

# Sintering behaviour of hydroxyapatite reinforced with 20 wt % $\text{Al}_2\text{O}_3$

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Hydroxyapatite reinforced with 20 wt %  $\text{Al}_2\text{O}_3$  was sintered at 1200, 1300 and 1400 °C. The sintering behaviour was investigated using X-ray diffraction and electron microscopy. Calcium aluminate phases were observed to be produced by the solid-state reaction between  $\text{Al}_2\text{O}_3$  and hydroxyapatite. As a hard phase these phases influence the densification of hydroxyapatite with 20 wt %  $\text{Al}_2\text{O}_3$  due to different sintering rates between the matrix and calcium aluminate.

## 1. Introduction

It is known that the densification behaviour of a crystalline powder can be dramatically influenced by an inert, second phase [1]. In particular, differential shrinkage is an important factor in the sintering of heterogeneous ceramic compacts. This behaviour is associated with the generation of transient stresses which may limit densification. Numerous models have been proposed to describe the densification behaviour [2–4]. These models describe how the formation of stresses is dominated by differential shrinkage between the ceramic matrix and inert, non-densifying coarse particles because the coarse particles act as a spherical domain or network to constrain the matrix shrinkage. The stresses can be analytically determined in the case where the chemical reaction between the matrix and particles is ignored. The present work was undertaken in an attempt to establish the effect of the sintering process on the densification of hydroxyapatite with 20 wt %  $\text{Al}_2\text{O}_3$ .

Hydroxyapatite has a superior biological response with the human body compared to metals and polymers [5]. However, the use of hydroxyapatite as a loaded implant is considerably limited by low mechanical reliability. Hydroxyapatite mixed with other materials appears to be a key to improve its fracture toughness. It has been found that the fracture toughness of hydroxyapatite reinforced with  $\text{ZrO}_2$  or  $\text{Al}_2\text{O}_3$  is increased [6, 7]. X-ray diffraction (XRD) results from hydroxyapatite mixed with  $\text{ZrO}_2$  sintered at 1200 °C revealed that the addition of  $\text{ZrO}_2$  resulted in a number of  $\alpha$ -tricalcium phosphate regions in the hydroxyapatite matrix [8]. When hydroxyapatite mixed with 20 wt %  $\text{Al}_2\text{O}_3$  was sintered at 1400 °C, calcium aluminate phases were produced by the reaction of the alumina and hydroxyapatite, and the sintered samples also revealed the presence of  $\alpha$ -tricalcium phosphate as the major phase, in addition to hydroxyapatite [9]. It would, therefore, be desirable to establish the effect of  $\text{Al}_2\text{O}_3$  on the sintering of hydroxyapatite. In this paper, hydroxyapatite with

20 wt %  $\text{Al}_2\text{O}_3$  sintered at different temperatures was characterized using electron microscopy and X-ray diffraction.

## 2. Experimental procedure

Hydroxyapatite powders were prepared by the reaction of  $\text{Ca}(\text{OH})_2$  and  $\text{H}_3\text{PO}_4$  in aqueous solution at pH 9–10. The Ca/P ratio of precipitated hydroxyapatite was kept at 1.67. The hydroxyapatite powders were mixed with 20 wt %  $\text{Al}_2\text{O}_3$  of average particle size 0.3  $\mu\text{m}$  in distilled water and dried by stirring on a hotplate. The mixed powders were then compacted into a cylinder at about 4200 psi (29 Mpa). The samples of hydroxyapatite with 20 wt %  $\text{Al}_2\text{O}_3$  were calcined at 900 °C in an air atmosphere for 3 h to promote crystallization and then sintered at 1200, 1300 and 1400 °C in air to establish the effect of the sintering temperature on the microstructure. The specimens were kept for 1 and 3 h at 1200 °C, for 2 h at 1300 °C, and also for 2 and 4 h at 1400 °C.

The sintered compacts of hydroxyapatite with 20 wt %  $\text{Al}_2\text{O}_3$  were characterized by XRD. Bulk specimens were polished for examination in a scanning electron microscope (SEM). For transmission electron microscopy (TEM), thin specimens were prepared using a dimpler and an ion-beam thinner in a standard technique. The thinned specimens were coated with carbon films and then examined in Jeol 4000FX equipped with an energy-dispersive X-ray analysis detector.

