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Thermal decomposition and reconstitution of hydroxyapatite in air atmosphere

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Abstract

In this paper, the decomposition and reconstruction behavior of hydroxyapatite (HAP) during heating and cooling in air atmosphere were studied. The commercial HAP were chosen and gradually heated to 1500°C and cooled to room temperature by a program controlled SiC heated furnace. X-ray diffraction (XRD) and Fourier-transformed infrared (FTIR) analysis were used to investigate the change of crystalline phases and functional groups of HAP at different temperatures. Weight change of samples was recorded by thermogravimetric analysis (TGA) during heating and cooling. The results revealed that HAP gradually releases its OH^- ions and transforms into OHAP in the temperature of 1000–1360°C. Above 1360°C, the OHAP would decompose into TTCP and αTCP phase. The OH^- stretching bands of HAP could be traced by FTIR even at the temperature of 1350°C which indicates HAP decomposition. HAP does not dehydrate completely before decomposition. We speculated that some oxyapatite (OAP) might be formed during dehydration with a great amount of OHAP still left in the system even up to the temperature of decomposition. In the temperature range of 1400–1500°C, there was no significant difference in XRD patterns, only TTCP and αTCP crystalline phases were observed. When the HAP gradually cools from 1500°C, a part of TTCP and αTCP would directly reconstruct into OAP around 1350°C. OAP existed in the temperature range of 1350–1300°C during cooling. When the temperature decreased to 1290°C, a part of TTCP and αTCP reconstructed into OHAP by rehydration reaction and OAP were rehydrated into OHAP as well. At 1100°C, the rest of TTCP and αTCP reconstitutes into HAP. As the temperature decreases, the OHAP is gradually rehydrated and reconstituted into HAP.

Keywords: Hydroxyapatite; Thermal behavior; Decomposition; Reconstruction

1. Introduction

Hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$) has excellent biocompatiblity, promotes faster bone regeneration, and direct bonding to regenerated bone without intermediate connective tissue. It has been developed and is currently used in clinical applications [1–3]. In recent years, the plasma-spraying technique has been widely investigated as a means of improving the biocompatibility of metal materials in vivo, by adding a HAP coating onto the metal implant surface [4–6]. Deposition of HAP on a metal surface involves introducing HAP powder into a high-temperature flame (usually over 10 000°C). These HAP particles are partly melted and may form a range of calcium phosphates including calcium oxide (CaO) or amorphous calcium phosphate upon decomposition [5,7]. When the high-temperature particles are impacted onto the cold metal substrate (usually below 150°C), the cooling rate of coatings can be as high as 10^8°C/s, which can lead to the formation of crystalline, non-crystalline and metastable crystalline products such as oxyhydroxyapatite (OHAP, $Ca_{10}(PO_4)_6(OH)_{2-x}O_x\square_x$), α-tricalcium phosphate (αTCP, $Ca_3(PO_4)_2$), tetracalcium phosphate (TTCP, $Ca_4P_2O_9$), calcium oxide (CaO) and amorphous apatite in HAP coatings [8–10]. It has been reported that OHAP, TTCP and αTCP have a greater tendency for dissolution and degradation than HAP in an aqueous environment [11], which will decrease chemical stability and enhance degradation of the coating in vivo.

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Recently, various plasma-spraying conditions and post-heat treatments have been studied for increasing the crystallinity of HAP coatings [8,12]. However, these HAP coatings contain numerous amorphous phases and complicated metastable phases, which made it difficult to elucidate the decomposition and reconstruction behavior of HAP coatings during the heat-treatment process. In the present paper we heated the commercial HAP powder from room temperature to 1500°C to investigate the thermal decomposition behavior of HAP in an air atmosphere. Additionally, the cooling rate of samples from 1500°C to room temperature were also controlled for exploring the reconstitution behavior of HAP during cooling. The XRD analysis was used to examine the phase transformation of HAP at different temperatures. The functional group change of HAP at different temperatures was observed by FTIR spectroscopy, and the weight change of samples were recorded by TGA during heating and cooling.

