JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE **11** (2000) 719–724

Effect of sintering parameters on the density and microstructure of carbonate hydroxyapatite

J. E. BARRALET[1], S. M. BEST[2], W. BONFIELD[2]*
[1]Biomaterials Unit, University of Birmingham, Dental School, St. Chad's Queensway, Birmingham B4 6NN, UK
[2]IRC in Biomedical Materials, Queen Mary and Westfield College, Mile End Road, London E1 4NS, UK
E-mail: j.e.barralet@bham.ac.uk

This work documents an investigation into the effect of water on the density and microstructure of carbonate hydroxyapatite in carbon dioxide sintering atmospheres. Carbonate apatites with carbonate contents of between 3.2 and 7.8 wt % were precipitated and the precipitates were formed into dry gels. Isothermal and isochronal sintering experiments were performed under dry carbon dioxide and wet carbon dioxide (containing 3 wt % water) atmospheres. The effect of carbonate content was studied by using two gels both with a green density of 37% and with carbonate contents of 5.8 and 7.8 wt %. Both isothermal and isochronal experiments demonstrated that bloating of the apatite occurred and this behavior was associated with the loss of carbonate from the apatite. It was found that only in wet carbon dioxide atmospheres fully dense translucent carbonate apatite could be formed. 93% dense carbonate apatite was formed after 4 h sintering at temperatures as low as 700 °C.

1. Introduction

Since mineral fluorapatite and synthesized hydroxyapatite (HA) were first sintered in the 1970s [1, 2] the use of HA in orthopaedic applications has become commonplace e.g. as a plasma sprayed coating on prosthetic joint stems, as a porous block or granule or more recently as a mouldable cement for bone augmentation. The HA lattice can accommodate a wide variety of defects and substitutions [3, 4] the biological effects of which are yet to be clarified. Human bone mineral is apatitic but differs from stoichiometric calcium HA in that it contains 4–8 wt % carbonate ions [5]. The extent of the effect of this ionic substitution upon the performance of this bioceramic if any are unknown, though *in vitro* and *in vivo* experiments have confirmed that carbonate ion substitution increases the solubility of HA [6, 7]. By being able to produce well characterized HA with differing carbonate contents, the effect of the carbonate substitution on the properties of the material may be understood. The mechanical properties of a polycrystalline ceramic are highly dependent on grain size, and porosity. Optimal mechanical strength is achieved at zero porosity and minimized grain size [8]. Previous workers have sintered carbonate hydroxyapatite (CHA), these studies have mainly been limited to isochronal studies [9, 12], and optimal sintering conditions have not been identified. These investigators used a variety of sintering atmospheres such as wet carbon dioxide, wet nitrogen, dry argon, and air. However no directly comparative investigations have previously been reported. By understanding the effects of the various sintering parameters on the microstructure of carbonate hydroxyapatite optimal sintering conditions can be selected for the production of a CHA with a given porosity and grain size. This paper describes the effect of three different sintering parameters; atmosphere, time and temperature, on the sintered microstructure and density of CHA of between 3.2 and 7.8 wt % carbonate substitution.

2. Methods

2.1. CHA preparation

A precipitation reaction based on that reported by Nelson and Featherstone [13] was used for the preparation of CHA. A mixture of 130 mM analytical grade (AR) tri-ammonium orthophosphate and between 10 and 32 mM AR sodium bicarbonate solution at pH >11 was dripped into a continuously stirred 210 mM solution of AR calcium nitrate 4-hydrate over a period of approximately 2 h at 3 °C. The resulting precipitates were aged for 24 h before being washed and filtered.

2.2. Characterization

The crystallite morphology resulting from the precipitation reaction was determined by transmission electron

---

*Now at Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge, CB2 3QZ, UK.

0957–4530

microscopy (TEM), with a JEOL 1200 EX2. The precipitates were examined in bright field mode and using electron diffraction at magnifications typically up to 50,000 ×, using an accelerating voltage of 100 kV. Carbon content was determined using a Control Equipment Corporation Model 240 XA CHN elemental analyzer and was found to be between 3.2 and 7.8 wt %. 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}. XRD patterns of CHA powders were collected using a Siemens D5000 diffractometer with the data analyzed using the Diffrac AT program. The phases present were determined by comparing the patterns with JCPDS standards.

