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Fabrication and Characterization of Hydroxyapatite/Zircinia Composite Using Powder Press Techingue

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ABSTRACT

The objective of this study was to fabricate and characterise of hydroxyapatite (HAP)/zirconia (TZP) composite using simple technique available in our laboratory and to investigate whether chemical reaction was occurred during sintering. Ten compacts (13.5mm * 3mm) were prepared .The bulk density, porosity and shrinkage values of the fired compacts were found significantly affected by both sintering temperature and addition of zirconia, whereas the sintering time has no significant effect. The biaxial flexural strength values were increased with a reduction of porosity and the latter was affected by both sintering temperature and addition of zirconia. Also it was noted that there is considerable scope for improvement the BFS values by redusing the porosity of these composites.

KEYWORDS Hydroxyapatite, zircinia, ceramics

Introduction

The objective of research concerned with structural ceramics is the generation of materials having high reliability. To achieve this objective, there are two fundamentally different approaches: flaw control and toughening. The flaw control approach accepts the brittleness of the material and attempts to control the large extremes of processing flaws. The toughening approach attempts to create microstructures that impart sufficient fracture resistance so that the strength becomes insensitive to the size of flaws. The former has been the subject of considerable research that identifies the most detrimental processing flaws, as well as the processing step responsible for those flaws. The latter has emerged more recently, and has the obvious advantage that appreciable processing and post processing damage can be tolerated without compromising the structural reliability. [4-6]

Composite such as zirconia toughened Al2O3 (ZTA), TiC-Al2O3 and SiC-Al2O3 are currently used as wear resistant bearings and cutting tools. Various combination of a low elastic modulus bioactive materials, and a higher elastic modulus bioinert materials, can yield composites with properties that are similar to those of bone. This type of composite should eliminate stress shielding of bone because there is no mismatch in elastic modulus across the implant-bone interface. In a study perfomed by Jianguo et al. (1992), 7 a range of high-strength hydroxyapatite composites (HAp/Oxide of Alumina, Titania or Zirconia) as well as pure hydroxyapatite, alumina, titania and zirconia were densified by hot isostatic pressing. The mechanical evaluation showed that the strength of the composite materials was 3-8 times higher than that of pure hydroxyaptite and close to that of the corresponding pure oxide. However, the authors did not give the sintering temperature to produce the fired ceramics, neither did they characterise their materials to show if there was decomposition of HAp or interaction between HAp and other oxide and so it is not clear if the processed materials were genuinely composites of the two starting materials or their reaction product.

Recently investigators have demonstrated that the mechanical reliability of HAp can be improved by reinforcing HAp with Al_2O_3.[4,9-13] The main problems in producing dense composites in this system are connected with the big difference in sintering temperature of the components, the enhanced tendency of HAp to decompose during sintering and the consequent interaction between HAp and reinforced phase. Several researcher have reported[12,14-16] on hydroxyapatite-zirconia composites with different volume ratio of zirconia particles. Most of these works reflect the difficulties of retaining the HAp and ZrO_2 phases in the composites due to difference in densification temperature (e.g. HAp start to densify at 1250 ^{O}C, whereas ZrO_2 start to densify at 1400 ^{O}C), and decomposition of HAp at 1400 ^{O}C into TCP. Takagi et al.[17-25] produced HAp/ZrO_2 composites using hot isostatic pressing (HIP) at 800-1150 ^{O}C at 100 MPa for 2 hours. No phase change was found in zirconia nor in the HAp phase. The strength and the toughness achieved were respectively 190 MPa and 2.3 MPa.m$^{1/2}$. These value were approximately 20% and 100% higher than the corresponding value for hydroxyapatite ceramics without zirconia.

Thus the possible benefits of a high strength, high toughness, bioactive HAp/zirconia have not as yet been fully explored. Although hydroxyapatite is a particularly attractive material for bone and tooth root implants[29], the principal limitation of this material is that it is brittle[30].