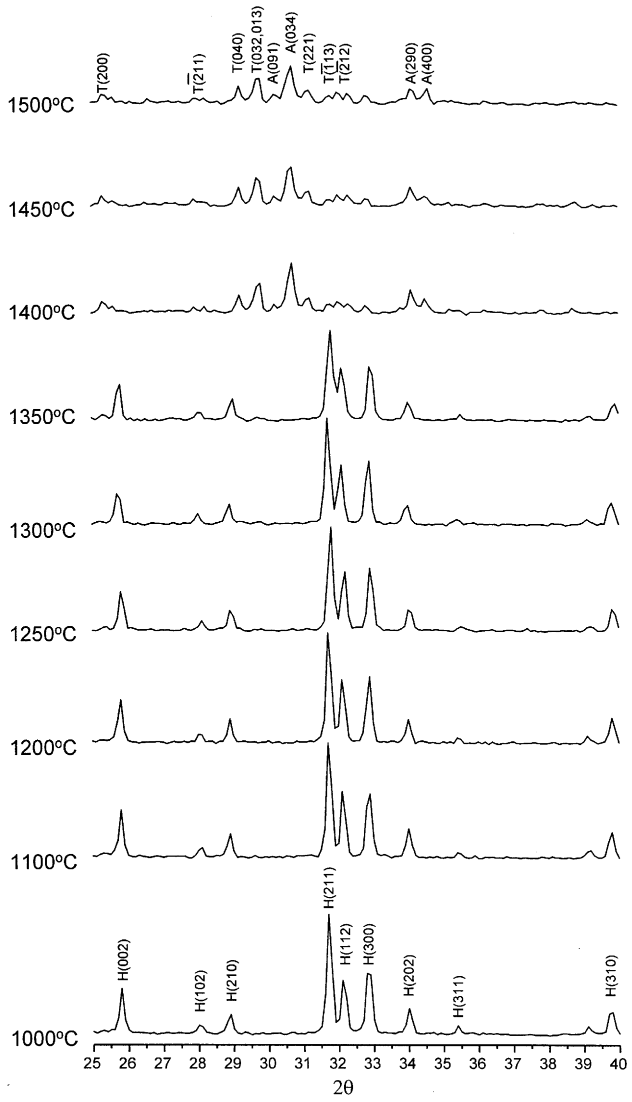

Fig. 1. X-ray diffraction patterns of HAP after heating to different temperatures (H : HAP, T : TTCP, A : αTCP).

2. Materials and methods

HAP powders were purchased from E. Merck (Darmstadt, Germany). It was placed in covered platinum crucibles and heated to different temperatures (1000–1500°C) at a heating rate of 10°C/min in an SiC heated furnace, and then maintained for 1 h. After heating, the samples were quenched to room temperature. In addition, the reconstruction of HAP was also studied in this study. The HAP powders were heated to 1500°C and cooled to different temperatures at a cooling rate of 10°C/min. The samples then were maintained for 1 h and quenched to room temperature.

The crystalline phases of specimens were determined by a Rigaku (Denki Co. Ltd., Tokyo, Japan) X-ray powder diffractometer with Cu K_α radiation and Ni filter. The scanning range of the samples was from 10 to 60° with a scanning speed of 4°/min. The infrared spectra were recorded using KBr pellets (1 mg sample per 300 mg KBr) on a Jasco FTIR (JASCO FTIR 410, Tokyo, Japan) grating instrument with slow scan and 0.1 slit width. The wavelength of the FTIR used in the experiment was in the range of 4000–400 cm^{-1} to evaluate the functional group of the specimens. TA/SDT2960 (TA instruments, Inc. 109 Lukens Drive New Castle, DE 19720) was used to study the thermal behavior of the specimens. The scanning temperature for the thermal analysis of the specimens was from room temperature up to 1500°C with a heating rate of 10°C/min and air flow rate of 90 ml/min. The total weight of the specimen for each thermal analysis was 40 mg and Al_2O_3 was as reference powder.