2.3. Green body fabrication

Filtration was used to form disc shaped monoliths as described previously [14]. As pH is known to influence gel packing the pH of the sol was measured for reference, but not altered by the addition of bases or acids as this could have interfered with the sintering behavior. Polymeric deflocculants were not employed as these may only partially decompose during sintering and mask the presence of carbonate. The filtered green bodies were dried slowly in cotton wool of 250 mm thickness at room temperature. When no mass loss was measured in a 24-h period the monoliths were placed in an oven at 80 °C for 24 h. After drying, the density was calculated by measuring the mass and sample dimensions. The sample dimensions were measured by determining the surface area of the top and bottom of the monolith using the Quantimet 570 image analysis system and the average thickness was measured using a micrometer. Pore size distributions of a 5.8 wt % CHA 37% relative density green pellet were measured by mercury porosimetry (Micrometrics ASA 200 mercury porosimeter using Autopore 9220 V3.01 software).

2.4. Sintering

The apatites were sintered in a Carbolite 1600 tube furnace using both dry CP grade carbon dioxide and 97% carbon dioxide with 3% water atmospheres, and a heating and cooling ramp of 2.5 °C min^{-1}. Sintered CHA densities were measured using Archimedes' method and grain size was determined from scanning electron micrographs (JEOL 6300) using a linear intercept method with measurements of at least 80 grains.

2.4.1. Sintering regimes

Isothermal sintering studies were performed using 37% dense, 7.8 wt % and 5.8% CHA. Specimens were sintered at 1000 °C for between 0 and 24 h in wet and dry carbon dioxide. The development of microstructure with time was observed using scanning electron microscopy. The effect of isochronal ($t = 4$ h) sintering temperature, carbonate content, furnace atmosphere composition and green relative density upon the microstructure was investigated. The effect of carbonate was determined using CHA of 3.2, 5.8 and 7.89 wt % CHA sintered at temperatures of between 700 and 1300 °C with green relative densities of between 30 and 40%.

3. Results

The precipitates were found to be apatitic and IR absorption bands in the 1450–1550 cm^{-1} range confirmed the presence of carbonate. All the precipitates were found to have primary particle sizes in the range 10–20 nm as determined from TEM investigation as previously reported [15].

3.1. Green body density

The green bodies were white brittle gel disc shaped monoliths approximately 3 mm thick and 10 mm diameter. The density was not related to carbonate content and was typically between 35 and 40%. Mercury porosimetry showed that a 7.8 wt % CHA green body with a green density of 37% had a monomodal pore size distribution about 9 nm, the specific surface area was 183.9 m^2 g^{-1}.

3.2. Isothermal sintering

CHA was sintered in both wet and dry carbon dioxide at 1000 °C and only CHA sintered in wet carbon dioxide reached full density. The ceramics that reached full density were observed to be translucent. However isothermal sintering in both atmospheres resulted in bloating at temperatures above 1100 °C. Fig. 1 shows the carbonate content of CHA as a function of time at 1000 °C when sintered in wet carbon dioxide atmosphere with a green carbonate content of 5.8 wt %. It can be seen that over 70% of the carbonate was lost from the 5.8 wt % CHA during sintering, during the ramp up to sintering temperature. After times of between 45 and 60 min a further 16% of the carbonate was lost, but thereafter the carbonate content appeared to be constant over the next 23 h. Fig. 2 shows the variation in density with time of 7.8 and 5.8 wt % CHA sintered in wet carbon dioxide at 1000 °C. At time $t = 0$ at 1000 °C the ceramics were already 99.0% dense (having sintered to a large degree during ramp up). After 30 min the density increased to 100%. The densification of the 7.8 wt % CHA seemed to

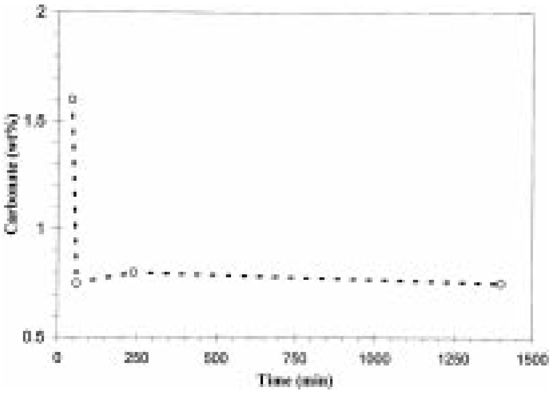


Figure 1 Carbonate content of 5.8 wt % CHA as a function of time during sintering at 1000 °C.