2. MATIALS AND METHODES

Table 1: The materials used in this study

Symbol	Manufacturer	Batch No.
HAp (PB)	Plasma Biotal Ltd, (Tideswell, Derbs, UK)	P120 ONS
HAp (EC)	Euro Crystals BV (Landgraaf, Holland)	91K12-1
Y-PSZ (M)	Mandoval Ltd, UK	C0523
Y-PSZ (U)	Unitec Ceramics, Stafford, UK	UCZ 373

Table.2: BFS and %TD data of composite prepared from co position of 70/30 wt.% Y-PSZ/HAp(PB)

Parameters	HAp/Y-PSZ (U)	HAp/Y-PSZ (M)
B.F.S (MPa)	269 ± 19	176 ± 10
T.D (%)	94 ± 0.4	85 ± 0.8

Table .3: Theoretical Densities of Various Composition Made from HAp and ZrO_2

Mixture / wt %	Mixture / vol %	Density / ρ m
100 wt % HAp	100 vol % HAp	3.156
90 wt % HAp : 10 wt % ZrO_2	94.5 vol % HAp : 5.5 vol % ZrO_2	3.315
70 wt % HAp : 30 wt % ZrO_2	81.7 vol % HAp : 18.3 vol % ZrO_2	3.685
50 wt % HAp : 50 wt % ZrO_2	66 vol % HAp : 34 vol % ZrO_2	4.148
30 wt % HAp : 70 wt % ZrO_2	45 vol % HAp : 55 vol % ZrO_2	4.745
10 wt % HAp : 90 wt % ZrO_2	18 vol % HAp : 82 vol % ZrO_2	5.542
100 wt % ZrO_2	100 vol % ZrO_2	6.05

Powder Characterisation

The particle size distribution of the starting milled HAp powder was determined using PSA (laser diffraction method). The standard methods of XRD (CuK radiation) and DTA was used to characterise the starting powders and the fired composites.

Specimens Preparation and Firing

Ten compacts (13.5mm 3mm) were prepared from each composition using powder press technique. The compacts were formed by applying a load of 3 tonnes for 1 min, removed from the die and fired at 1450°C in air atmosphere for 6 h. Compacts formed from a composition of 50 wt % HAp/50 wt % ZrO_2 were fired from 1100 to 1450°C for a sintering time of 3, 6 or 12 h.

Microstructure Examination

Polished section were prepared by vacuum impregnating compacts with epoxy resin, followed by polishing with SiC paper and diamond pastes down to 1 m. Back scattered imaging was used for polished sections (after coated with carbon) of various composition of ZrO_2:HAp composite, fired at 1450°C for 6 h to examine the microstructure and to show the distribution of zirconia within the HAp matrix. Energy dispersive X-ray analysis (EDX) was employed to identify the phases of the composite material

3.RESULTS

PSA data are presented in Figure 9.1. The mean particle size of zirconia is 0.5 ± 0.4 m and for the milled hydroxyapatite is 2.6 ± 1.4 m which was significantly reduced compared to the starting HAp powder (5.12m, see section 8.5.1). The milling process reduces the particles size which may lead to better homogeneity and densification process of HAp with ZrO_2, and enhanced sinterability.

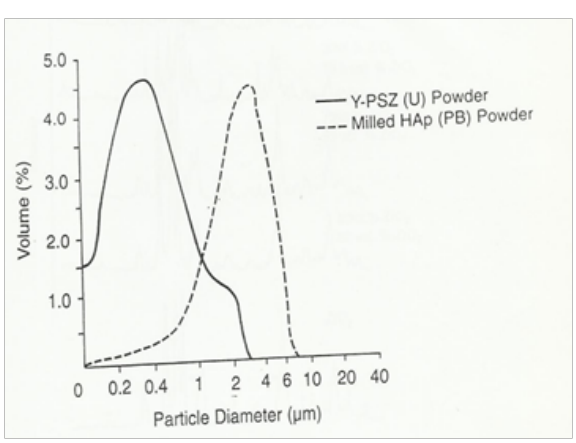


Figure 1: Particles size distribution of HAp(PB) after milling, compared with Y-PSZ (U) strating powder.

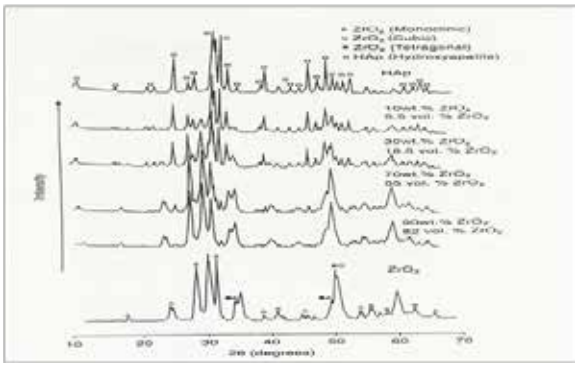


Figure 9.2 shows the X-ray diffraction patterns of the starting powder of various compositions of ZrO_2/HAp composite. All green powders showed only the diffraction peaks of tetragonal, cubic, or monoclinic zirconia and hydroxyapatite.

Figure .2: XRD traces of various compositions of green Y-PSZ(U):HAp(PB) composite.

