

Thermal reconstruction behavior of the quenched hydroxyapatite powder during reheating in air

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Abstract

Commercial hydroxyapatite (HAP) powders were quenched from 1500°C to room temperature and reheated at different temperatures by a program controlled SiC-heated furnace to investigate the reconstruction behavior of quenched HAP powder in air. X-ray diffractometer (XRD) and Fourier-transformed infrared (FTIR) analysis were used to examine changes in crystalline phases and functional groups of quenched HAP powders at different temperatures. Weight changes of the quenched powders during heating were recorded by thermogravimetric analysis (TGA). The XRD results showed that the quenched HAP powder was composed of two crystalline phases of tetracalcium phosphate (TTCP) and α -tricalcium phosphate (α TCP). There was no other calcium phosphate phases to be traced. When quenched HAP powders were reheated, TTCP gradually reconstructed into HAP around 500°C and yield Ca(OH)_2 . α TCP did not convert to HAP at a temperature lower than 700°C but the transformation of α TCP to β TCP was observed during heating. α TCP reacted with Ca(OH)_2 , the product of reconstruction of TTCP, to form more HAP at temperatures over 700°C. In addition, the CO_3^{2-} ion was incorporated into the lattice of the reconstructed HAP around 500°C. The intensity of CO_3^{2-} ion in FTIR decreased as the temperature increased and totally disappeared around 900°C. Above 1000°C, reconstructed HAP lost OH ions and transformed into oxyhydroapatite. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Hydroxyapatite; Plasma-spray; Decomposition; Reconstruction

1. Introduction

Hydroxyapatite [HAP , $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] is the main mineral constituent of human bone. It has been developed and made available for experimental or clinical application because of its excellent biocompatibility, faster bone regeneration, and direct bonding to regenerated bone without intermediate connective tissue [1–3]. In recent years, as a means of improving the biocompatibility of metal materials in vivo, coating HAP onto metal implant surfaces using a plasma-spraying technique has been widely investigated [4–6]. Such coatings should inject HAP powder into a plasma, which are then heated to very high temperatures (usually over 10000°C) and propelled to cold metal substrates (usually below 150°C) at high speeds to form coatings on the surfaces of metals [6,7]. These extreme

heat-treatment conditions then lead to the formation of non-crystalline or metastable crystalline products such as oxyhydroxyapatite (OHAP, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{2-x}\text{O}_x$ □ $_x$), α -tricalcium phosphate (α TCP, $\text{Ca}_3(\text{PO}_4)_2$), tetracalcium phosphate (TTCP, $\text{Ca}_4\text{P}_2\text{O}_9$), calcium oxide (CaO) and amorphous apatite in HAP coatings [8–10]. It has been reported that OHAP, TTCP and α TCP undergo dissolution and degradation more rapidly than HAP in an aqueous environment [11], which decreases chemical stability and enhances degradation of the coatings in vivo.

Recently, various plasma-spraying conditions and post-heat treatments have been studied for increasing the crystallinity of HAP coatings [8,12,13]. However, these coatings contain numerous amorphous phases and complicated metastable phases, which make elucidation of the reconstruction behavior of HAP coatings during post-heat treatment difficult. In the studies, commercial HAP powders were heated to 1500°C and quenched to room temperature. The quenched powders were reheated to different temperatures to investigate the reconstruction behavior of HAP

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during post-heat treatment. XRD analysis was used to examine the phase transformation of HAP quenched pow-

ders at different temperatures. The functional group changes of specimens at different temperatures were ob-