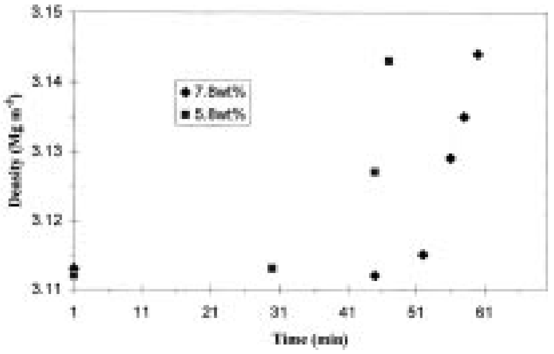


Figure 2 Sintered density of 5.8 and 7.8 wt % CHA after times of up to 1 h at 1000 °C in wet carbon dioxide atmosphere.

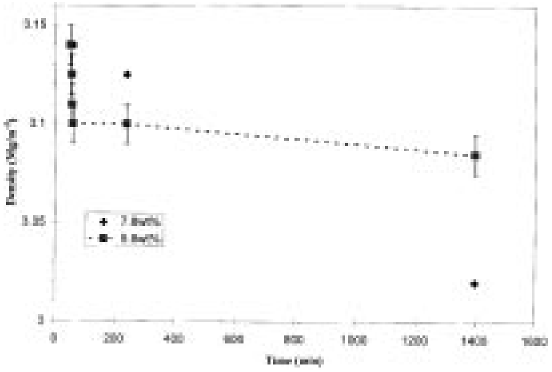


Figure 3 Sintered density of 5.8 and 7.8 wt % CHA after times of between 45 min and 24 h at 1000 °C in wet carbon dioxide atmosphere.

lag behind the 5.8 wt % CHA by 10–15 min. It can be seen in Fig. 3 that between 48 and 60 min the 5.8 wt % CHA then decreased in relative density by 1.5%, between 1 h and 24 h the density remained constant. The 7.8 wt % CHA also decreased in density from 100% to 95.8 wt %.

Fig. 4 shows the effect of sintering time on the grain size of 5.8 wt % CHA. The grain size of the 7.8 wt % CHA was greater than that of the 5.8 wt % CHA at all sintering times, the rate of grain growth decreased with time for both materials.

The change in density of CHA sintered at 1000 °C in dry carbon dioxide with time is shown in Fig. 5. A $t = 0$ at 1000 °C the densities of the CHA were much lower, 52 and 64% relative density for 7.8 wt % and 5.8 wt % CHA respectively. The 5.8 wt % CHA again decreased in density between 40 and 60 min to 55%, after this time the density did not change significantly. The 7.8 wt % CHA increased in density to 72% after 1 h and the density did not vary significantly over the following 23 h.

The microstructures of 7.8 wt % CHA isothermally sintered in wet and dry carbon dioxide atmospheres for 0, 60, and 1440 min are displayed in Fig. 6. After sintering for 1440 min in wet carbon dioxide some intergranular porosity is evident along the grain boundaries. In dry carbon dioxide the microstructure consisted of an interconnected network of what appear to be grains though no boundaries were visible up to 4 h. At 24 h the microstructure consisted of barrel shaped grains connected at the ends which form an open network.

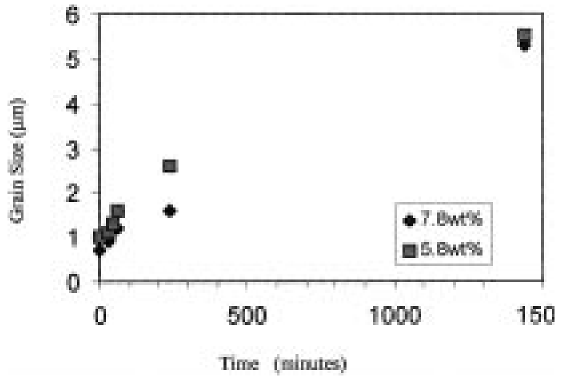


Figure 4 Grain size of 5.8 and 7.8 wt % CHA as a function of sintering time at 1000 °C in wet carbon dioxide.

