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Thermal decomposition of synthesised carbonate hydroxyapatite

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Heat treatments are used when sintering hydroxyapatite to make porous blocks and granules and during plasma spraying of coatings. Calcium : phosphorus ratio is known to affect the thermal decomposition behavior of hydroxyapatite. Hydroxyapatite with carbonate ions substituted for phosphate ions is more similar in composition to bone mineral. While it has been shown that carbonate apatite may be sintered, relatively little is known about its high temperature stability. Various atmospheres have been used in investigations into the thermal stability of hydroxyapatites and carbonate hydroxyapatites, including nitrogen, wet carbon dioxide air, water vapor and wet oxygen, but few of these studies were directly comparable. Previous work has shown that loss of carbonate from CHA at high temperature is time dependent, which suggests that rapid high temperature treatment may prevent carbonate loss during processing. This study investigated the effect of dry carbon dioxide, carbon dioxide containing 3% water, nitrogen and nitrogen containing 3% water on the phase composition of hydroxyapatite containing between 1.0 and 11.5 wt % carbonate rapidly heated to temperatures of between 700 and 1400 °C. Carbonate ion substitution was observed to decrease the temperature at which crystallisation occurred to a minimum of 700 °C for 11.8 wt % carbonate apatite heated in wet atmospheres. Atmosphere was found to appreciably affect the crystallization temperature and phase transformations of carbonate apatite containing 7.8 wt % carbonate. In wet and dry carbon dioxide atmospheres, crystallisation began in this material at 1100 and 900 °C, βTCP was formed at 1500 and 1300 °C respectively. The high temperature decomposition of carbonate hydroxyapatite would appear to depend on the composition of the apatite and the atmosphere in which it is heated.

Introduction

Stoichiometric hydroxyapatite (HA) is structurally similar to biological apatite found in human enamel, dentine and bone. Hydroxyapatite is used in orthopedic applications as filler for bone defects and as a coating for joint prostheses. Heat treatments are used when sintering HA to make porous blocks and granules and during plasma spraying of coatings. The calcium : phosphorus ratio is known to affect the thermal decomposition behavior of HA, and β tricalcium phosphate (βTCP) /HA mixtures are often produced by heating non-stoichiometric HA above 800 °C [1–4]. It has also been observed that water vapor can influence the decomposition temperature of non-stoichiometric HA [5]. Carbonate hydroxyapatite (CHA) is more similar chemically to biological apatites, which can contain up to 8 wt % carbonate ions [6]. Carbonate ions can substitute hydroxyl ions or phosphate ions in HA forming A type or B type CHA, respectively, or both sites may be occupied simultaneously, giving an AB type CHA [7, 8]. These substitutions alter the calcium and phosphorus weight percentages of the apatite by changing the formula weight, the calcium vacancy concentration and the amount of phosphate [9]. It has been reported that HA which has a calcium : phosphorus ratio higher than the stoichiometric value of 1.67 (such as B type CHA) will decompose into HA and calcium oxide in air at temperatures greater than 1000 °C [10, 11]. However previous studies have indicated that a predominantly B type CHA sintered in wet carbon dioxide for 4 h at 1300 °C did not show any evidence of decomposition [12]. Various atmospheres have been used in investiga-

TABLE I Composition and morphology of the precipitates used in this study

Sample	Wt %				Morphology	Dimension (nm)	Ca/P
	Ca	P	H	CO_3			
sHA	39.8	18.5	0.2	0			1.67
H1	37.3	17.5	0.3	1.0	Acicular	~ 500 × 10	1.65
H2	36.4	17.0	0.4	2.5	Spheroidal	~ 15	1.66
H3	36.0	16.3	0.5	7.8	Spheroidal	~ 15	1.71
H4	35.0	14.2	0.8	11.8	Spheroidal	~ 15	1.91

tions into sintering behavior of HA and CHA, including nitrogen, [11] wet carbon dioxide [13], air, [14], carbon dioxide [5, 11, 12] water vapor [5] and wet oxygen, [15], though differences were noted in final density and decomposition temperature, these studies were not directly comparable due to differences in starting material and sintering regime. Previous work has shown that loss of carbonate from CHA at high temperature is time dependent [12], which indicates that rapid high temperature treatment may prevent carbonate loss during processing. This study investigates the effect of dry carbon dioxide, carbon dioxide and 3% water, nitrogen and nitrogen and 3% water on the phase composition of hydroxyapatite containing between 0 and 11.5 wt % carbonate rapidly heated to temperatures of between 700 and 1400 °C.

