High temperature characteristics of synthetic hydroxyapatite

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The characteristics of synthetic hydroxyapatite sintered at high temperature were studied by means of X-ray diffraction, infrared and differential thermal analysis, and thermogravimetric analysis. The results show that synthetic HAp with a Ca/P ratio near 1.67 is stable when sintered in dry or wet air below 1200 °C. Even after long times, no tricalcium phosphate (TCP) can be observed. Beyond 1200 °C, HAp loses its OH groups gradually and is transformed to oxyapatite [$Ca_{10}O(PO_4)_6$ or $Ca(PO_4)_6O$. $\square$]. At 1450 °C oxyapatite dissociates into the products α-$Ca_3(PO_4)_2$, $Ca_2P_2O_7$ and $Ca_4P_2O_9$.

1. Introduction

The properties of hydroxyapatite (HAp) at high temperature are important for the design of experiments to obtain the ceramic by sintering. During the past two decades, a lot of research into the characteristics of HAp has been done, but some basic principles of HAp are still not very clear. The main problems are (1) under which conditions HAp is stable; (2) how HAp is decomposed. Many investigators agree that HAp is stable in water vapour atmosphere up to 1200 °C [1], while some reported that HAp may be partly decomposed (in the temperature range 800–1200 °C) into tricalcium phosphate, [2, 3]. In this paper, the stability of HAp, the loss of OH⁻ group and the decomposition of HAp are studied by X-ray diffraction (XRD), differential thermal analysis (DTA), and thermogravimetric analysis (TGA).

2. Specimen Preparation

HAp was prepared in our laboratory by precipitation from aqueous solution according to the following reaction [4].

$$5Ca(NO_3)_2 + 3(NH_4)_3PO_4OH$$

$$\rightarrow Ca_5(OH)(PO_4)_3 + 10NH_4NO_3$$
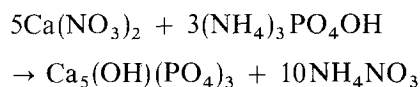
The Ca/P ratio of the green product was 1.67 ± 0.02. It was fired from room temperature through 1550 °C in air in 50 °C temperature intervals. Having been fired, specimens were drawn from the oven quickly to preserve their crystal phase and tested by instruments.

3. Testing Results
3.1. XRD spectra
Fig. 1 shows XRD spectra of HAp fired from room temperature through 1550 °C in air. From this figure we can see that below 700 °C, the peaks are wide and the intensity is weak, which means that the crystallization of the material is poor. Beyond 750 °C the crystallization is getting better with increasing temperature. Above 1200 °C the spectra change a little; the intensity of some peaks varies and some peaks have a little shift at high 2θ angle. At 1450 °C the spectrum indicates that the structure of HAp collapses. New products are $Ca_3(PO_4)_2$, $Ca_2P_2O_7$ and $Ca_4P_2O_9$. Their X-ray diffraction patterns are identified by different symbols.

3.2. Infrared spectra
Fig. 2 depicts fourier transform infrared spectra of HAp. For the spectra below 1200 °C, peaks at 3571 and 630 cm^{-1} are due to OH, 1410 cm^{-1} is CO_3, 875 cm^{-1} is HPO_4, 1640 cm is water and the other is due to PO_4 in HAp. After 1100 °C, the quantity of OH is lost almost completely and the spectrum is different from pure HAp. At 1450 °C the spectrum changes again.

3.3. DTA-TGA test results
Fig. 3 shows the DTA-TGA test results of HAp with temperature increasing from room temperature to 1580 °C and then decreasing to 750 °C. The TGA curve shows that the lost quantity of HAp from 900 to 1480 °C corresponds to every HAp molecule losing one H_2O molecule. The DTA curve is smooth. No absorbing or releasing heat peak is observed below 1400 °C. Between 1420 and 1450 °C there are two absorbing heat peaks which almost overlap each other. With decrease of temperature, a heat releasing peak is present at 1430 °C.