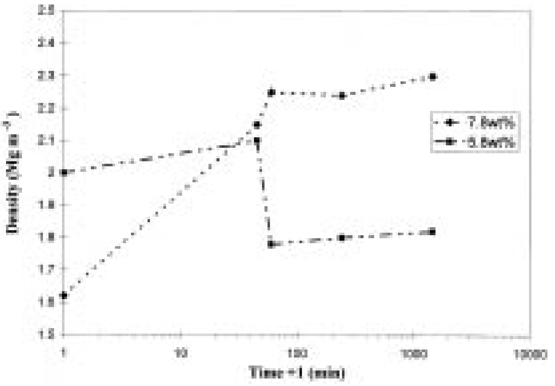


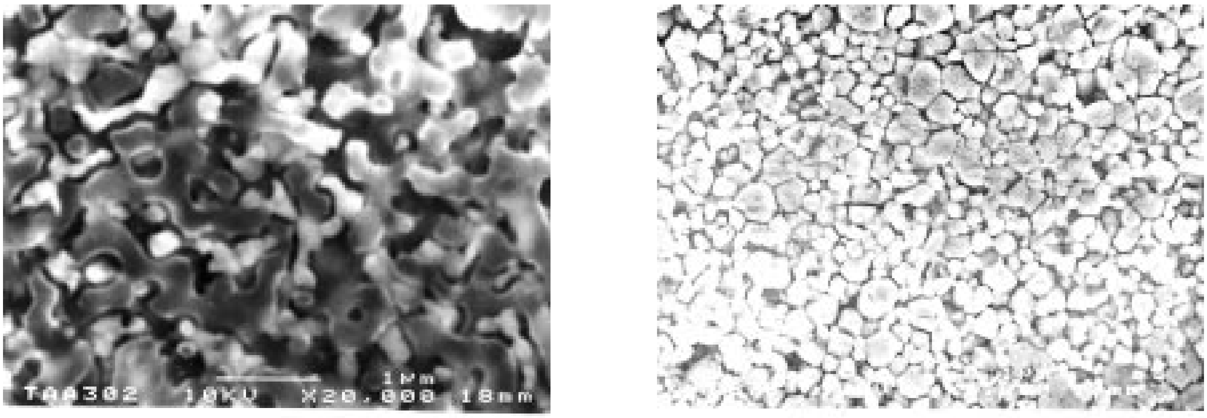
Figure 5 Sintered density of 5.8 and 7.8 wt % CHA after times of up to 24 h at 1000 °C in dry carbon dioxide atmosphere.

3.3. Isochronal sintering

The main difference observed between the sintering atmospheres was that wet carbon dioxide yielded translucent ceramics whereas dry carbon dioxide produced white opaque ceramics The difference in optical properties was noted from above 1150 °C up to the maximum temperature of investigation, 1300 °C. XRD confirmed that 3.2% CHA sintered in wet carbon dioxide for 4 h was comprised of a single phase of hydroxyapatite. SEM revealed that large intergranular pores were visible in the material sintered in dry carbon dioxide and smaller intragranular pores were also evident. However, when sintered in a wet carbon dioxide atmosphere, intergranular porosity was not evident although some crack like pores were seen within some grains. The effect of sintering temperature on grain size was hard to compare for different carbonate apatites since the temperature at which densification occurred varied with green density and carbonate content. Table 1