Methods

CHA was prepared based on a method described previously [16], by reacting equal volumes of 130 mM solution of tri-ammonium orthophosphate at pH > 11 and a 210 mM solution of calcium nitrate 4-hydrate, while stirring over a period of approximately 2 h at 3 °C. Between 0 and 320 mM sodium bicarbonate was added to the phosphate solution in order to produce CHA of differing carbonate contents. The resulting precipitates were aged for 24 h at room temperature before being washed and filtered. Carbon content was determined using a Control Equipment Corporation Model 240 XA CHN elemental analyzer. Calcium, phosphorus and sodium measurements were made with a Perkin Elmer Plasma 40 Emission Spectrometer. Infrared spectra were recorded on a Nicolet 800 FTIR spectrophotometer using a photoacoustic sampling technique (MTEC Photoacoustic PAC200 system). Spectra were obtained between wavenumbers 400–4000 cm^{-1}. Precipitate morphology was investigated using transmission electron microscopy (TEM), (JEOL 1200 EX2). For the high temperature X-ray studies, the apatite powder to be measured was suspended in a small amount of Analar grade acetone (BDH) and then carefully pipetted onto the platinum foil heating stage of a Bühler high temperature stage attached to a Siemens D5000 diffractometer. The sample was then heated on the platinum strip in increments of 100 °C. At each temperature step, and the sample allowed to equilibrate at that temperature for 1 min. Then data were collected in flat plate geometry, with a Ni filtered CuKα radiation. Data were collected by a position sensitive detector at a fixed position, collecting data over a range of approximately $10°2\theta$ between 26 and $36°2\theta$. During the experiment, the atmosphere in the high temperature stage was purged with the appropriate gas, either carbon dioxide or nitrogen. These gases were also used wet by passing through a water trap prior to entering the high temperature stage, thus giving four different atmospheres for study. Data were initially converted using Powder v2.0 software and then phase identification was carried out using a combination of software packages. Initial identification was made using the JCPDS database. However, due to peak shifts due to sample measurements at elevated temperatures, patterns were also generated using Powder Cell v2.3 using data obtained from both JCPDS and also from the ICSD database at the Daresbury Laboratories.

Results

Apatite characterization

The composition and morphology of apatites prepared in the method of this investigation has been reported in detail previously [9]. Table I shows the composition and crystal morphology of the apatites used in this study. H1 and H2 were prepared at 70 and 3 °C respectively in the absence of added bicarbonate ions. The carbonate in these apatites probably originated from atmospheric carbon dioxide. H1 had carbonate IR bands at 1455 and 1419 cm^{-1}, which have been ascribed to CO_3^{2-} for PO_4^{3-}, or B type substitution, whereas H2 had additional bands at 1550 and 1530 cm^{-1}, which have been ascribed to OH^- for PO_4^{3-}, or A type substitution [8, 17]. H1 consisted of acicular crystals approximately 500 nm in length and 10 nm in width, whereas H2 consisted of agglomerates of spheroidal crystals approximately 10–20 nm in diameter. Fig. 1 is a transmission electron micrograph showing the sizes of morphologies of H1 and H2. H3 and H4 were prepared in the presence of added bicarbonate ions and had a similar morphology to H2. These apatites had IR bands characteristic of AB type apatites. The Ca/P ratio increased with increasing carbonate content from 1.65 at 1 wt % carbonate to 1.91 at 11.5 wt % carbonate. Conventional XRD confirmed the phase purity of the apatites.

