Introduction

Hydroxyapatite [HAp] clearly has a great potential for biomedical applications because of its similarity in chemical composition and crystallA2 0 scn.278 4[hic structure to human hard tissue [1,2]. However, relatively poor strength and fracture toughness have restricted its extensive applications. A great deal of work has been done on the research and development of HAp ceramics as biomaterials [3-7]. One possible solution for improving the mechanical properties is microwave sintering of HAp [8-11].

Microwave sintering of HAp has been studied by Fang et al. [12-14]

Experimental Procedure

Raw materials

Four commercially available pre-calcined HAp powders, including P81, P88, P120 and P149 (Plasma Biotal Ltd., Tideswell, Derbyshire, England), were used. BM16 powder was prepared by bead milling P149 HAp powder, with sixteen passes. Table 1 shows the average particle size and speci c surface area of the HAp powders used in this work. For sintering studies, the powders were uniaxially pressed into pellets of 12.7 mm diameter.

Microwave hybrid heating:A 1.5 kW, 2.45 GHz variable-power microwave furnace (Ceramic Engineering, Sydney, Australia), with proportional power control (amplitude variation) and built-in mode stirrer, was used at the 65% power level for all experiments.

HAp is only weakly microwave-absorbent at low temperatures. It therefore cannot be heated from room temperature without a susceptor. However, like most ceramics, its microwave absorption capability increases with temperature [28]. erefore, a microwave hybrid heating procedure was required to heat the HAp samples from room temperature to the critical temperature (T_{crit}) above which HAp can e ciently absorb microwave radia cylindrical ZrO_2 or rod-like SiC susceptors tion.

A cylindrical clay-bonded silicon carbide susceptor (d = 60 mm, h=20 mm) was positioned around the sample. e susceptor was placed inside an alumina brick (120 × 120 × 80 mm), which was surrounded by a layer (240 × 240 × 200 mm) of brous aluminosilicate insulation (Kaowool, Morganite Industrial Products, Sydney, Australia). is arrangement is shown schematically in Figure 1. For each experimental run, one sample was placed at the centre of the susceptor. e temperature was measured with an infrared pyrometer, which was calibrated during the cool-down cycle using a Pt - Pt13Rh thermocouple. A standard heating rate of ~10,000 °C/h and soak time of 10 min were used. e mode stirrer was used at all times to produce a more uniform microwave eld distribution across the cavity.

Conventional heating: An electric furnace (300 × 200 × 120 mm) with SiC elements (Gallenkamp, London, UK) was used for the conventional heating of the control samples. A standard heating rate of 300°C.h^{-1} (the furnace maximum) and soak time of 60 min were used in all cases. No serious overshooting was observed by such a high heating rate. Two sets of experimental trials were carried out.

Comparative densi cation and decomposition behaviour:Pellets from each of the HAp powders were sintered at a range of temperatures from 900°C to 1400°C in 100°C steps by microwave and conventional heating. A er sintering, the apparent density and %HAp yield of the pellets were measured according to the methods described by Ruys et al. [29].

E ect of microwave soak time:To investigate the e ect of microwave soak time, one pellet from each powder was microwave sintered at 1100°C using soak times of 1, 3, 10 and 30 min. No conventionally sintered controls were used in this study. A er sintering, the apparent density of the pellets was measured to determine the e ects of microwave soak time on the densi cation behaviour of HAp ceramics.

Results and Discussion

Comparative densi cation behaviour

Figures 2-6 present the sintering curves of the HAp powders sintered by microwave and conventional heating. ey reveal that, with microwave sintering, densi cation began at ~900°C-1000°C, which was ~100°C-150°C lower than for conventional sintering. ese data show that the maximum densities were achieved at ~1200°C-1400°C (the sintering plateau temperature for microwave heating) for microwave heating as compared with ~1300°C-1400°C (the sintering plateau temperature for conventional heating) for conventional heating. In other words, microwave heating below the conventional heating plateau temperature signi cantly improved densi cation. However, the densities obtained above the conventional heating plateau temperature were similar for microwave or conventional heating.

e densities attained a er sintering at 1100°C using microwave and conventional sintering are shown in Figure 7. ese data show