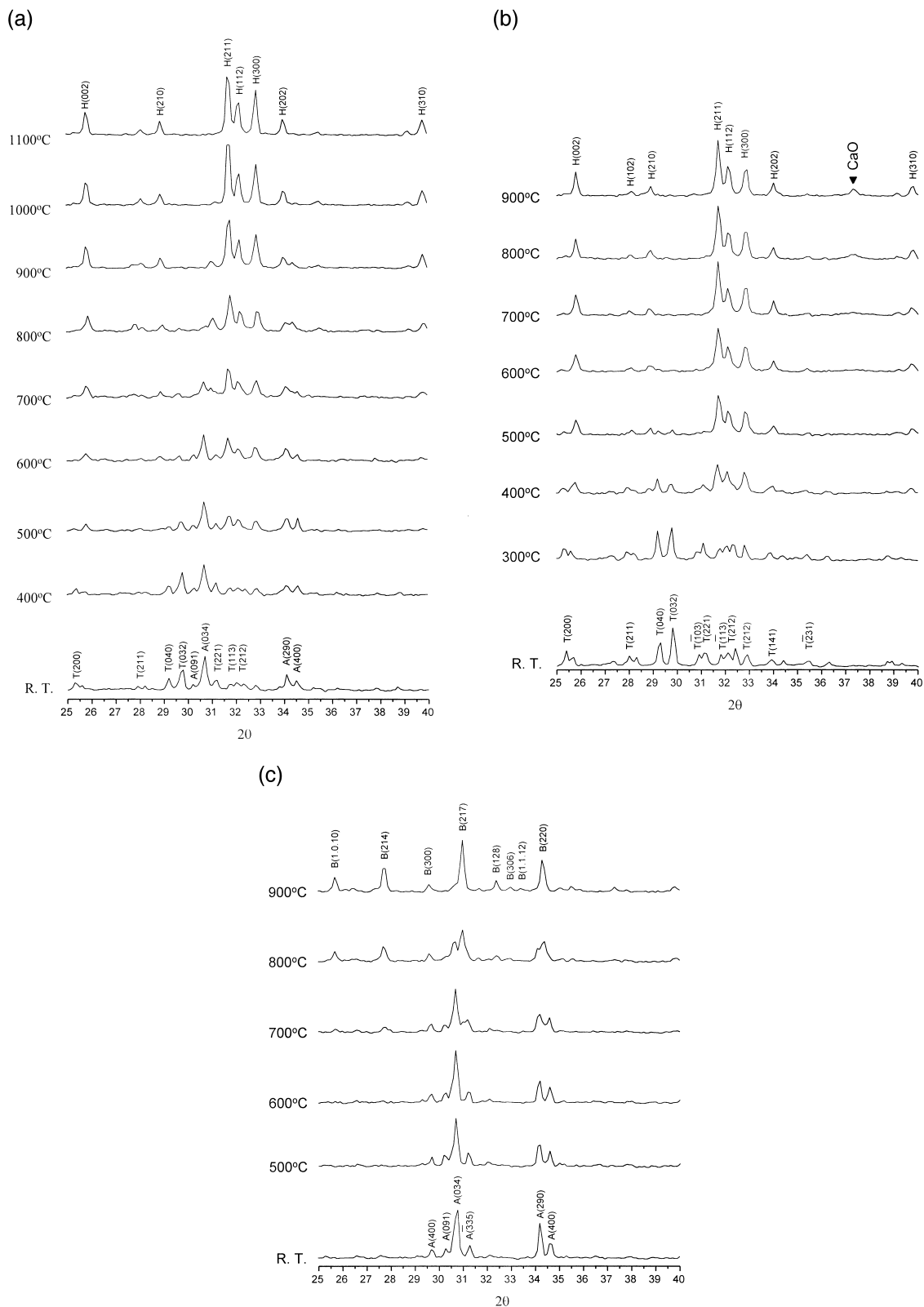


Fig. 1. (a) X-ray diffraction patterns of quenched HAP powder reheated at different temperatures (H: HAP, T: TTCP, A: α TCP) (b) X-ray diffraction patterns of TTCP heated at different temperatures (H: HAP, T: TTCP) (c) X-ray diffraction patterns of α TCP heated at different temperatures (A: α TCP, B: β TCP).

served by FTIR spectroscopy, and the weight changes were recorded by thermogravimetric analysis (TGA) during heating.

2. Materials and methods

HAP powder was purchased from E. Merck, 64271 Darmstadt, Germany. It was placed in covered platinum crucibles and heated to 1500°C at the rate of 10°C/min in a SiC-heated furnace, and then maintained for 1 h. The HAP powder was then quenched to room temperature. To investigate the reconstruction behavior of quenched HAP powder, we reheated the quenched powder at different temperatures (400–1100°C for 1 h) and then quenched the powder to room temperature again.