3. Results

3.1. Crystal structure analysis

Fig. 1 summarized the XRD patterns of HAP powder heated at the temperature of 1000–1500°C. There was no significant difference in XRD patterns from 1000–1350°C, it showed a stoichiometric hydroxyapatite characterized pattern (XRD JCPDS data file No. 9-432). At 1400°C, the HAP was decomposed into TTCP and αTCP. There was no crystalline phase to be traced but TTCP and αTCP in the temperature of 1400–1500°C. Fig. 2 showed the results of XRD analysis of HAP powder cooling down from 1500°C with a cooling rate of 10°C/min. There was no phase transformation until a temperature of 1350°C. Characteristic peaks of the reconstruction of HAP such as (2 1 1) were burgeoned out on the XRD pattern at 1300°C, the intensity

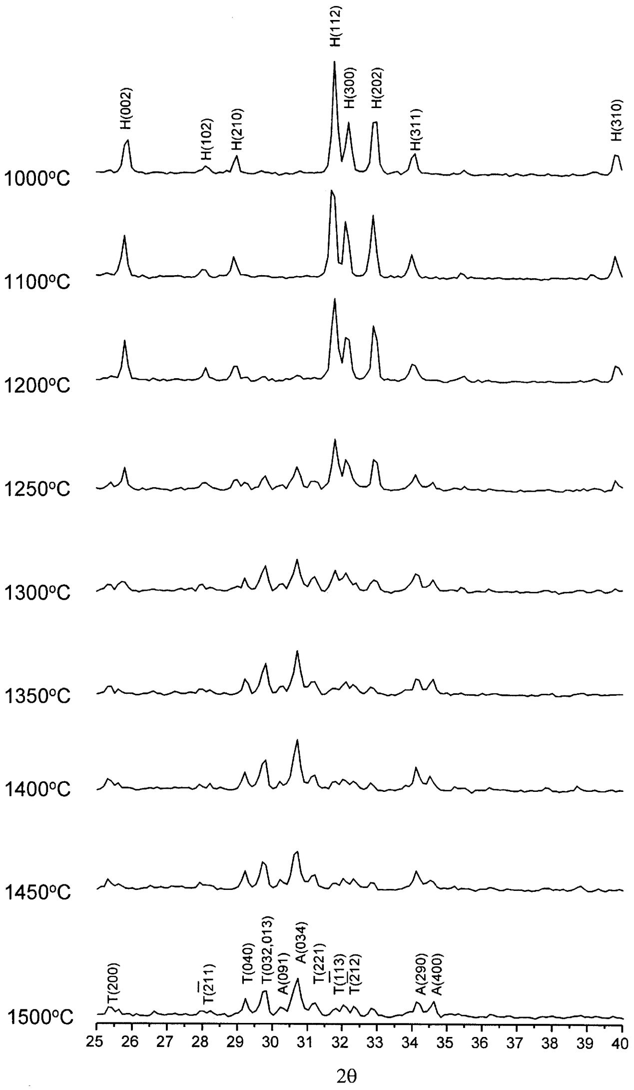

Fig. 2. X-ray diffraction patterns of HAP after cooling from 1500°C to the temperatures indicated (H : HAP, T : TTCP, A : αTCP).

gradually increasing with the temperature decrease. When the cooling down to 1100°C, TTCP and αTCP completely convert into HAP structure, where all the characterized peaks of TTCP and αTCP disappear from the XRD pattern.

3.2. FTIR spectrum analysis

FTIR patterns of HAP heated at different temperatures are depicted in Fig. 3. At 1000°C, it shows a typical FTIR spectrum of HAP. As the heating temperature increases, the librational and stretching band of OH^- at 635 and 3572 cm^{-1} gradually decrease in their intensity and the bands at 945 and 1025 cm^{-1} corresponding to oxyhydroxyapatite functional group appear around 1200°C. When the temperature is over 1300°C, the librational OH^- bands disappear. The stretching band of OH^- was still observed even at the temperature of 1350°C. A broad band from 1200 to 950 cm^{-1} was formed when the temperature was increased up to 1400°C, which corresponded to TTCP and αTCP. It was unchanged on increasing the temperature from 1400 to 1500°C.