## 3. Results and discussion

It has been observed in hydroxyapatite–alumina blended powders that spherical agglomerates of hydroxyapatite are surrounded by  $\text{Al}_2\text{O}_3$  particles and that uniform mixtures can be achieved [9]. XRD patterns from hydroxyapatite with 20 wt %  $\text{Al}_2\text{O}_3$  sintered at different temperatures are shown in Fig. 1. It can be seen that the XRD diffractograms are very

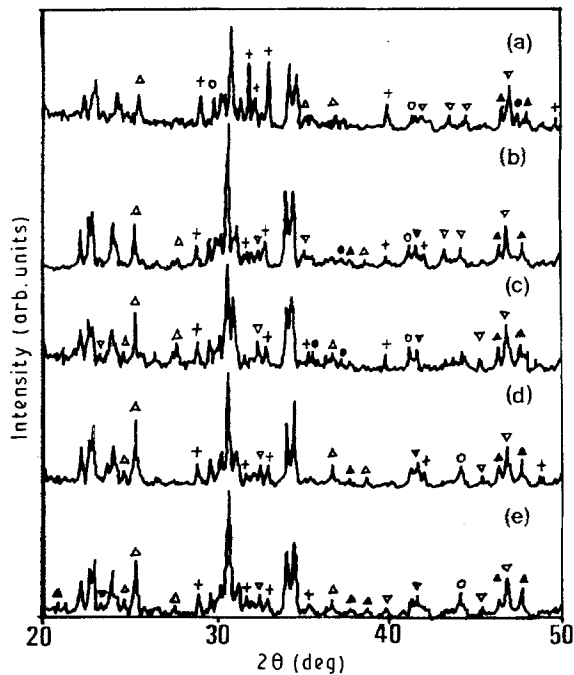


Figure 1 X-ray diffraction patterns from hydroxyapatite reinforced with 20 wt %  $\text{Al}_2\text{O}_3$  sintered at (a) 1200 °C for 1 h, (b) 1200 °C for 3 h, (c) 1300 °C for 2 h, (d) 1400 °C for 2 h and (e) 1400 °C for 4 h, showing characteristics of tricalcium phosphate with a small number of other compounds: (+)  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ , (▼)  $\beta\text{-Ca}_3(\text{PO}_4)_2$ , (▲)  $\text{Ca}_3\text{Al}_2\text{O}_6$  ( $\text{C}_3\text{A}$ ), (●)  $\text{CaAl}_2\text{O}_4$  (CA), (△)  $\text{CaAl}_4\text{O}_7$  ( $\text{CA}_2$ ), (▽)  $\text{Ca}_5\text{Al}_6\text{O}_{14}$  ( $\text{C}_5\text{A}_3$ ), (○)  $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  ( $\text{C}_{12}\text{A}_7$ ).

complicated and that new compounds are being produced by the solid-state reaction between hydroxyapatite and alumina. Compared with standard X-ray diffraction patterns, the XRD results reveal that the major phase of the sintered samples is  $\alpha$ -tricalcium phosphate rather than hydroxyapatite. It is clear from the XRD patterns of hydroxyapatite with 20 wt %  $\text{Al}_2\text{O}_3$  sintered at 1200 °C for 1 and 3 h that major peaks of  $\alpha$ -tricalcium phosphate appear to arise in comparison with the major peaks of hydroxyapatite at the angles ( $2\theta$ ) of 31.76, 32.18 and 32.89° as shown in Fig. 1a and b. After increasing the sintering temperatures to over 1300 °C, the amount of hydroxyapatite is reduced by further decomposition (Fig. 1c, d and e). Furthermore, there is no evident trace of  $\text{Al}_2\text{O}_3$  in the XRD traces. This indicates that  $\text{Al}_2\text{O}_3$  is completely consumed by the solid-state reaction. Extra peaks on the XRD diffractograms can also be seen. The extra peaks may be produced by calcium aluminates which have been preliminarily identified as  $\text{Ca}_3\text{Al}_2\text{O}_6$ ,  $\text{CaAl}_2\text{O}_4$ ,  $\text{CaAl}_4\text{O}_7$ ,  $\text{Ca}_5\text{Al}_6\text{O}_{14}$  and  $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ . Thus the formation of the calcium aluminates accompanies the decomposition of hydroxyapatite.