TTCP and α TCP were heated at different temperatures to investigate their thermal behavior individually during heating. TTCP was synthesized by heating an equimolar mixture of commercially obtained CaCO_3 and CaHPO_4 (May and Baker, Dagenham, UK; Sigma, USA) at 1500°C for 1 h in a furnace and then quenching the mixture to room temperature. α TCP was prepared by mixing HAP and CaHPO_4 with a molar ratio of 2:1. The mixture was heated in air for 1 h at 1400°C and then quenched to room temperature.

The crystalline phases of specimens were determined by Rigaku X-ray powder diffractometry with $\text{CuK}\alpha$ 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/300-mg KBr) on a Jasco FTIR grating instrument with slow scan and normal-slit width. The weight change of the specimens during heating and cooling were recorded by TGA in the heating range of 20–1500°C with a heating rate of 10°C/min under a flowing air atmosphere.

3. Results

3.1. Crystal structure analysis

Fig. 1a summarizes the XRD patterns of quenched HAP powder reheated at different temperatures. The quenched HAP powder showed a TTCP/ α TCP biphasic crystalline structure (Fig. 1a — R.T.). There were no other calcium phosphate crystalline phases to be observed while the HAP powder was quenched from 1500°C and reheated to 400°C. When the reheating temperature was over 500°C, the peaks of HAP gradually burgeoned out and the characteristic peaks of TTCP gradually decreased in intensity. But the peaks for α TCP did not show any changes in intensity. At 700°C, a part of α TCP was transformed into β TCP which