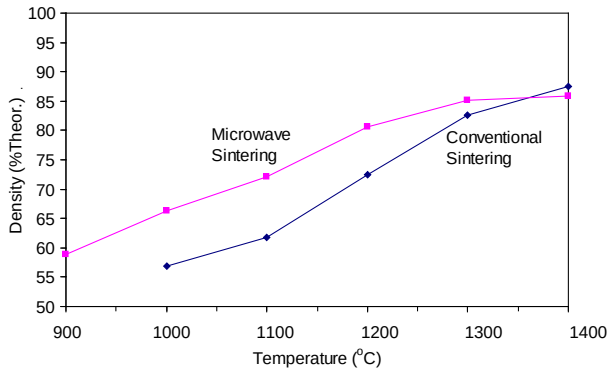


Figure 2: Comparative sintering curves for P81 HAp sintered by microwave and conventional heating.

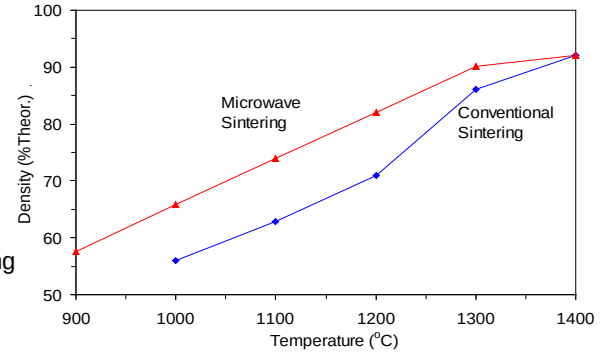
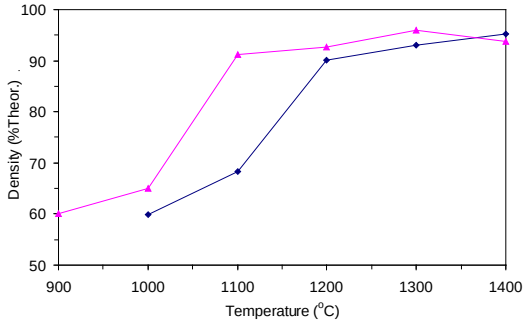


Figure 3: Comparative sintering curves for P88 HAp sintered by microwave and conventional heating.



that microwave heating signi cantly improved densi cation for each of the powders trialled. Overall, the improvement in densi cation by microwave heating at 1100°C was of the order of ~11-30%. Although the soaking time for the microwave and conventionally processed samples are di erent, the comparison is valid below the composition temperature, where no decomposition occurs. At higher temperature, however, using identical soaking times would be more reliable.

erefore the main di erence between microwave and conventional heating in this trial was the fact that densi cation occurred at lower temperatures for the former. is is advantageous in the case of HAp since lower sintering temperatures reduce the risk of decomposition. erefore, it appears that microwave sintering o ers a solution to the problem of trying to achieve maximal densi cation of HAp without the

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was crystalline while the structure of the surface was amorphous. e existence of an amorphous layer on the surface of the microwave sintered grains suggests the presence of a liquid phase at the particle surfaces during microwave sintering. is would enhance densi cation.

It has also been suggested that, in microwave sintering, the temperature between particles is higher than the apparent or measured temperature and the supposed formation temperature of the liquid phase [55]. is temperature heterogeneity will decrease the liquid viscosity in the grain boundaries. Moreover, the vibration rate and amplitude of the liquid molecules will be increased by preferential coupling of the microwaves with the liquid formed in the grain boundaries. is also will reduce the liquid viscosity. e presence of a liquid with low viscosity increases the rate of grain rearrangement, thereby enhancing the densi cation rate.

is theory has been con rmed by Tiegs et al. [56-59], who have shown that preferential coupling of microwaves with the grain boundaries in microwave heated Si_3N_4-based ceramics leads to improved densi cation. Ferber et al. [60] established that the improved creep resistance of microwave-heated Si_3N_4(6Y_2O_3-2Al_2O_3) was due to the preferential coupling of microwave radiation with the intergranular phases. It has been suggested that relatively small temperature gradients across the grains can induce a driving force to encourage densi cation [54].