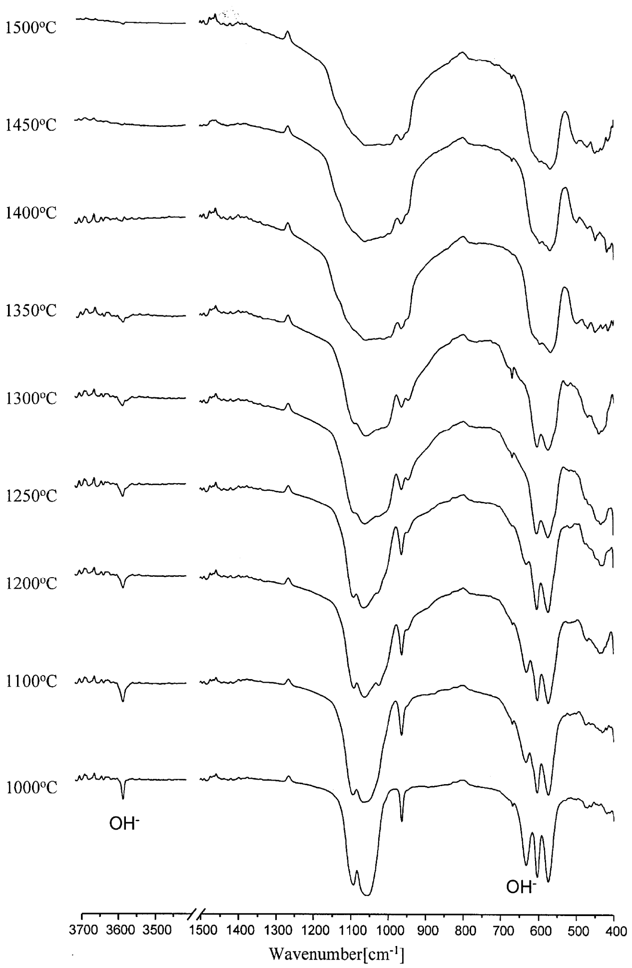

Fig. 3. FTIR spectra of HAP heated at different temperatures.

Fig. 4 shows FTIR spectra of HAP powder at different temperatures, where HAP was cooled down from 1500°C with a cooling rate of 10°C/min. There was no significant change in the FTIR spectrum while the temperature cooling down from 1500–1350°C. When the temperature down to 1300°C, the broad band in the region of 1200–950 cm^{-1} for TTCP and αTCP would gradually narrow down. The stretching band of OH^- at 3572 cm^{-1} could be traced by FTIR at 1250°C, and the intensity increased with the decrease of temperature. The librational band of OH^- at 635 cm^{-1} appeared at the temperature of 1200°C and the intensity would increase with the decrease of temperature.