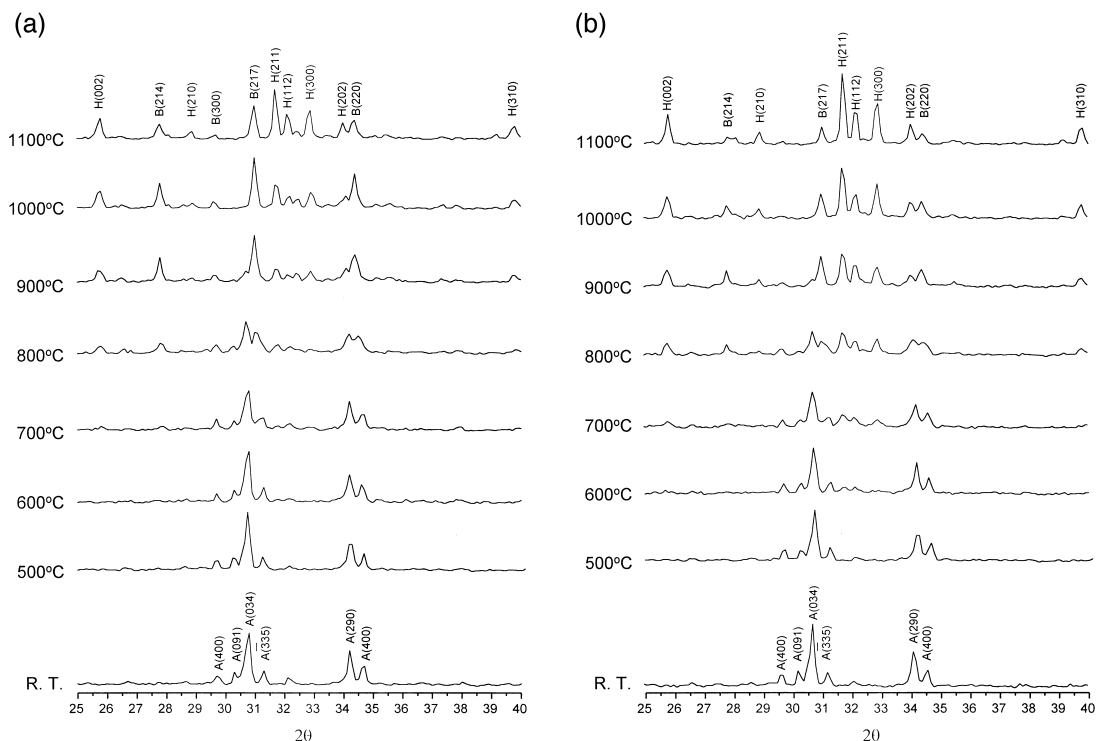
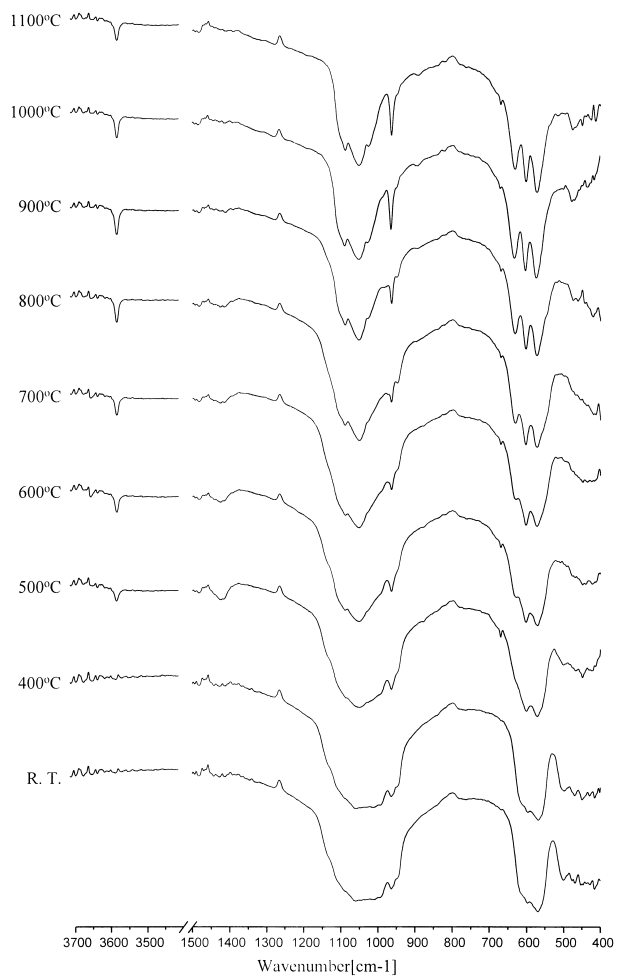
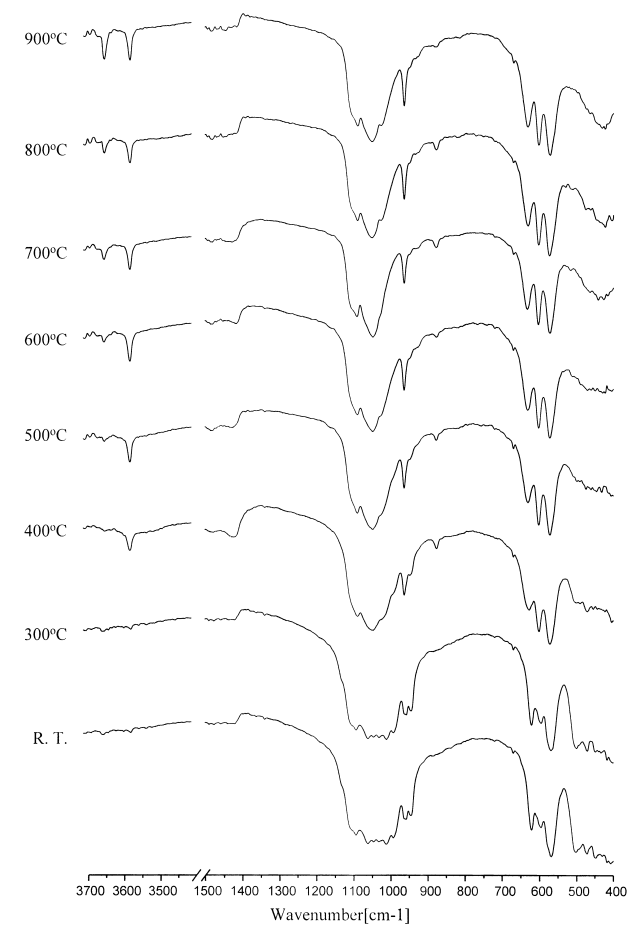


Fig. 2. (a) X-ray diffraction patterns of the mixture of α TCP and CaO with a molar ratio of 3:1 heated at different temperatures (A: α TCP, B: β TCP, H: HAP) (b) X-ray diffraction patterns of the mixture of α TCP and $\text{Ca}(\text{OH})_2$ with a molar ratio of 3:1 heated at different temperatures (A: α TCP, B: β TCP, H: HAP).