High temperature XRD

The temperatures at which crystallization and decomposition occurred are summarized in Table II. With the exception of minor compositional differences, H1 and H2 differed predominantly in crystallinity. It can be seen in that in all test atmospheres these materials decomposed into HA and βTCP at 800 °C. βTCP formed in H1,

TABLE II Summary of high temperature XRD data

Sample	Atmosphere	HA crystallization temperature (°C)	1st decomposition temperature (°C)	Phase formed	2nd decomposition temperature (°C)	Phase formed
H1	CO_2	None	800	β TCP	1200	α
	N_2	None	800	β TCP	1200	α
	$CO_2 + H_2O$	None	800	β TCP	1200	α
	$N_2 + H_2O$	None	800	β TCP	1200	α
H2	CO_2	None	800	β TCP	1300	Super α
	N_2	None	800	β TCP	1200	α
	$CO_2 + H_2O$	None	800	β TCP	1200	Super α
	$N_2 + H_2O$	None	800	β TCP	1200	Super α
H3	CO_2	900	1300	β TCP	—	
	N_2	900	1200	αTCP	—	
	$CO_2 + H_2O$	1100	1500	β TCP	—	
	$N_2 + H_2O$	800	1400	αTCP	—	
H4	CO_2	800	1300	αTCP	—	
	N_2	700	1200	αTCP	—	
	$CO_2 + H_2O$	800	1400	αTCP	—	
	$N_2 + H_2O$	700	1100	αTCP	—	

then transformed into αTCP at 1200 °C in all test atmospheres, while βTCP formed in H2 transformed into αTCP at 1200 °C only in dry nitrogen. However in all other test atmospheres, βTCP formed in H2 appeared to transform into super αTCP. Fig. 2 shows the XRD patterns of H2 in (a) wet nitrogen and (b) wet carbon dioxide at temperatures of between 600 and 1400 °C.

H3 and H4 both increased in crystallinity during heating as determined by a sharpening of the 211, 112, 300 and 202 peaks. Crystal growth of H3 was detected at between 800 and 1100 °C, whereas at higher carbonate content, (H4) it was detected at between 700 and 800 °C. Decomposition into αTCP occurred in H3 at 1200 °C in dry nitrogen and at 1400 °C in wet nitrogen. However, in carbon dioxide atmospheres βTCP was formed at 1300 °C in dry carbon dioxide, at 1500 °C in wet carbon dioxide. Fig. 3 shows the XRD patterns of H3 in (a) wet carbon dioxide and (b) wet nitrogen at temperatures of between 700 and 1500 °C. H4 decomposed into αTCP at 1100 °C in wet nitrogen, 1200 °C in dry nitrogen, at 1300 °C in dry carbon dioxide and at 1400 °C in wet carbon dioxide. X-ray diffraction data showing decomposition of H4 in wet nitrogen and wet carbon dioxide are shown in Fig. 4.

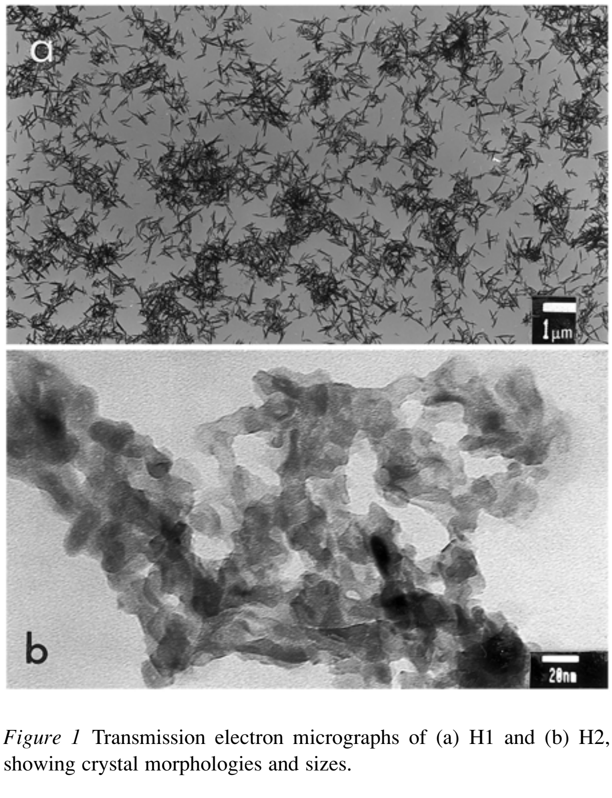

Figure 1 Transmission electron micrographs of (a) H1 and (b) H2, showing crystal morphologies and sizes.