When samples of hydroxyapatite reinforced with 20 wt %  $\text{Al}_2\text{O}_3$  sintered at 1200 and 1300 °C were polished for SEM observation, it was found that the samples were very brittle and friable. Fig. 2a, b and c show the porous structure of hydroxyapatite reinforced with 20 wt %  $\text{Al}_2\text{O}_3$ . Massive open pores were produced when the samples were sintered at 1200 and 1300 °C. Correspondingly, a typical TEM micrograph taken from the sample sintered at 1200 °C for 1 h is shown in Fig. 3a. It is very clear that a porous structure of hydroxyapatite is produced. The calcium

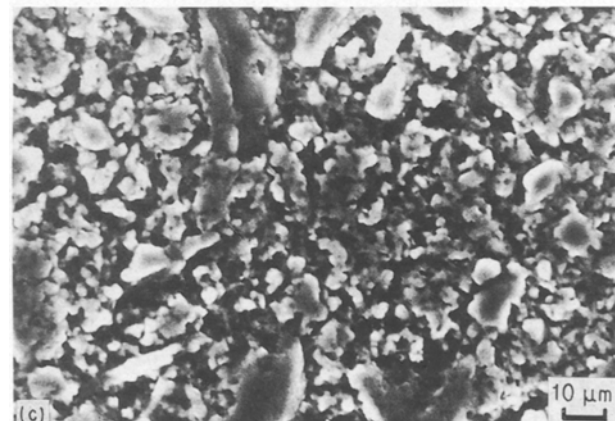
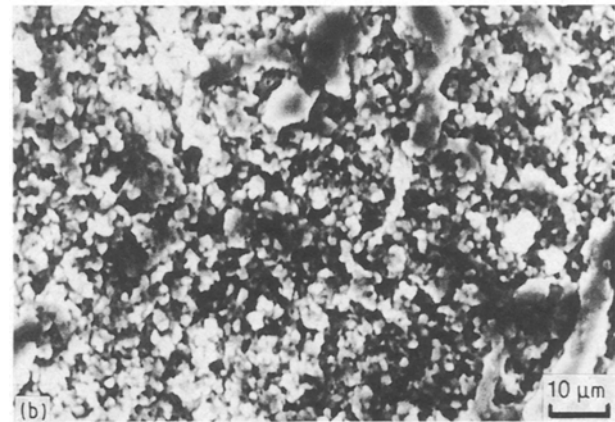
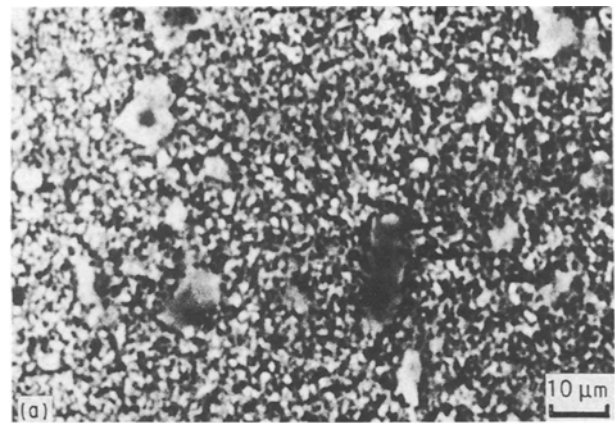


Figure 2 SEM micrographs showing porous hydroxyapatite reinforced with 20 wt %  $\text{Al}_2\text{O}_3$  sintered at (a) 1200 °C for 1 h, (b) 1200 °C for 3 h and (c) 1300 °C for 2 h.

aluminates as agglomerates also appear to be in a porous structure as shown in Fig. 3a. Apparently, the solid-state reaction between alumina and hydroxyapatite leads to the formation of calcium aluminate and alumina no longer exists, since the diffusion of  $\text{Al}^{3+}$  and  $\text{Ca}^{2+}$  ions occurs during sintering. It has been found that dense hydroxyapatite can be achieved by sintering at 1150–1200 °C [10, 11], which is distinctly different from the behaviour of hydroxyapatite with 20 wt %  $\text{Al}_2\text{O}_3$ . Alumina can be seen to have a major effect on the sintering of hydroxyapatite and to react with hydroxyapatite to form calcium aluminates. TEM observation shows that the calcium aluminates are spherical domains dispersed in the matrix of calcium phosphate. Also there seems to be a difference