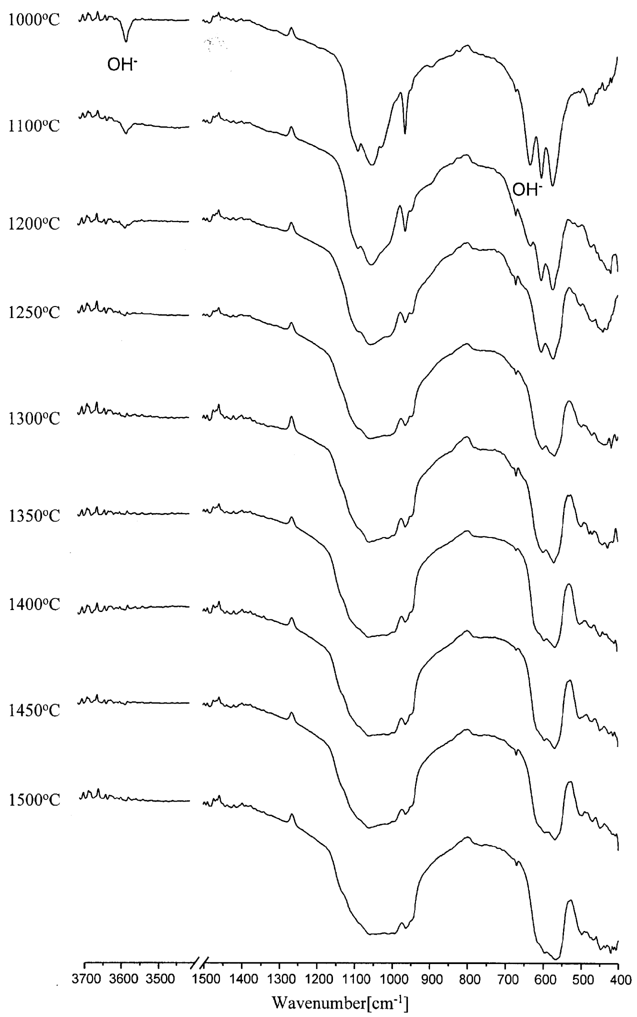

Fig. 4. FTIR spectra of HAP cooled from 1500°C to different temperatures.

3.3. Thermogravimetric analysis

Fig. 5 shows the thermogravimetric curve of HAP powder heated from room temperature to 1500°C and then cooled to room temperature. When the temperature is in the range of 100–400°C, HAP powder quickly loses its weight. There is no apparent change in weight in the temperature range of 400–800°C. The weight of HAP then slowly decreases with increasing temperature upto 800°C. An inflection can be observed at 1360°C and a fast weight loss occurrs thereafter. On increasing the temperature up to 1400°C, the weight of HAP slightly increases as the temperature rises. In the cooling curve, a small weight loss is recorded when the temperature cools down from 1500 to 1290°C. The weight then quickly increases at the temperature of 1290–1240°C. When the temperature cools down to 1240°C, the weight gradually increases with a moderate rate. The weight is more or less constant once the temperature is below 900°C.

4. Discussion

It has been reported that the structure of HAP heated at high temperature would be modified by many factors, including the synthesis methods and conditions, amount and type of impurities present, atmosphere of heating, additives, and other factors such as sample size, particle size, and heating rate of the sample [2,3,14]. As known, hydroxyapatite has two types of water in its structure—adsorbed and lattice water [15]. Adsorbed water—characterized reversibility, thermal instability from 25 to 200°C, and weight loss without any effect on lattice parameters. Lattice water is irreversibly lost at the temperature of 200–400°C, which causes a contraction in the a-lattice dimension during heating. At higher temperature, the hydroxyapatite gradually dehydrates, which lead to the release of OH^- ions and then transforms to OHAP. OHAP has a large number of vacancies in its structure, a bivalent oxygen ion and a vacancy substitute for two monovalent OH^- ions of HAP, which can be presented by a formula: $Ca_{10}(PO_4)_6(OH)_{2-2x}O_x\square_x$, where $\square$ stands for a vacancy. In the limit, when $x = 1$, oxyapatite ($Ca_{10}(PO_4)_6O$, OAP) is formed [14,16,17]. The HAP dehydration does not occur instantly but over a wide temperature range, which has been reported to mainly depend on the partial H_2O pressure during heating. If performed under vacuum, HAP loses its OH^- at a lower temperature, about 850°C. If HAP is heated in a H_2O stream, the structure of HAP is then preserved up to 1100°C [13,14]. It is generally denied for the existence of OAP, and moreover it is generally thought that the complete dehydration of HAP might cause lattice destruction, giving rise to a mixture of tricalcium phosphate and tetracalcium phosphate. Trombe and Montel [17] demonstrated the formation and existence of OAP by very rigidly controlled condition. It is particularly important to eliminate all traces of water when OAP is to be prepared. The range of temperature for OAP stability is very narrow around 800–1050°C.