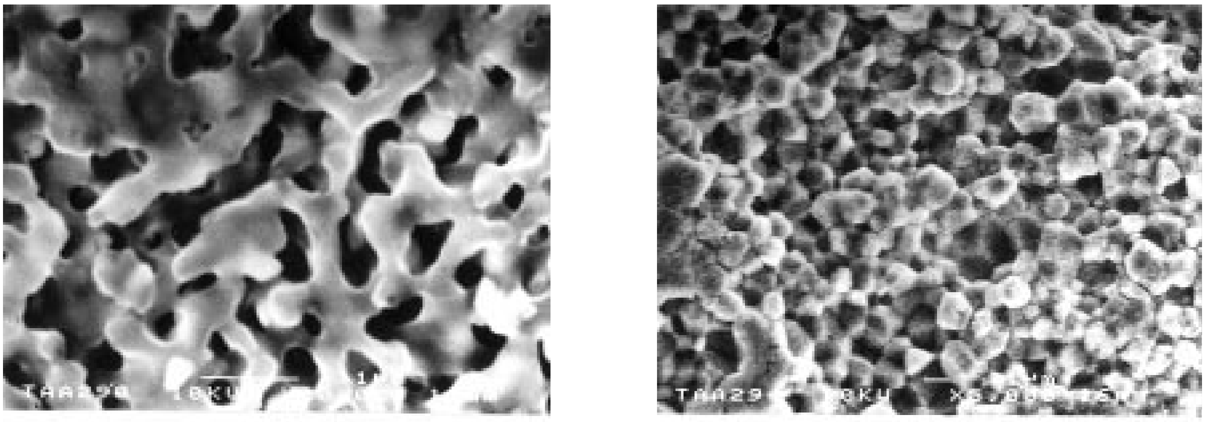
TABLE I The effect of sintering atmosphere and temperature on the grain size of a 3.2 wt % CHA sintered for 4 h

	Grain size (µm) ± sd	
Temperature (°C)	Carbon dioxide	Wet carbon dioxide
1150	1.14 ± 0.12	0.67 ± 0.07
1250	6.15 ± 0.84	5.05 ± 0.63
1300	10.85 ± 1.31	8.20 ± 0.94



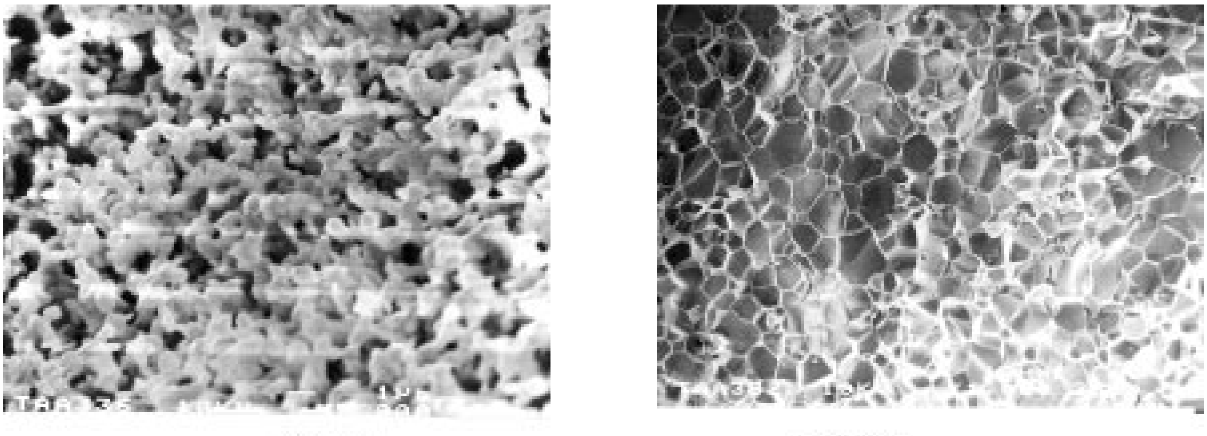
0 minutes

0 minutes



45 minutes

60 minutes



24 hours

24 hours

(a)

(b)

Figure 6 Microstructure of 7.8 wt % CHA sintered in wet (a) and dry (b) carbon dioxide atmospheres at 1000 °C for times of up to 24 h.