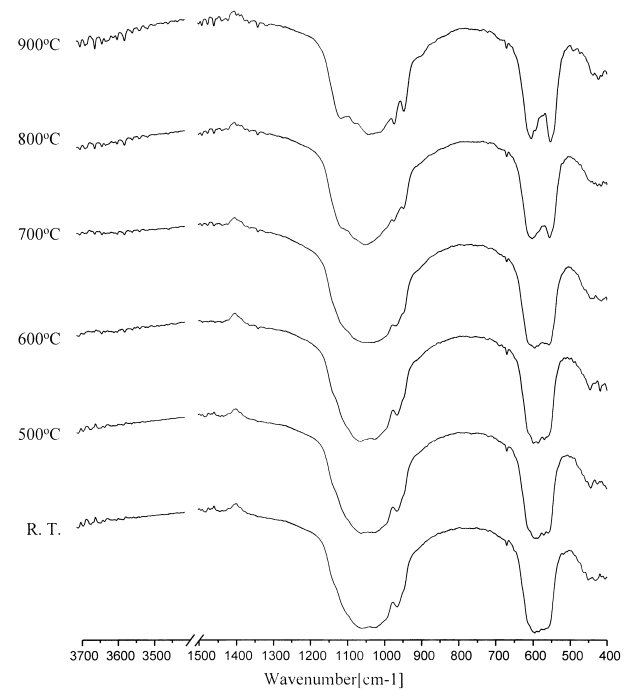
(a)



(b)



(c)



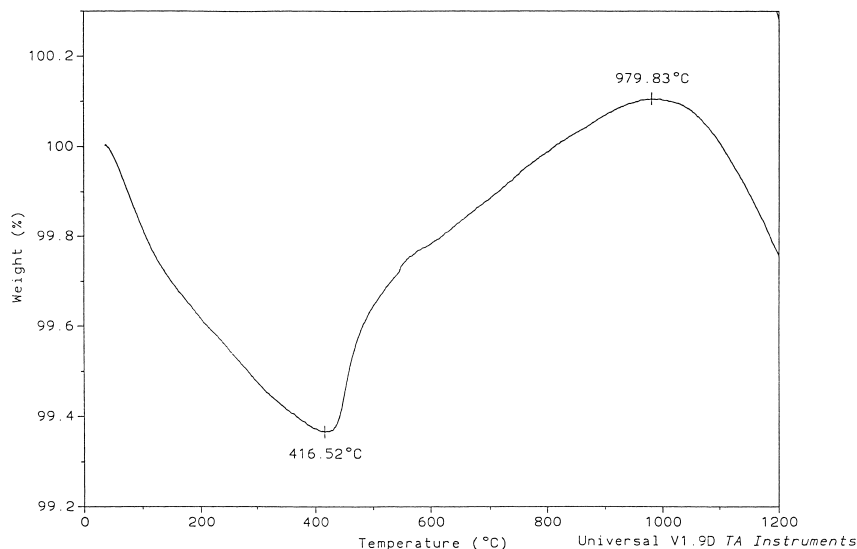


Fig. 4. TGA result of quenched HAP powder heated from room temperature to 1200°C.

caused the peaks of α TCP to decrease slightly. TTCP-characterized peaks reheated to a temperature above 900°C completely disappeared because all the TTCP was converted to HAP. This same scenario occurred on α TCP to β TCP transformation. α TCP gradually turned into β TCP with reheated temperature increases, and the peaks of α TCP totally disappeared when the temperature reached 900°C. At temperatures up to 1100°C, only HAP was observed in the XRD pattern.