In this study, it is difficult to observe HAP transformation to OHAP by XRD because most of the characteristic peaks of the two compounds overlap one another. The presence of OHAP in HAP can, however, be detected by FTIR. HAP has two types of OH band—OH stretching and librational absorption bands at 3572 and 630 cm^{-1}, respectively. As shown in Fig. 3, the intensity of the peak at 630 cm^{-1}, which corresponds to the OH^- librational mode diminishes with a temperature increase until 1300°C where it is no longer distinguishable from the background. The OH^- stretching mode at 3572 cm^{-1} also decreased with the increase of temperature. The OH^- stretching band seems more stabilized than the OH^- librational mode at higher temperatures. The OH^- stretching band could be detected in the FTIR curve even at a temperature up to 1350°C. The OH^- librational 630 cm^{-1} mode is missing in the biological

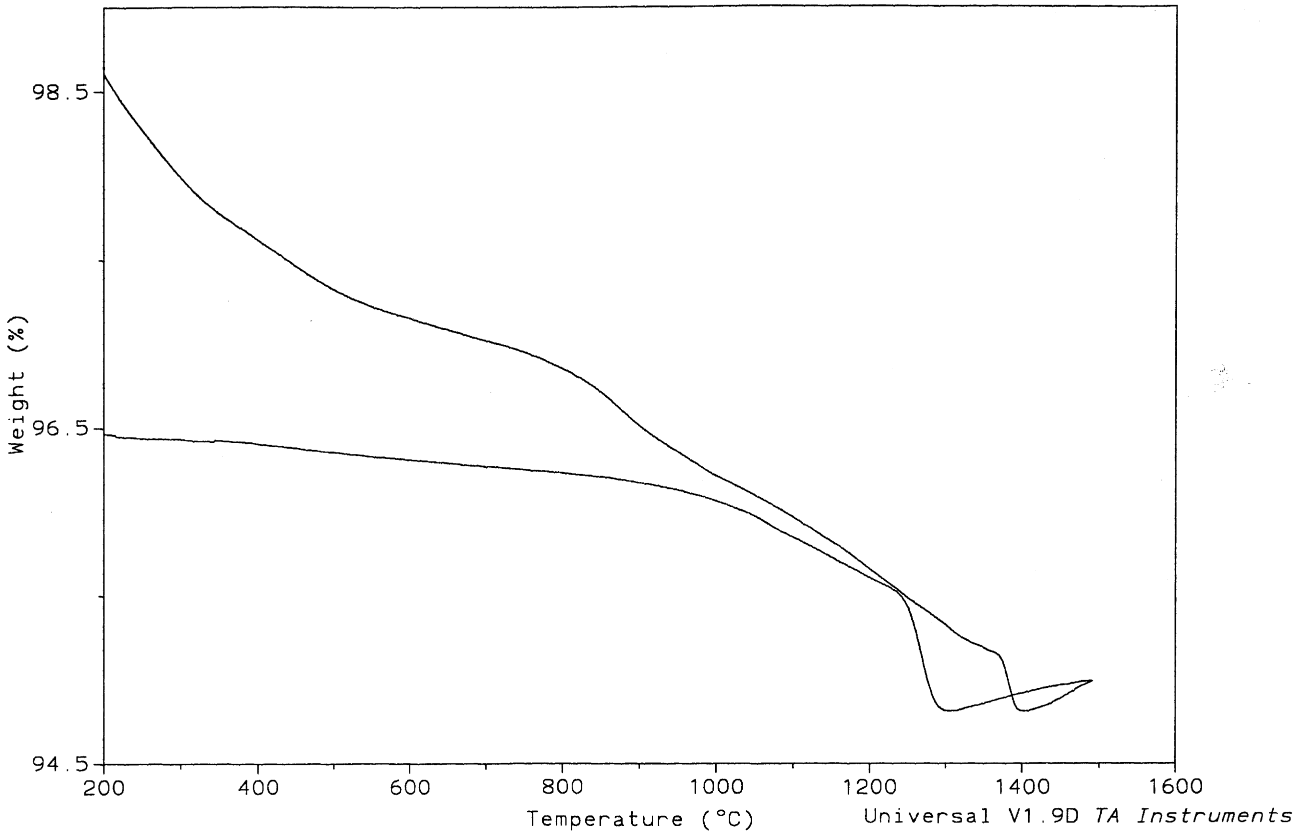

Fig. 5. TGA results of HAP heated from 200 to 1500°C and then cooled to 200°C.

apatite pattern, but present in the synthetic HAP pattern, although OH is present in both materials. The space group of biological HAP (non-stoichiometric hydroxyapatite) has been determined by X-ray diffraction methods to be $P6_3/m$. However, theoretical considerations suggest the space group of synthetic HAP (stoichiometric hydroxyapatite) should be $P6_3$. It has been proposed that the hydroxyl ions in HAP are displaced by some 0.3 Å along the hexagonal screw axis, destroying the mirror plane and consequently altering the space group from $P6_3/m$ to $P6_3$. The absence of the OH^- librational 630 cm^{-1} mode during heating is the result of stoichiometric HAP changing to non-stoichiometric HAP.