shows the effect of sintering atmosphere and temperature on the grain size of 3.2% CHA. Generally as the carbonate content increased, the sintering temperature required for a given degree of densification decreased, but at lower temperatures (800–900 °C), densification and grain growth had not been appreciably initiated in CHA containing low levels of carbonate ions. In addition, bloating was observed to occur and the effect of this was greatest in higher carbonate content apatites. The effect of temperature and sintering atmosphere on the sintered density of 30% green density 5.8 and 7.8 wt % CHA is shown in Figs 7a and b. In wet carbon dioxide 5.8 wt % CHA was 92% dense after 4 h sintering at 700 °C. full density was reached between 800 and 900 °C. Bloating occurred between 900 and 1100 °C and the density reduced to 77%, little further densification occurred between 1100 and 1300 °C. After sintering at 800 °C 7.8 wt % had hardly densified. Densification occurred between 900 and 1200 °C and again bloating was evident but at a higher temperature than 5.8 wt % CHA. In a dry carbon dioxide atmosphere after 4 h sintering 5.8 wt % CHA only began to densify at temperatures above 1150 °C, however at 1300 °C bloating again appeared to have occurred. 7.8 wt %

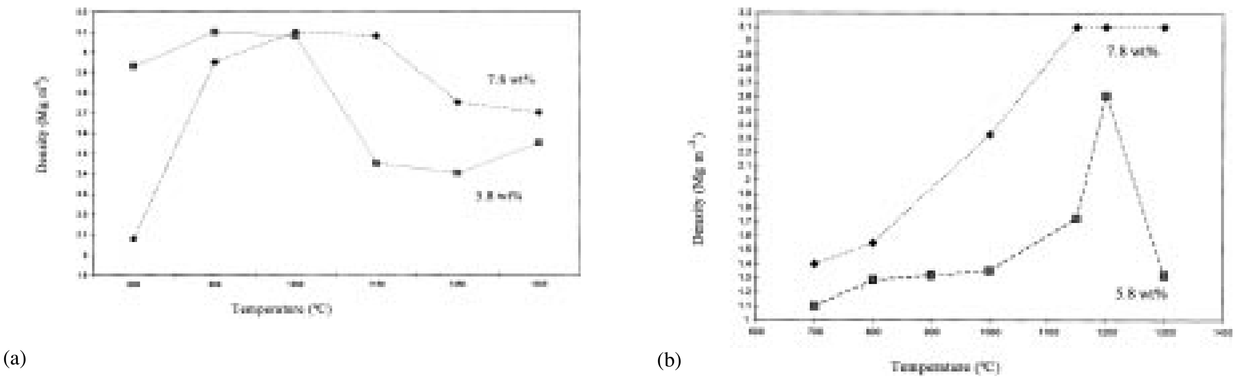


Figure 7 The effect of temperature on the sintered density of 30% green density 5.8 and 7.8 wt % CHA in (a) wet carbon dioxide and (b) dry carbon dioxide.

CHA began to densify at a lower temperature (1000 °C) than 5.8 wt % CHA, however at temperatures of between 1150 and 1300 °C the 7.8 wt % CHA sintered to nearly full density and no bloating appeared to occur.