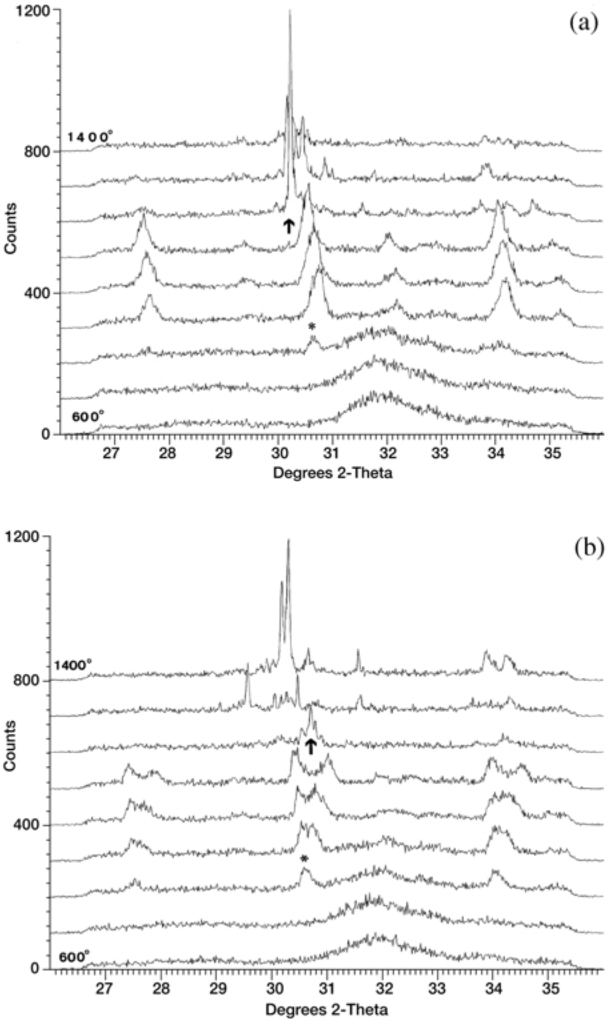

Figure 2 XRD patterns of H2 at temperatures of between 600 and 1400 °C in (a) wet nitrogen and (b) wet carbon dioxide. (First decomposition marked * second decomposition marked ↑.)

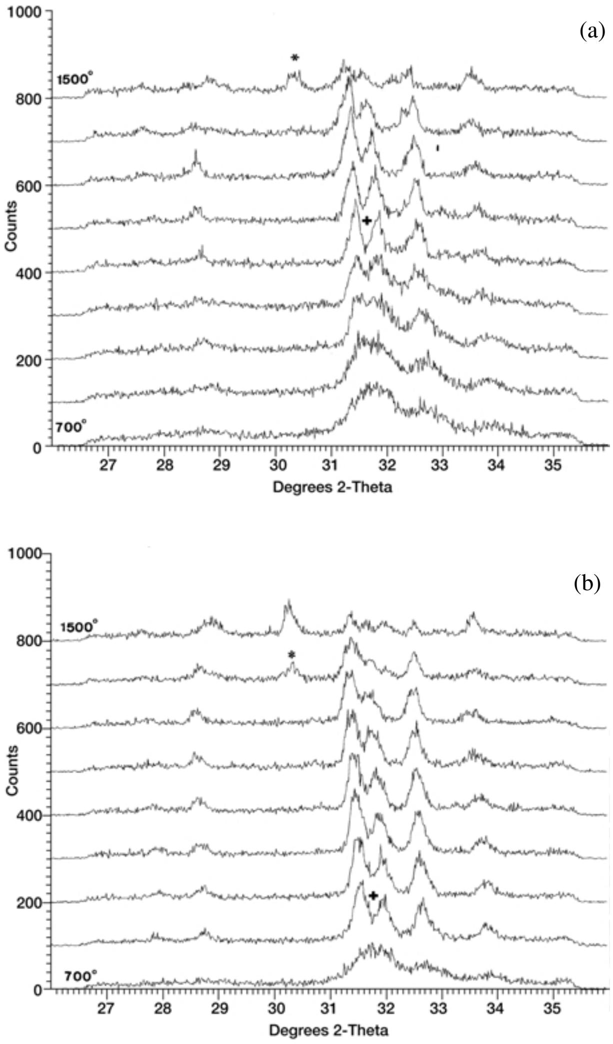

Figure 3 XRD patterns of H3 at temperatures of between 700 and 1500 °C in (a) wet nitrogen and (b) wet carbon dioxide. (Apatite crystallization marked +, first decomposition marked *.)