To further understand the phase transformation of both TTCP and α TCP during heating, TTCP and α TCP were separately prepared and heated to different temperatures. As seen in Fig. 1b, TTCP were gradually converted to HAP at temperatures over 400°C. Above 700°C, the main characteristic peak of CaO burgeoned out on the XRD pattern, and its intensity increased as the reheating temperature increased. Fig. 1c shows the XRD results of α TCP heated at different temperatures. At 700°C, a part of α TCP would transform to β TCP. When the temperature rose to 900°C, all the α TCP were converted to β TCP. There were no HAP-characterized peaks observed during heating.

Fig. 2a shows the XRD patterns of the mixture of α TCP and CaO with a molar ratio of 3:1, heated at different temperatures in an air atmosphere. The phase transformation of α TCP to β TCP occurred around 700°C. The characterized peaks of HAP appeared at a temperature of 900°C and the intensity increased with the temperature increase. XRD results of the mixture of α TCP and $\text{Ca}(\text{OH})_2$ with a molar ratio of 3:1 heated from room temperature to 1100°C are shown in Fig. 2b. α TCP started to transform into β TCP at 700°C. At that time, HAP-characterized

peaks on the XRD pattern were seen and the peaks increased in intensity as reheating temperatures increased.

3.2. FTIR spectrum analysis

The FTIR spectra of quenched HAP powders reheated at different temperatures are summarized in Fig. 3a. There was no significant difference in the FTIR spectrum when the reheated temperature increased from room temperature to 400°C. The spectrum was in agreement with that of TTCP and α TCP. As the heating temperature increased, broad bands for TTCP and α TCP in the region of 1200 to 950 cm^{-1} would gradually narrow down. An OH^- stretching band at 3572 cm^{-1} and a small OH^- librational band at 635 cm^{-1} appeared at 500°C, where their intensity increased with the temperature increase. Above 1000°C, the intensity of the two OH^- absorption bands would gradually decrease. Additionally, the intensity of the structural CO_3^{2-} bands at 1470–1412 cm^{-1} had a positive tendency when the reheated temperature increased from room temperature to 500°C. Thereafter, the bands gradually decreased as the temperature increased and completely disappeared around 900°C.

Fig. 3b summarizes the FTIR spectrum of TTCP heated at different temperatures. There were no significant differences in FTIR spectra between room temperature and 300°C. At 400°C, PO_4^{3-} bands of HAP appeared at 960, 1075, and 1100 cm^{-1} . OH^- bands of HAP at 3572 and 635 cm^{-1} could also be traced. An absorption band at 3640 cm^{-1} corresponding to H_2O was observed at 500°C, where the intensity increased with the reheated tempera-

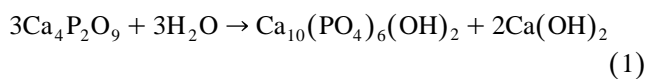
ture. When α TCP was reheated at different temperatures (as seen in Fig. 3c), the bands for TCP gradually burgeoned out at 1118, 973, 945, 603, 586, 649 and 540 cm^{-1} around 700°C, where their intensity also increased as the temperature increased. OH^- bands were not detected in any one of FTIR spectrum.

3.3. Thermogravimetric analysis

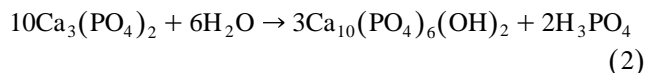
Fig. 4 shows the thermogravimetric curve of HAP quenched powder heated from room temperature to 1200°C. At temperatures in the range from room temperature to 415°C, the HAP quenched powder quickly lost weight. A turning point was observed at 415°C and then a fast weight increase occurred. At temperatures up to 600°C, the weight of HAP quenched powder increased gradually at a moderate rate. Above 980°C, the sample weight did not increase but rather decreased as the temperature increased.