4. Discussion

Although a number of different furnace atmospheres have been investigated for the sintenng of CHA no significant differences in sintering behavior have previously been described. The rationale for sintering in carbon dioxide atmospheres is that carbonate loss may be reduced during sintering. However, despite sintering in a carbon dioxide atmosphere significant loss of carbonate did occur in this study as shown in Fig. 1. The rate of loss was initially rapid and an equilibrium value appears to have been reached after 30 min. The rate of carbonate loss is likely to be dependent on the surface area of the ceramic which changed during densification from $\sim 2 \times 10^{2}$ to $\sim 2 \times 10^{-4}\,\mathrm{m}^{-2}\,\mathrm{g}^{-1}$. Given that carbonate is lost as carbon dioxide clearly some atomic rearrangement must occur resulting in an apatitic structure which will differ from biological apatite. Therefore if a synthetic analogue of biological apatite were required it would seem that very short sintering times would be desirable to minimize carbonate loss. This loss of carbonate appeared to correlate to the decrease in density that was observed in both isothermal and isochronal sintering studies. Such a decrease in density of CHA during sintering has been observed by other workers [9, l6, 17], and it seems likely that the loss of carbon dioxide from the CHA is responsible for this phenomenon. Both isothermal and isochronal sintering studies showed that a wet carbon dioxide sintering atmosphere could yield a fully dense translucent ceramic whereas densification did not proceed to completion in dry carbon dioxide. A wet carbon dioxide atmosphere is more reducing than a dry carbon dioxide atmosphere at the temperatures used in this investigation and reducing atmospheres have been implicated in preventing pore/boundary breakaway in other ceramic systems [18]. Water has been observed to increase the densification rate of a number of systems when present in the sintering atmosphere [19, 20]. The sintering temperature for densification of silica gels is known to depend upon the water content of the gels [21]. At 3000 ppm full density is attained at 1150 °C and the density increases to a maximum value then decreases with sintering time. Gels with a water content of <10 ppm full density is reached at 1200 and l250 °C and bloating does not occur. At an even lower water content, ($\ll$ l0 ppm) densification did not occur at temperatures below 1320 °C. The reasons for this were attributed to a reduction in viscosity of the gel caused by water. It is feasible that the water in the wet carbon dioxide atmosphere used in this study also softened the CHA at a lower temperature than in dry carbon dioxide, enabling full densification to occur. However previous investigations using air and a similar quantity of water as a sintering atmosphere for CHA did not result in a dense ceramic at 1250 °C whereas a wet carbon dioxide atmosphere did [22]. Table I shows that the grain size of 3.2 wt % CHA was greater when sintered in dry carbon dioxide than in wet carbon dioxide at sintering temperatures between 1150 and 1300 °C, this implies that the presence of water increases the densification: grain growth ratio. Fig. 7 shows that the effect of carbonate on sintered density is dependent on furnace atmosphere composition. In wet carbon dioxide atmosphere, 5.8 wt % CHA is practically fully dense after sintering for 4 h at 800 °C, whereas 7.8 wt % CHA is only 68% dense. Bloating of the 5.8 wt % CHA occurred at some temperature above 900 °C so that at 1100 °C the relative density was less than 80%, however the 7.8 wt % CHA was fully dense. Above 1100 °C bloating occurred and the density was appreciably lower. In dry carbon dioxide little densification of 5.8 wt % CHA occurred at temperatures up to 1000 °C. At 1200 °C after 4 h sintering, the 5.8 wt % CHA was 84% dense and bloating occurred at higher temperatures. However the 7.8 wt % CHA began densification above 800 °C and was fully dense at 1150 °C and no bloating occurred at up to 1300 °C. It might reasonably be expected that the degree of bloating to depend upon the quantity of carbonate present in the apatite prior to sintering and the loss of carbon dioxide to generate a more deficient structure in which diffusion rates and therefore sintering rates would be higher. Though the expected difference in sintering rate is observed in dry carbon dioxide the reverse appears to be the case in wet carbon dioxide for the green densities, carbonate contents, carbon dioxide/water ratio and sintering times investigated. One explanation may be that differing degrees of carbonate loss may occur in different atmospheres and further work is required to confirm this. Although termed isochronal sintering, it is clear form the isothermal investigation that significant sintering occurs during the ramp up to sintering temperature. Fig. 7a shows that substantial densification occurs at temperatures as low as 700 °C. A sample sintered at 1000 °C with a 2.5 °C min^{-1} heating and cooling ramp will have been at a temperature of greater than 700 °C for 4 h in addition to the ''isochronal'' sintering time. In order to understand the effect of sintering temperature more clearly the heating ramps should be as fast as possible without causing cracking to the sample. In an attempt to minimize the effect of any sintering that may occur during the ramping of the furnace, a piece of 5.8 wt % CHA was slowly ($\sim$ 1 min) introduced manually into the tube furnace in order to replicate the temperature profile obtained by microwave sintering [23] and was found to sinter to full density at 900 °C after 10 min.

5. Conclusions

Sintering CHA is a complex process since so many parameters change during the sintering process including surface area, carbonate content, vacancy concentration, grain size and pore size and connectivity. While it is possible to make observations about specific sintering conditions further work is required in order to fully understand the effect and interactions of these variables. However it can be concluded that CHA can sinter to full density in wet carbon dioxide atmosphere. This is an important finding since this method avoids the need for complex sintering techniques such as hot isostatic pressing that has previously been employed to produce fully dense translucent hydroxyapatite ceramics, [2, 24, 25]. Few hydroxyapatites are completely free of carbonate since carbon dioxide it is often present in the reaction solutions unless precautions to remove it are taken. Therefore this finding may have implications for a number of hydroxyapatite heat treatments such as plasma spraying. It has been shown that in order to produce dense CHA, sintering time can be an important parameter to control since full density may be achieved over a very narrow range of sintering times.