4. Discussion

4.1. Room temperature to 700 °C

It is known that under proper conditions, such as pH value, temperature and time, amorphous calcium phosphate, or ACP, $(Ca_{10}HPO_4(PO_4)_6)$ is transformed into defective hydroxyapatite $Ca_9(HPO_4)$ $(PO_4)_5(HO)$ (DHA) and perfect HAp [5]. The relative quantities of the two products are determined by the Ca/P ratio. If the ratio is near 1.67, the product may be HAp and little DHA. On the other hand, the lower the Ca/P ratio, the more DHA would be found. The two materials have similar crystal structures and belong to the same space group $P6_3/m$ and their XRD spectra are identical. That means whatever the product is, either pure HAp or a mixture of DHA and HAp, the XRD spectra are not different. By using transmission electron microscopy, we see that the synthetic material is needle-like, 50 nm long and 10–20 nm thin, so the XRD peaks in this temperature range are wide and
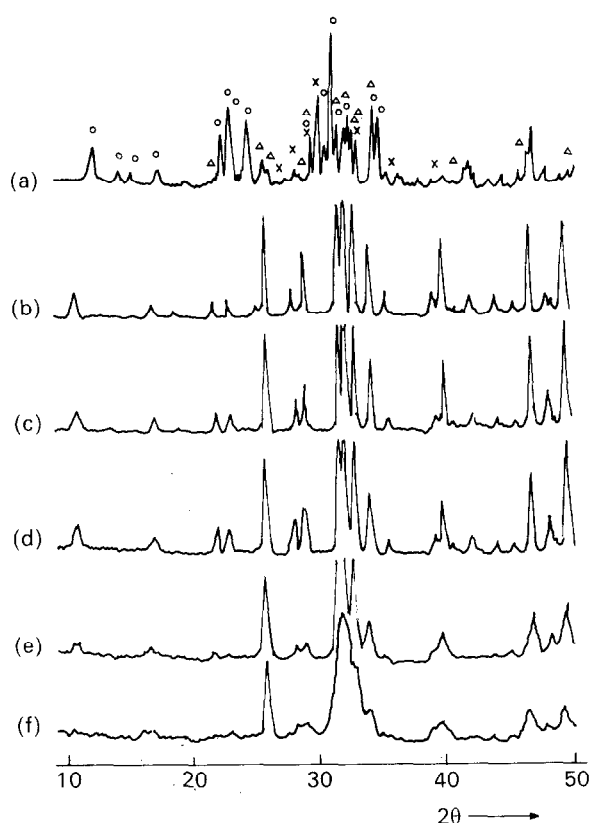
weak. From TR spectra, CO_3^{2-} and HPO_4^{2-} are observed. The quantity of these ions is very small because we used boiled water to reduce CO_2 and the Ca/P ratio of product is near 1.67. DHA is present in small amounts.

4.2. 750–1200 °C

At 750 °C, DHA is decomposed as follows:

$$Ca(HPO_4)(PO_4)_5(OH) \rightarrow 3Ca_3(PO_4)_2 + H_2O$$
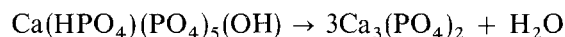
Because the Ca/P ratio of green material is 1.67 ± 0.02 and very close to the theoretical Ca/P ratio 1.67 of HAp, the quantity of DHA must be small and TCP may not be produced. The quantity is below the testing limit of XRD and infrared analysis. After this reaction, all material is HAp, its XRD spectra agree with ASTM standard card. Several researchers reported that [2, 3, 6] TCP was observed beyond 800 °C and HAp decomposes partly. They suggested the following reaction:

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

But the existence of CaO cannot be observed and it cannot be explained why only a part of HAp was decomposed. In this experiment, pure HAp cannot transform to TCP. To check this result, HAp was sintered at 900 °C in air for 24 h and at 1200 °C for 12 h: no decomposition can be observed by XRD and infrared analysis. The DTA test also shows no phase transformation in this process. It is concluded that

Figure 1 XRD spectra of HAp fired from room temperature through 1550 °C in air in steps of 50 °C, each of 30 min. (×) $Ca_2P_2O_7$, (○) a-TCP, (△) $Ca_4P_2O_9$. (a) 1550 °C, (b) 1350 °C, (c) 1100 °C, (d) 850 °C, (e) 700 °C, (f) 100 °C.
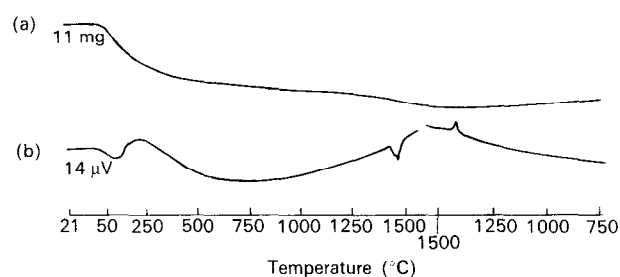

Figure 3 (a) TGA and (b) DTA test results of HAp temperature increasing from room temperature to 1580 °C and then decreasing to 750 °C.
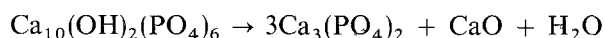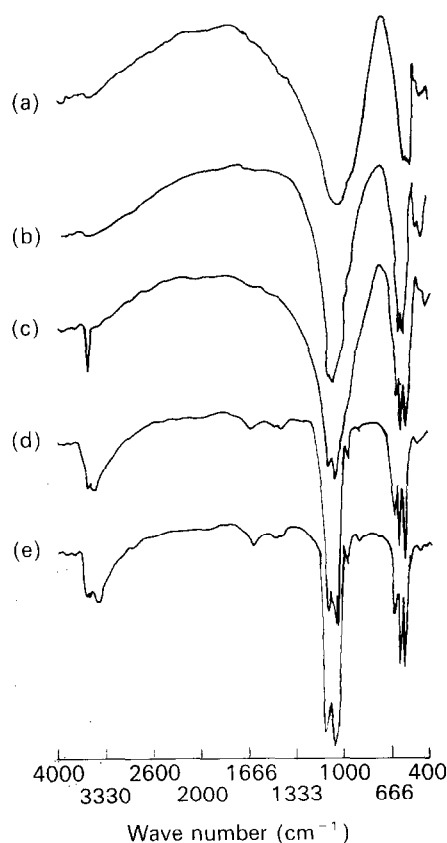