Fig. 5 shows the TGA curve of HAP, a continuous curve with a weight loss at the temperature from 800 to 1360°C. When the temperature reaches 1360°C, a significant weight loss appears which extends over the temperature region of 1360–1400°C. According to the equilibrium phase diagram of CaO/P_2O_5, HAP will decompose into TTCP and αTCP at 1350°C [18]. From the XRD results (Fig. 1), the decomposition of HAP to TTCP and αTCP at 1350–1400°C with a significant weight change (approximately 0.75 wt%) attributed to dehydration. But the OH^- stretching mode of HAP still appeared at 1350°C (Fig. 3)—the commencement HAP decomposition. It indicated that the HAP did not dehydrate completely before decomposition. We speculated that some of the OAP might be formed during dehydration and there was a great amount of OHAP remaining in the system even up to the temperature of decomposition. According to the reaction, OAP decomposed into TTCP and αTCP:

$$Ca_{10}(PO_4)_6O \rightarrow 2Ca_3(PO_4)_2 + Ca_4P_2O_9 \tag{1}$$

and does not involve any change in weight.

From the XRD analysis (Fig. 1), only TTCP and αTCP appeared after HAP decomposition. There was no significant difference in XRD patterns at the temperature of 1400–1500°C. Some investigators reported that the calcium phosphates such as $Ca_2P_2O_7$ and CaO, could be observed during HAP decomposition. These reactions were described as follows [19]:

$$2Ca_{10}(PO_4)_6O \rightarrow 2Ca_3(PO_4)_2 + Ca_2P_2O_7 + 3Ca_4P_2O_9 \tag{2}$$

or

$$Ca_{10}(PO_4)_6(OH)_2 \rightarrow 3Ca_3(PO_4)_2 + CaO + H_2O. \tag{3}$$

In the present study, no other crystalline phases could be detected other than TTCP and αTCP at the temperature of 1400–1500°C. According to the phase diagram of CaO/P_2O_5 and the study of the thermal decomposition reaction of HAP, it is impossible that $Ca_2P_2O_7$, CaO and P_2O_5 will appear in the system. CaO and $Ca_2P_2O_7$ could be traced only in non-equilibrium conditions such as a sudden temperature increase or decrease, typical of the thermal spray or plasma spray process.

It is known that TTCP and αTCP could reconstitute into HAP during cooling. The reconstitution temperature of HAP has been reported to be dependent on cooling rate and atmosphere [12,13]. The cooling rate of high-temperature molten HAP particles deposited on a cold metal substrate by the plasma-spraying technique could be as high as 10^8°C/s, which led to a large amount of TTCP and αTCP on the substrate where a small amount of CaO and $Ca_2P_2O_7$ could also be traced. McPherson et al. [20] reheated HAP coatings in air at 600°C that resulted in recrystallization of the glass phase and formation of HAP with water vapor. de Groot et al. [21] thought that TTCP and αTCP are more stable than HAP in dry atmosphere, which is difficult to convert into HAP in vacuum. Chen et al. [12] studied the effect of increasing the crystallinity of HAP coatings by post-heat treatment and found that TTCP and αTCP could convert to HAP by reactions of hydration in a humid atmosphere. They suggested that TTCP and αTCP could covert into HAP by the reactions of hydration:

$$3Ca_4P_2O_9 + 3H_2O \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 2Ca(OH)_2 \tag{4}$$

and

$$10Ca_3(PO_4)_2 + 6H_2O \rightarrow 3Ca_{10}(PO_4)_6(OH)_2 + 2H_3PO_4. \tag{5}$$