4. Discussion

During the last decade, plasma-sprayed HAP coatings have become increasingly popular in the field of prosthetic replacements. To deposit HAP on metal surfaces, HAP powder should be introduced to high temperatures, which would result in partial melting and decomposing to an amorphous or metaphase calcium phosphate. When the high temperature particles were impacted onto cold metal substrates, the cooling rate of coatings were as high as 10^8 °C/s, which led to the formation of a large amount of non-crystalline or metastable crystalline products on HAP coatings. Studies in vitro and in vivo have been reported in which the biodegradation of HAP coatings depend on their crystallinity [13]. For increasing the crystallinity of HAP coatings, the reconstruction behavior of HAP has attracted more and more attention in recent years. Gross et al. [9] heated an amorphous phase of HAP coating in dry and moist atmospheres. The latter gave rise to more extensive crystallization. McPherson et al. [14] found that heat treatment of HAP coatings in air at 600°C resulted in crystallization of the glass phase and a reaction with water vapor forms HAP. Zyman et al. [8] heated HAP coatings at 630°C, the temperature at which the amorphous phase was crystallized and completely crystalline HAP coatings were obtained. Chen et al. [12] studied increasing the crystallinity of HAP coatings by post-heat treatment and found that TTCP and α TCP could convert to HAP by hydrolytic reaction in humid atmospheres. They suggested that TTCP and α TCP be converted to HAP by a series of hydrolytic reactions:



and

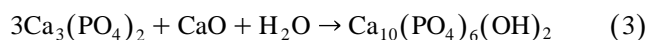


In this study, commercial HAP powders were decomposed to TTCP and α TCP at high temperatures. Some investigators reported that CaO could be observed while HAP decomposed [15,16]. However, only TTCP and α TCP crystalline phases appeared on the XRD pattern and no other calcium phosphate phases could be traced when HAP powder was quenched from 1500°C to room temperature (as seen in Fig. 1a). According to the phase diagram of CaO/ P_2O_5 [17], a liquid phase begins to form at 1570°C and the only solid phase existing above 1700°C is calcium oxide. CaO was not detected in the study because the decomposed temperature of HAP was lower than 1700°C. In thermal spray or plasma spray processes, the temperature to melt HAP powder was over 10000°C which caused CaO to be left in the system while being quenched from such a high temperature.

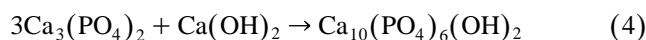
When the HAP powder was quenched from 1500°C, all the HAP would disappear and be decomposed into TTCP and α TCP. They are then supposed to be reconstructed into HAP when the quenched HAP powder is reheated up to 500°C (Fig.1a). It was worth noting that only TTCP-characterized peaks decreased in intensity at a temperature of 500°C, but the characteristic peaks for α TCP did not change. This may reflect that the HAP at that temperature might directly transform from TTCP, where α TCP did not join in this reaction. Ribound [17] and Chow [18] suggested that TTCP is less stable than TCP because the crystal structure of TTCP is similar to HAP which promotes the crystal growth of HAP. To further understand the phase transformations of TTCP during heating, the TTCP were heated at different temperatures individually. As seen in Fig. 1b, TTCP were converted to HAP at the temperature of 400°C. The results of FTIR analysis showed that the OH^- bands were traced at temperatures up to 400°C (Fig. 3a). We believe that the hydrolytic reaction — Eq. (1) — occurred in this system during heating. According to Eq. (1), TTCP would react with the OH^- group to yield HAP and $\text{Ca}(\text{OH})_2$. It was difficult to trace the characteristic peaks of $\text{Ca}(\text{OH})_2$ in XRD patterns because most of the peaks were overlapped with those of HAP. However, the main characteristic peaks of CaO could be detected on the XRD pattern at temperatures above 700°C (Fig. 2a), accompanied by the appearance of H_2O bands as seen in FTIR spectra (Fig. 3b). We proposed that $\text{Ca}(\text{OH})_2$ should exist in this system when TTCP was converted to HAP and CaO came from the dehydration of $\text{Ca}(\text{OH})_2$ during heating.

