to accompany the improvement of the crystallinity. CO$_3^{2-}$ remains above these temperature and is gradually released with increasing temperature. Both specimens are well-crystallized hydroxyapatite with a small amount of CaO as a by-product above 900°C. Decomposition of CAK can be expressed as

\[
\begin{align*}
\text{CO}_2 & \quad \text{Ca}_{9.25}\text{K}_{0.15}(\text{PO}_4)_{5.12} (\text{CO}_3)_{0.88} (\text{OH})_{1.73} \rightarrow \quad x\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + y\text{NaCaPO}_4 + z\text{CaO} \quad (5)
\end{align*}
\]

where x and y are determined to satisfy the weight balance of the equation. Based on Eq. (5), the composition was calculated to be approximately 95 wt% of the apatite phase and 5 wt% of CaO.

For CANa, rhenanite (NaCaPO$_4$) formed above 900°C owing to the presence of Na$^+$ ions in CANa. It has been reported that rhenanite also forms as a decomposition product of bone mineral in meat and bone meal above 500°C$^{23}$. When biological apatites, such as dental enamel and bone, are heated to above 1,000°C, α-TCP usually forms as a decomposition product. For CANa, the sodium content is so high that rhenanite forms instead of α-TCP. Because formation of rhenanite causes the Ca/P molar ratio to be too high to form stoichiometric hydroxyapatite, the excess Ca forms CaO. If decomposition completely proceeds, based on XRD analysis, the process can be expressed as

\[
\begin{align*}
\text{CO}_2 & \quad \text{Ca}_{9.27}\text{Na}_{1.33}(\text{PO}_4)_{4.96} (\text{CO}_3)_{1.04} (\text{OH})_{1.80} \rightarrow \quad x\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + y\text{NaCaPO}_4 + z\text{CaO} \quad (5)
\end{align*}
\]

The composition was calculated to be 68 wt% apatite, 24 wt% rhenanite, and 8 wt% CaO based on the above equation. These values for the by-products seem to be too large compared with the intensities of the diffraction peaks in the XRD patterns. Some Na would remain in the apatite lattice. Rhenanite has been found to be more bioactive than hydroxyapatite, and a biphasic material of rhenanite and hydroxyapatite has great potential as a bone substitute with good resorbability and osteoinductivity$^{23-25}$. Rhenanite and carbonate apatite biphasic material is also promising as a bone substitute, and the present study will be the basis for fabricating the biphasic material.
CONCLUSION

The chemical formulas of CAK and CANa were determined to be Ca$_{8.72}$K$_{0.12}$(PO$_4$)$_{4.96}$(CO$_3$)$_{1.04}$(OH)$_{1.80}$ and Ca$_{8.72}$Na$_{1.33}$(PO$_4$)$_{4.96}$(CO$_3$)$_{1.04}$(OH)$_{1.80}$, respectively. The carbonate apatites are both B-type, that is, CO$_3$$^2$ ions substitute PO$_4$$^3$ ions. Coupled substitution of (Ca$^{2+}$+PO$_4$$^{3-}$) by (Na$^+$+CO$_3$$^{2-}$) is dominant for CANa because of charge balance and the similarity of the ionic radii of Ca$^{2+}$ and Na$^+$. TG analysis shows that the final weight loss at 1,200°C is about 11.2% for CAK and 13.9% for CANa. Carbonate loss gradually occurs above 150°C immediately after release of adsorbed water and remarkable weight loss occurs above 400°C. Carbonate ions remain even at a final temperature of 1,200°C. The crystallinity of the apatite phase improves between 800 and 850°C for CAK and 750 and 800°C for CANa, corresponding to rapid loss of carbonate ions. For both CAK and CANa, a small amount of CaO forms above 900°C. In addition to CaO, NaCaPO$_4$ also forms above 900°C. Although the lattice parameters of the carbonate apatites vary with temperature in different ways, the final values of the a and c lattice parameters reach constant values of 0.9421 and 0.6881 nm, respectively, which are the lattice parameters of stoichiometric hydroxyapatite.

REFERENCES