Acknowledgments

The authors gratefully acknowledge the financial support of the EPSRC, which made this work possible.

References

1. E. A. MONROE, *J. Dent. Res.* **50** (1971) 860.
2. H. AOKI, *Reports of Inst. for Med. Dent. Engineering, TMDU, Tokyo* **7** (1973) 113.
3. J. C. ELLIOTT, in ''Structure and Chemistry of the Apatites and Other Calcium Orthophosphates'' (Elsevier, Amsterdam, 1994) p. 63.
4. R. Z. LEGEROS, in ''Calcium Phosphates in Oral Biology and Medicine'' (Karger, Basel, 1991) p. 82.
5. F. C. M. DRIESSENS, in ''Bioceramics of Calcium Phosphate'' (CRC Press, Bocca Raton, Florida, l983) p. 1.
6. D. G. A. NELSON, *J. Dent. Res.* **60(C)**, (1981) 1621.
7. J. E. BARRALET, H. AOKI, M. AKAO and H. AOKI, in press *J. Biomed. Mater. Res.* (1999).
8. W. D. KINGERY, H. K. BOWEN and D. R. UHLMAN, in ''Introduction to Ceramics'' (John Wiley and Sons, New York, 1976) p. 808.
9. L. G. ELLIES, D. G. A. NELSON and J. D. B. FEATHERSTONE, *J. Biomed. Mater. Res.* **22** (1988) 541.
10. Y. DOI, T. KODA, N. WAKAMATSU, T. GOTO, H. KAMEMIZU, Y. MORIWAKI, M. ADACHI and Y, SUWA, *J. Dent Res.* **72** (1993) 429.
11. Y. DOI, T. SHIBUTANI, Y MORIWAKI, T. KAJIMOTO and Y. IWAYAMA, *J. Biomed. Mater. Res.* **39** (1998) 603.
12. P. LAYROLLE, A. ITO and T. TATEISHI. *J. Am. Ceram. Soc.* **81** (1998) 1421.
13. D. G. A. NELSON and J. D. B. FEATHERSTONE, *Calcif. Tiss. Int.* **34** (1982) 569.
14. J. E. BARRALET, S. BEST and W. BONFIELD *Biomed. Mater. Eng.* **6** (1996) 101.
15. J. E. BARRALET, S. BEST and W. BONFIELD *J. Biomed. Mater. Res.* **41** (1998) 79.
16. Y. SUWA, H. BANNO, H. SAITO, Y. DOI, T. KODA, M. ADACHI and Y. MORIWAKI, in Proceedings of the 6th International Symposium on Ceramics in Medicine, Philadelphia, November 1993, edited by P. Ducheyne and D. Christiansen (Butterworth-Heinemann Ltd., Oxford, 1993) p. 381.
17. J. C. MERRY, E. R. GIBSON, S. M. BEST and W. BONFIELD, *J. Mater. Sci.: Mats in Med.* **9** (1998) 779.
18. A. MOCELLIN and W. D. KINGERY, *J. Am. Ceram. Soc.* **56** (1973) 309.
19. I. YASUMOTO, *J. Phys. Chem.* **88** (1984) 4041.
20. F. VILA, O.N. VENTURA, J.A. VALERA and E. LOGO, *J. Molec. Struc. (Thermochem)* **305** (1994) 175.
21. J. PHALOPPOU, T. WOIGNIER and J. ZARZYCKI, in ''Ultrastructure Processing of ceramics, glasses and composites'' (John Wiley and Sons, NY, 1984) p. 70.
22. J. E. BARRALET, *Thesis, University of London* (1995) 166.
23. Y. FANG, D. K. AGRAWAL, D. M. ROY and R. ROY, *J. Mater. Res.* **9** (1994) 180.
24. K. UEMATSIJ, M. TAKAGI, T. HONDA, N. UCHIDA and K. SAITO, *J. Am. Ceram. Soc.* **72** (1989) 1476.
25. J. LI and J. L. HERMANSSON, *Interceram* **39** (1990) 13.

Received 9 September
and accepted 13 December 1999