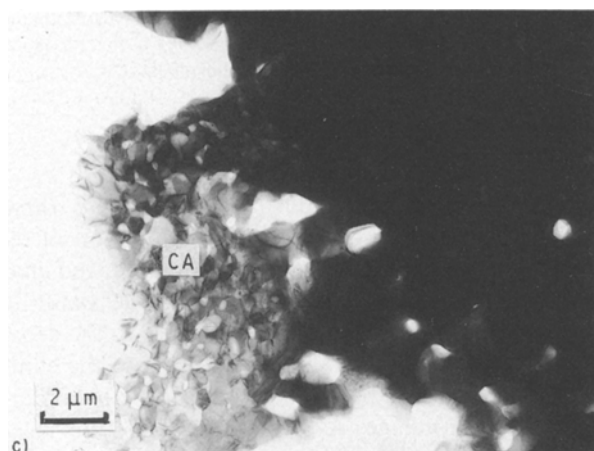
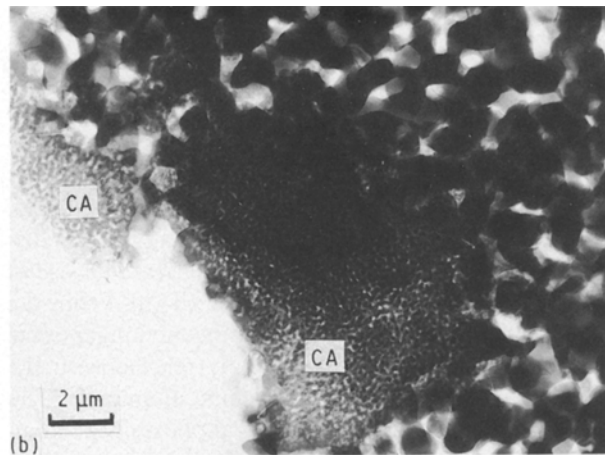
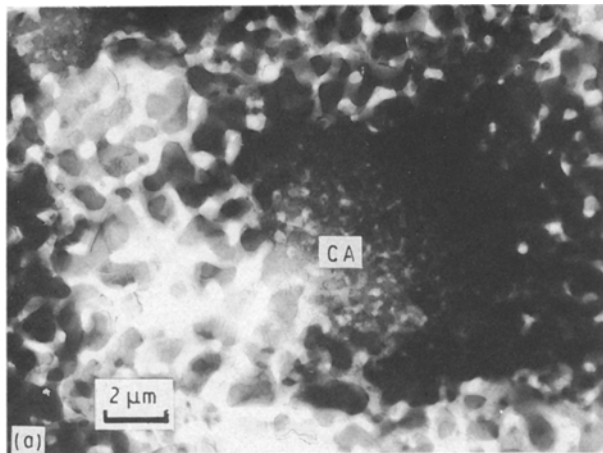


Figure 3 TEM micrographs showing hydroxyapatite reinforced with 20 wt %  $\text{Al}_2\text{O}_3$  sintered at (a) 1200 °C for 1 h, (b) 1200 °C for 3 h and (c) 1300 °C for 2 h; CA = calcium aluminate.

in the sintering rates between the matrix and calcium aluminate phases. Therefore, it is proposed that the calcium aluminates act as hard phases constraining the shrinkage of the matrix in addition to its own densification. This constraint could influence the grain growth and densification of the calcium phosphate and cause the cracks, voids and pores in the matrix.

Similarly, Fig. 3b and c respectively exhibit the porous structure of hydroxyapatite reinforced with 20 wt %  $\text{Al}_2\text{O}_3$  sintered at 1200 °C for 3 h and at 1300 °C for 2 h. Obviously, extensive grain growth has occurred in both the matrix and calcium aluminates and many pores have become isolated when the sample was sintered at 1300 °C for 2 h. Fig. 4a and b are typical TEM micrographs taken from the samples sintered at 1200 °C for 1 h and at 1300 °C for 2 h showing the porous calcium aluminates. Compared with the samples sintered at 1200 °C, the porosity is obviously reduced as the sintering temperature increases. The primary pores are produced by neck growth on the grain boundaries during sintering. As with neck growth and grain growth, the pores on the grain boundaries may be left behind by the moving boundary or migrate with the boundary, gradually agglomerating at grain corners. The effect of the constraint on the matrix will be reduced as grain growth and the elimination of pores, related to the shrinkage, takes place in the calcium aluminates. The relief of the local constraint will gradually allow the matrix to densify. Apparently, in the temperature range 1200