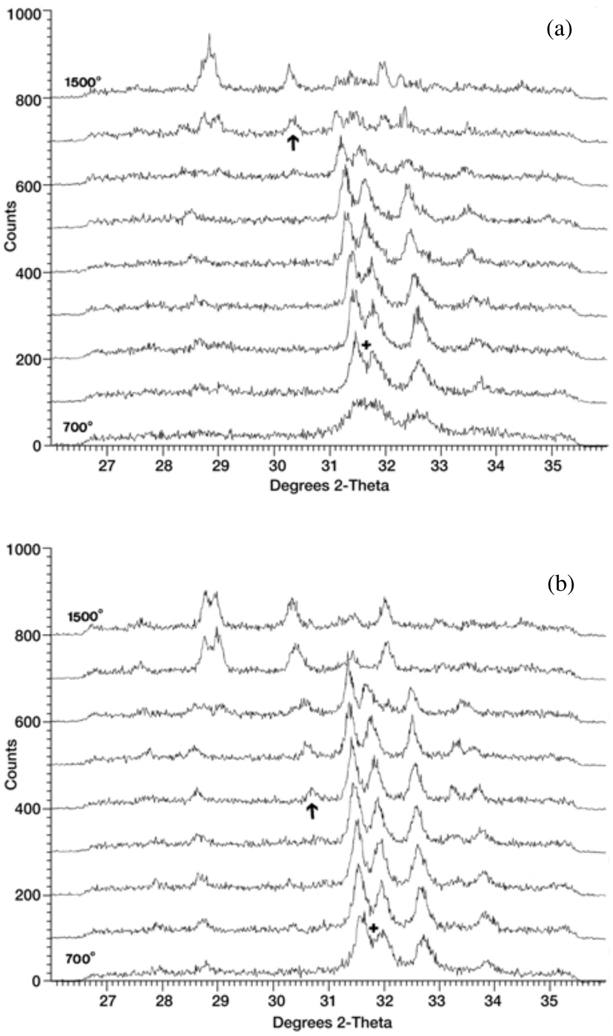

Figure 4 XRD patterns of H4 at temperatures of between 700 and 1500 °C in (a) wet nitrogen and (b) wet carbon dioxide. (Apatite crystallization marked +, first decomposition marked ↑.)

Discussion

H1 and H2 were essentially carbonate free calcium deficient apatites and had Ca/P ratios of 1.65 and 1.66 respectively and contained small amounts of carbonate as an impurity. The preparation method used was essentially based on that reported by Hayek and Newsley [18] for the production of stoichiometric HA (sHA), except the calcium : phosphate ion ratio of the reactant solutions used in this study was calcium deficient (1.62) giving rise to calcium deficient (Ca-def) apatites. It is well known that Ca-def HA might be expected to decompose at temperatures greater than 900 °C into βTCP:

$$\text{Ca-def HA} \rightarrow x\ \text{sHA} + y\beta\ \text{TCP} + \text{water} \qquad (1)$$

In fact quantification of the amount of βTCP produced after heating at 1000 °C forms the basis of a Ca : P ratio measurement technique for Ca-def Ap [19]. One might expect atmosphere to have an influence on the decomposition temperature or rate of decomposition of H1 and H2 but this was not observed. It is known that loss of carbonate during heating is time dependent even at 1000 °C [12], and so in this experiment at 800 °C, where the total heating time was less than 120 min it is probable that some carbonate remained. The lack of any effect of atmosphere on this transformation would indicate that this decomposition is independent of moisture content and the presence of carbon dioxide. Crystallinity did however appear to affect the $\beta \rightarrow \alpha$ transformation behavior, since H1 (which was more crystalline than H2), formed αTCP in all test atmospheres while H2 formed what was identified as super αTCP in all atmospheres except nitrogen. In wet CO_2 an unidentified highly crystalline intermediate phase appeared to be formed at 1200 °C (platinum background peaks were discounted). This result is significant since super α has only ever been reported at temperatures greater than 1400 °C [20].