It is interesting that the characterized peaks for CaO or $\text{Ca}(\text{OH})_2$ did not show up in XRD patterns when quenched HAP powder (TTCP/ α TCP) was reheated. According to Eqs. (1) and (2), TTCP and TCP could be converted to

HAP individually by hydrolytic reaction. However, only the transformation of α TCP to β TCP was observed when we heated α TCP from 500°C to 900°C (as seen in Fig. 1c). There were no HAP characteristic peaks observed in XRD patterns or OH⁻ bands traced in the FTIR spectrum (Fig. 3c). These results reflected that α TCP did not convert to HAP by heat-treatment in air atmosphere and no hydrolytic reaction occurred in the system. We suggested that α TCP could not be converted to HAP in a quenched HAP powder (TTCP/ α TCP) as in the study. But α TCP might react with CaO or Ca(OH)₂ — the products of TTCP converted to HAP — and then turn into HAP. Chen et al. [12] heated a mixture of β TCP and CaO with a molar ratio of 3:1 at 650°C for 1 h in air and found that almost all the TCP were converted to HAP during heating, but most of the CaO in the mixture remained unchanged. Bonel et al. [19] studied an HAP/Ca(OH)₂ system and reported that TCP could react with CaO to lead to the formation of HAP at 1000°C in humid air, according to the reaction:



In this study, we mixed α TCP and CaO with a molar ratio of 3:1 and heated it at different temperatures in air. Results showed that α TCP reacted with CaO and then were converted to HAP around 900°C (Fig. 2a). If we heated the mixture of α TCP and Ca(OH)₂ with a molar ratio of 3:1, the reaction would occur at a lower temperature than 700°C (Fig. 2b). The temperature was in agreement with that of α TCP converted to HAP in the quenched HAP powder system. Therefore, we proposed that the reconstruction of quenched HAP powder (TTCP/ α TCP) during reheating was through the following reactions: Initially, TTCP would transform into HAP and Ca(OH)₂ around 500°C by hydrolytic reaction [as seen in Eq. (1)]. Ca(OH)₂, the product of TTCP hydrolytic reaction, could then react with α TCP to yield more HAP by the equation of



When quenched HAP powder were reconstructed into HAP, the carbonate ions could be traced by FTIR at around 500°C (Fig. 3a). It is well known that carbonate ion is important in biological apatites [20]. Some reports showed that carbonated HAPs are more reactive than pure HAP in biological environments [21,22]. It has been reported that the carbonate content of plasma-sprayed HAP coatings could be obtained by immersing the coatings into physiologically simulated solution or by treating with carbonate atmosphere [23,24]. LeGeros et al. [25] assumed that the carbonate content could decrease the solubility of the HAP coating in a physiological environment. In this study, the appearance of the carbonate ions in the system reflected that the CO₃²⁻ ion could be incorporated into the HAP lattice simply by reheating quenched HAP powder in air.

When heating the whole bone, Biltz et al. [20] found that the structural CO₃²⁻ ion in the whole bone did not change at 450°C. The structural CO₃²⁻ ion would gradually decrease at temperatures over 550°C and completely disappear around 900°C. In this study, the carbonate ion in the reconstructed HAP also gradually decreased with reheated temperatures up to 500°C and totally disappeared around 900°C. TGA curves showed that the weight of the reconstructed HAP decreased as the temperature increased over 980°C (Fig. 4). The bands of OH⁻ ions in the reconstructed HAP also gradually decreased as the temperatures increased (Fig. 3a). The reconstructed HAP would gradually dehydrate and transform into OHAP during reheating, where the CO₃²⁻ ion and OH⁻ ion would gradually be released from the lattice and lead to weight loss at temperatures over 900°C.

5. Conclusions

When quenched HAP powder (TTCP/ α TCP) were reheated, TTCP were reconstructed into HAP and yielded Ca(OH)₂ at around 500°C. α TCP were not converted to HAP but the transformation of α TCP to β TCP was observed during heating. α TCP reacted with Ca(OH)₂, the product of reconstruction of TTCP, to form more HAP at the temperatures over 700°C. In addition, the CO₃²⁻ ion was incorporated into the lattice of the reconstructed HAP at around 500°C. The intensity of the CO₃²⁻ ion in FTIR decreased as the temperature increased and disappeared at around 900°C. Above 1000°C, reconstructed HAP lost OH ions and were transformed into oxyhydroapatite.

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