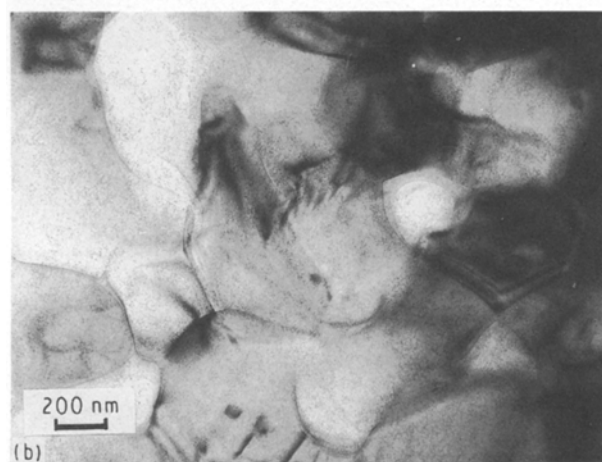
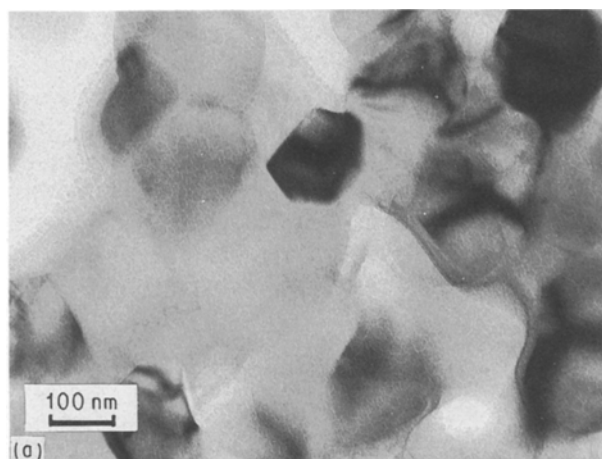


Figure 4 TEM micrographs showing calcium aluminate phase from hydroxyapatite reinforced with 20 wt %  $\text{Al}_2\text{O}_3$  sintered at (a) 1200 °C for 1 h and (b) 1300 °C for 2 h; CA = calcium aluminate.

to 1300 °C, the porous structure of hydroxyapatite reinforced with 20 wt %  $\text{Al}_2\text{O}_3$  is caused by an incomplete sintering process. The realization of full densification at this stage is therefore likely to be limited. In this case, the addition of  $\text{Al}_2\text{O}_3$  to hydroxyapatite will retard the process of the densification.

When samples of hydroxyapatite reinforced with 20 wt %  $\text{Al}_2\text{O}_3$  were sintered at  $1400^\circ\text{C}$ , there was a dramatic change in the microstructure. The porosity of the samples was considerably reduced. Fig. 5a and b show SEM micrographs of the hydroxyapatite reinforced with 20 wt %  $\text{Al}_2\text{O}_3$  sintered at  $1400^\circ\text{C}$  for 2 h and 4 h, respectively. There is a large number of calcium aluminate particles which are uniformly distributed in the calcium phosphate matrix. The size of the particles is in the range of 2 to  $10\ \mu\text{m}$ . From the XRD results, it is known that alumina no longer exists in the samples because it has fully reacted with the calcium oxide to produce calcium aluminate. The products of the reaction are several phases depending upon the reaction between  $\text{CaO}$  and  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$  being contributed by the decomposition of hydroxyapatite [9].

Further observation using TEM on the samples was also undertaken. Fig. 6 is a typical TEM micrograph of hydroxyapatite reinforced with 20 wt %  $\text{Al}_2\text{O}_3$  sintered at  $1400^\circ\text{C}$  for 2 h showing the interface between the calcium phosphate and calcium aluminate. Clearly, further sintering at  $1400^\circ\text{C}$  up to 4 h appears to have no significant effect on the morphology of hydroxyapatite reinforced with 20 wt %  $\text{Al}_2\text{O}_3$ . It is found that the addition of alumina to hydroxyapatite not only leads to the formation of calcium aluminates, but also influences the densification during sintering as compared with pure hydroxyapatite. In general, the