H3 and H4 had higher carbonate contents than H1 and H2 and lower phosphate contents, and thus had a higher Ca/P ratio. In the case of H3, the atmosphere did affect the temperature at which crystal growth was detected. This crystal growth temperature was 900 °C in dry nitrogen and dry carbon dioxide, 800 °C in wet nitrogen and, most notably was elevated to 1100 °C in wet carbon dioxide. Atmosphere appeared to have little effect upon the crystal growth temperature of H4, which was lower than that of H3, (700–800 °C). This finding is in agreement with the observation that increasing carbonate substitution reduces grain growth temperature of apatite [11, 21].

HA with a calcium phosphate ratio greater than 1.67 is known to decompose on heating into sHA and CaO [11]. However, no evidence for the presence of CaO was detected in any of the XRD data. Although the most intense peak for CaO is around 37°2θ at room temperature, at temperatures greater than 1300 °C this peak is shifted to ~ 35° due to lattice expansion. This result suggests that the formation of CaO did not occur during the rapid heating regime used in this study. sHA decomposes above 1000 °C into tetracalcium phosphate and αTCP according to the reaction [22]:

$$Ca_{10}(PO_4)_6(OH)_2 \rightarrow Ca_4(PO_4)_2O + 2\alpha Ca_3(PO_4)_2 + H_2O \qquad (2)$$

It has been reported [23] that the temperature at which reaction (2) proceeds increases with water vapour pressure, from 1325 °C at 0.6 kPa to 1477 °C at 9.8 kPa. In this study, the water vapour pressure was either 0 or 3 kPa so one might expect tetracalcium phosphate to be formed at temperatures of between 1300 and 1500 °C, depending on the test atmosphere, but none was observed indicating that equilibrium was not reached in the heating regime used in this study.

H3 decomposed into αTCP in dry nitrogen at 1200 °C and βTCP at 1300 °C in dry carbon dioxide. In wet atmospheres, the decomposition occurred at a temperature 200 °C higher. While water might be expected to stabilize hydroxyapatite by preventing the formation of oxyapatite [24], the reason why nitrogen and carbon dioxide affect the phase of TCP formed is not understood. H4 decomposed at similar temperatures, but αTCP was formed in all atmospheres implying that either carbonate content or calcium phosphate ratio affects the high temperature formation of α- or βTCP. Previous workers studying high temperature decomposition of CHA with a similar carbonate content to − 4 reported the formation of βTCP at 1000 °C in dry carbon dioxide. This discrepancy may be due to the differences in heating rate (5 °C min^{-1} compared with 30 °C min^{-1} in this study).

Conclusions

The precipitation temperature and thus the crystallinity of calcium deficient apatite does affect the high temperature stability of the material. There is some evidence for the formation of super αTCP at temperatures as low as 1200 °C, but further experiments are required to determine whether the observed phase is stable at temperatures greater than 1200 °C or results from the formation of an unstable intermediate phase. Carbonate ion substitution was observed to decrease the temperature at which crystallization occurred, reaching 700 °C for 11.8 wt % carbonate apatite heated in wet atmospheres. Atmosphere was found to appreciably affect the crystallization temperature and phase transformations of carbonate apatite containing 7.8 wt % carbonate ions. In dry atmospheres, crystallization occurred at 900 °C, but in wet carbon dioxide crystallisation occurred at 1100 °C. In wet and dry carbon dioxide, βTCP was formed at 1500 and 1300 °C respectively, whereas in wet and dry nitrogen αTCP was formed at 1200 and 1400 °C respectively. Hence the high temperature decomposition of carbonate hydroxy apatite would appear to depend on composition of the apatite and the atmosphere in which it is heated.

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