Figures 3-7 shows that the temperature for the onset of densi cation for either microwave or conventional heating was lower for the powders with smaller particle size and higher surface area (such as BM16 and P120). e sintering characteristics of a powder depend on the surface area, particle size, particle size distribution, morphology and reactivity [61]. For a given chemical reactivity, densi cation at a given temperature will be enhanced with a ner particle size, higher surface area, and appropriate size distribution for dense particle packing. e temperature at which the maximum density was achieved also depended on the particle size and surface area of the powders. In case of BM16 impurities also have possibly a ected the density. It was lower for the powders with a smaller particle size and higher surface area.

Figure 7 shows that the densi cation enhancement of microwave heating was strongly dependent on the particle size of the powders. e densi cation enhancement for the ne HAp powders, such as BM16 and P120, was much greater than that for the coarser HAp powders, such as P81, P88 and P149. Compared with conventional sintering, microwave sintering of ne powder (BM16) at 1100°C led to a ~30% (64.5% versus 94.5% dense) densi cation enhancement whereas it led to only a ~11% increase in densi cation of coarse powder (62.8% versus 73.9% dense). is enhanced e ect with ner powders suggests that the particle size of the powders and, by association, the grain boundary area strongly in uenced the degree of microwave densi cation. ese accords with the theories discussed previously, where preferential coupling of grain boundaries with microwaves is one of the densi cation enhancement mechanisms of microwave sintering [49,51]. Since the ne powders have a higher surface area and higher grain boundary area, they are more susceptible to preferential grain boundary coupling.

Comparative decomposition behaviour: e %HAp yields of the samples sintered by microwave and conventional heating are shown in Table 2. e data reveal that the decomposition e ect was slightly higher for microwave sintering than for conventional sintering. HAp decomposition is a di usion controlled mechanism [62]. Since microwave heating presumably enhances di usion rates [44-56], it is possible that it could enhance HAp decomposition. However, the data suggest that the e ect of microwave heating on densi cation was much more signi cant than that on decomposition.

Tables 2 and Table 3, and Figure 6 show that, compared with conventional sintering, microwave sintering of BM16 powder at 1100°C led to a ~30% (64.5% versus 94.5% dense) densi cation enhancement whereas, it led to only a 5% increase in decomposition (76% versus 81%). e fact that densi cation is enhanced much more than decomposition is a positive result, which points to practical bene ts in processing of reinforced HAp biomaterials. e reason for this strong enhancement of densi cation (compared with a weak enhancement of decomposition) is that the decomposition rate during microwave heating was probably increased by the induced higher di usion rate, whereas densi cation was enhanced by both the induced higher di usion rate and the preferential grain boundary coupling mechanism. erefore, any disadvantage in decomposition should be partially compensated by advantages in densi cation.

E ect of microwave soak time: A number of combinations of powder type and soak time were trialled at a soak temperature of 1100°C. e results are shown in Figure 8. ese data indicate that, for three pure HAp powders (P88, P120 and P149), increasing soak times led to a slight improvement in densi cation level, although little improvement occurred for soak times above 3 to 10 min. erefore, a 3 min soak

[illegible] 1100°C was adequate [illegible] densi cation.

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31. Fang Y, Roy DM, Cheng J, Roy R, Agrawal DK (1993) Microwave Sintering of +\GUR[\DSDWLWH %DVHG &RPSRVLWHV ,Q &ODUN '(7LQJD :5 /DLD -5 (GV Microwaves: Theory and Applications in Materials Processing II, American &HUDPLF 6RFLHW\ :HVWHUYLOOH 2+

32. Janney MA, Kimrey HD (1988) Microstructure Evolution in Microwave Sintered $OXPLQD ,Q - %OHQLQJHU - +DQGZHUNHU & (GV $GYDQFHV LQ 6LQWHULQJ $PHULFDQ &HUDPLF 6RFLHW\ :HVWHUYLOOH 2+

33. Fanslow GE (1991) Microwave Enhancement of Chemical and Physical 5HDFWLRQV 0DWHU 5HV 6RF 3URF ,Q 6\QGHU :% -U 6XWWRQ :+ ,VNDQGHU MF, Johnson DL (Eds.), Microwave Processing of Materials II, Materials Research Society, Pittsburgh, PA, 43-48.

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35. .DQQH\ fect of P:C10 E5760065700051270028(1995) Microwave