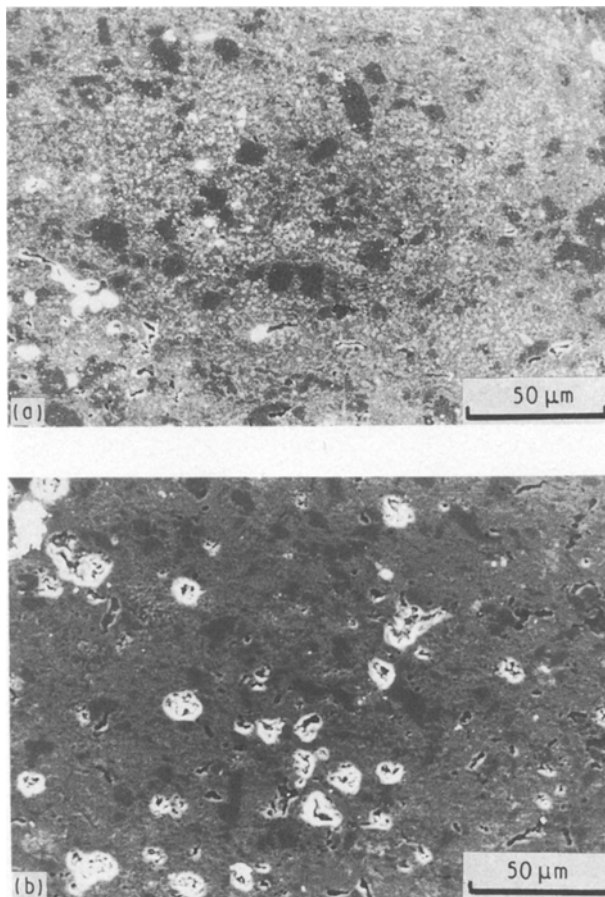


Figure 5 SEM micrographs showing overall microstructure of hydroxyapatite reinforced with 20 wt %  $\text{Al}_2\text{O}_3$  sintered at  $1400^\circ\text{C}$  for (a) 2 h and (b) 4 h (black particles are calcium aluminates).

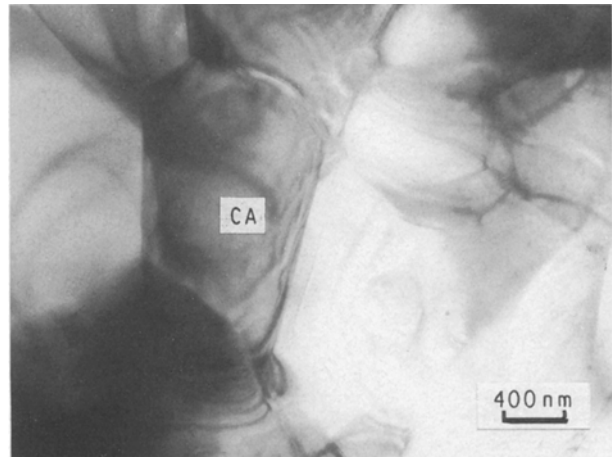


Figure 6 A typical TEM micrograph taken from hydroxyapatite reinforced with 20 wt %  $\text{Al}_2\text{O}_3$  sintered at  $1400^\circ\text{C}$  for 2 h showing calcium aluminate and calcium phosphate; CA = calcium aluminate.

process of densification during sintering has three stages: neck growth, diffusion and elimination of residual pores. The residual pores are removed and become isolated in the final stage. As the sintering temperatures increase from  $1200$  to  $1400^\circ\text{C}$ , the densification of the calcium aluminates leads to the elimination of residual pores and grain growth accompanied by shrinkage. As a result of this, the local constraint will be considerably relieved and the matrix will consequently be allowed to densify. In this stage, the porosity of the calcium phosphate matrix will be reduced to reach full densification. Obviously, the addition of the alumina influences the sintering behaviour of hydroxyapatite because the sintering rates are different between the calcium phosphate matrix and calcium aluminates. The sintering results suggest that higher temperatures are desirable for achieving dense hydroxyapatite reinforced with 20 wt %  $\text{Al}_2\text{O}_3$ , which is distinctly different from the result for pure hydroxyapatite [10].

#### 4. Conclusion

The addition of  $\text{Al}_2\text{O}_3$  to hydroxyapatite leads to a solid-state reaction between the alumina and  $\text{CaO}$  which is supplied by the decomposition of hydroxyapatite. Calcium aluminates are consequently produced by the solid-state reaction. Calcium aluminates have a different sintering rate from that of the calcium phosphate matrix and therefore influence the sintering behaviour of hydroxyapatite. The different sintering rates between calcium aluminate and calcium phosphate phases result in the need for higher sintering temperatures of over  $1400^\circ\text{C}$  in order to achieve the complete densification of hydroxyapatite with 20 wt %  $\text{Al}_2\text{O}_3$ .

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