As Eqs. (4) and (5), TTCP and αTCP would reconstruct into HAP by a series of hydration reactions, which would catch OH^- ions back into the HAP lattice and lead to weight increase. In our study, there was no significant weight change to be recorded in TGA and no OH^- bands (stretching or librational mode) to be traced in FTIR analysis during cooling from 1500–1300°C (Fig. 4). The HAP peaks appeared in the XRD pattern once the temperature reached 1300°C, Fig. 2. It seemed that the TTCP and αTCP were directly converted into OAP as the following reaction with no weight change involved

$$2Ca_3(PO_4)_2 + Ca_4P_2O_9 \rightarrow Ca_{10}(PO_4)_6O. \tag{6}$$

Water vapor or OH^- ions were not involved at the beginning of the reconstruction reaction of HAP. This transformation occurs without a phase change. OAP seems existent in this system during cooling. Trombe et al. [17] reported that the OAP is a highly unstable structure, which does not exist at temperatures lower than 800°C (under 10^{-4}–10^{-6} Torr). They found that a small weight increase occurs during cooling of OAP from 1000°C to room temperature, which represents partial rehydration upon cooling to 800°C. In the study, the stability range of OAP was very narrow, approximately 1350–1300°C. As the temperature decreased, OAP would be rehydrated into OHAP. A significant weight increase was recorded by TGA in the temperature range of 1290–1240°C. In the temperature range of 1290–1240°C, the characterized peaks of HAP could be observed obviously and the intensity of the peaks increased as the temperature decreased. FTIR results (Fig. 4) showed that only a slight OH^- stretching band (at 3572 cm^{-1}) was present at 1250°C. While at 1200°C, the intensity of OH^- bands could be observed more clearly. It is postulated that TTCP and αTCP can gradually convert into OAP, and then form OHAP with an uptake of OH^- ions at 1290–1240°C. TTCP and αTCP would completely disappear at 1100°C as OH^- bands of HAP are detected in the FTIR spectrum. As the temperature further decreases, OHAP gradually rehydrates and reconstitutes into HAP.

5. Conclusions

In this study, HAP was heated from room temperature to 1500°C in an air atmosphere. It would gradually release OH^- ions and transform to OHAP around 1000–1360°C. Above 1360°C, the OHAP would decompose into TTCP and αTCP. The OH^- stretching bands of HAP could be detected at 1350°C, the commencement of HAP decomposition. It indicated that the HAP did not dehydrate completely before being decomposed. We speculated that some OAP might be formed during dehydration and there was a great amount of OHAP still left in the system even up to decomposition temperature. From 1400 to 1500°C, there were no significant difference in XRD patterns, only TTCP and αTCP could be observed. We thought that the thermal decomposition of HAP was through the following phase transformations: HAP → HAP + OHAP (transform from part of HAP) → HAP + OHAP + OAP (transform from part of OHAP) → TTCP + αTCP.

When HAP was heated to 1500°C and then cooled at a rate of 10°C/min, a part of TTCP and αTCP reconstructed into OAP at 1350°C because no OH^- stretching bands were traced and no weight increase was recorded. We could detect TTCP and αTCP in the XRD pattern at 1100°C. It reflected that a part of TTCP and αTCP initially converted into OAP around 1350°C and then exist in the temperature range of 1350–1300°C during cooling. When cooling to 1290°C, a part of TTCP and αTCP convert into OHAP by rehydration. At 1100°C, the rest of TTCP and αTCP completely reconstitute the HAP phase. OHAP then gradually rehydrates and reconstitutes HAP as the temperature decrease. We believe that the phase transformation of HAP down from 1500°C should be through the following steps: [TTCP/αTCP] → [TTCP/αTCP] + OAP (transform from part of [TTCP/αTCP], 1350–1300°C) → [TTCP/αTCP] + OHAP (transform from OAP and part of [TTCP/αTCP],1290–1240°C) → [TTCP/αTCP] + OHAP + HAP (convert from [TTCP/αTCP] and OHAP, 1240–1100°C) → HAP (below 1100°C).

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