Figure 2 Infrared-spectra of HAp sintered from room temperature to 1550 °C in air for 30 min. (a) 1500 °C, (b) 1350 °C, (c) 1100 °C, (d) 700 °C, (e) RT.

pure HAp is stable when it is sintered in air at 1200 °C and it does not decompose.

4.3. 1200-1400 °C

In this temperature range, HAp loses its OH^- gradually. From infrared spectra it can be seen that HAp almost loses its OH completely at 1300 °C. The TGA test shows that every HAp molecule loses a H_2O. The reaction is [7, 8]:

$$2OH \rightarrow O + H_2O \uparrow$$

$$Ca_{10}(OH)_2(PO_4)_6 \rightarrow Ca_{10}(PO_4)_6O \cdot \square + H_2O$$
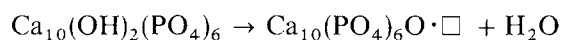
$\square$ is vacancy and $Ca_{10}(PO_4)_6O \cdot \square$ is called oxyapatite. One of the places which were occupied by two OH groups in one HAp unit cell, is now occupied by an oxygen atom and the other is vacant. The parameters of HAp and oxyapatite were given by computer. At 1150 °C the material is pure HAp, $a_0 = b_0 = 0.9421$ nm, $c_0 = 0.6882$ nm, this result agrees well with the result of other investigators. The parameters of oxyapatite are $a = b = 0.9404$ nm, almost the same as that of HAp. Parameter c is not determined. We get two c values, 0.6882 nm and 1.3758 nm. Notice that the latter is just two times larger than the former. We cannot explain this result. To test the stability of oxyapatite, we put it in water for 48 h and heated it in water vapour at 120 °C for 24 h and then dried it at 80 °C. Infrared spectra show that neither water nor OH groups can enter the crystal lattice of oxyapatite. Research into the structure and characteristics of oxyapatite should be pursued.

4.4. 1400-1550 °C

Oxyapatite decomposes at about 1450 °C. This decomposition corresponds to the absorbing heat peak of the DTA curve. The reaction is

$$2Ca_{10}(PO_4)_6O \rightarrow 2Ca_3(PO_4)_2$$
$$+ Ca_2P_2O_7 + 3Ca_4P_2O_9$$
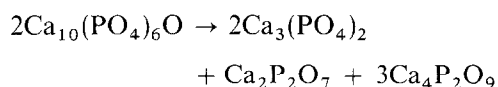
The following table shows the analytical results of XRD spectra sintered at 1550 °C in air for 30 min as calculated by computer.

TABLE I Analytical results of XRD spectra

Products	Stan. lines	Testing lines	RF	ASTM card No.
$Ca_3(PO_4)_2$	18	18	556	90348
$Ca_2P_2O_7$	18	16	406	20647
$Ca_4P_2O_9$	18	17	328	110232

It should be noted that tricalcium phosphate is in the $\bar{\alpha}$ phase at this temperature [9], but the XRD spectrum that we get is a pattern of α-TCP because the test was done after the temperature was decreased from 1550 °C to room temperature. Comparing the two DTA peaks we discover that the absorbing peak is bigger; it is an overlap of two absorbing heat peaks. The first one is due to the decomposition of oxyapatite and the other is due to the decomposition of α-TCP into $\bar{\alpha}$-TCP. We suggest that the first product of decomposition is α-TCP but at this temperature α-TCP is unstable and is transformed into $\bar{\alpha}$-TCP soon. When temperature decreases to 1430 °C, $\bar{\alpha}$-TCP transforms into α-TCP completely and heat is released. The transformation between α-TCP and $\bar{\alpha}$-TCP is reversable.

5. Conclusion

Pure synthetic HAp, with Ca/P ratio is near 1.67, is stable when it is sintered in dry or wet air for long times below 1200 °C. In this process, no TCP can be observed. Beyond 1200 °C HAp loses its OH^- groups gradually and is transformed to oxyapatite $Ca_{10}(PO_4)_6O$. At 1450 °C, oxyapatite is decomposed and the products are $\bar{\alpha}$-TCP, $Ca_2P_2O_7$ and $Ca_4P_2O_9$. $\bar{\alpha}$-TCP turns into α-TCP at lower temperatures.

Acknowledgement

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