XRD data for the fired composites made from composition of 70/30 wt% HAp/ZrO_2 and for 30/70 wt% HAp/ZrO_2 are shown in Figures 9.3 & 9.4 respectively, for composites which were powder pressed and fired in air atmosphere at various sintering temperatures for 6 h. All specimens showed only the diffraction peaks of zirconia and of hydroxyapatite up to 1250 ^{O}C. No sign of phase change was found either in zirconia or hydroxyapatite phase. The specimen annealed at 1350 ^{O}C and higher shows strong peaks of cubic zirconia and weak peaks of tricalcium phosphate (TCP), which is the decomposition product of hydroxyapatite. Peaks attributable to calcium zirconate were detected as well.

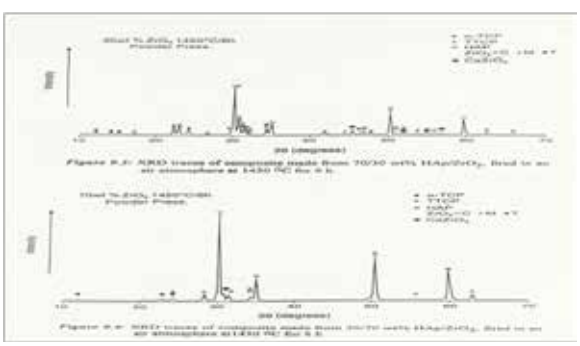


Figure 9.5 a and b shows DTA curves of 70/30 and 30/70 wt% HAp/ZrO_2 composite powder respectively, which indicate that there was an endothermic effect at 1350 ^{O}C which is due to the decomposition of HAp into TCP for the former composite because higher amount of HAp than the latter, whereas for the latter composite

there was an endothermic peak situated at about 1200 which indicates the transformation of monoclinic to tetragonal zirconia. At about 1450 ^{O}C further endothermic peaks were observed, which is due to decomposition of HAp and/or an interaction between CaO and zirconia to form calcium zirconate, which was confirmed by the XRD results.

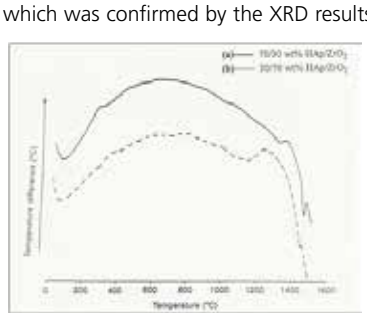


Figure 5: DTA Curve analysis for composite made from (a) 70/30 wt% HAp/ZrO2 and (b) 30/70 wt% HAp/ZrO2.

Back scattered images are presented in Figure 9.6 a,b,c, and d, for a polished section of various composites made from compositions of 10, 30, 50 and 70 wt% ZrO_2 respectively, fired at 1450 ^{O}C for 6 h. These show that the composite start out as a matrix of HAp with a fine dispersion of zirconia and gradually alter to a zirconia matrix with a dispersion of HAp. The porosity (dark black regions) appeared to decrease with zirconia addition as can be seen in Figures 9.6. EDX (Table C.5, appindex C), analysis showed that the dark regions correspond to the calcium phosphate phase, and the bright regions correspond to the zirconia. The wet mixing method used in present study has the potential to obtain homogenous microstructure of green compacts as can be seen in the BSI of powder pressed composites in Figures 9.6.

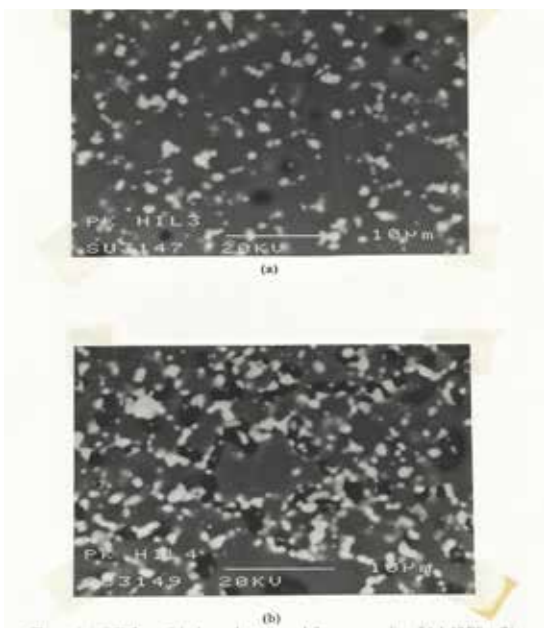
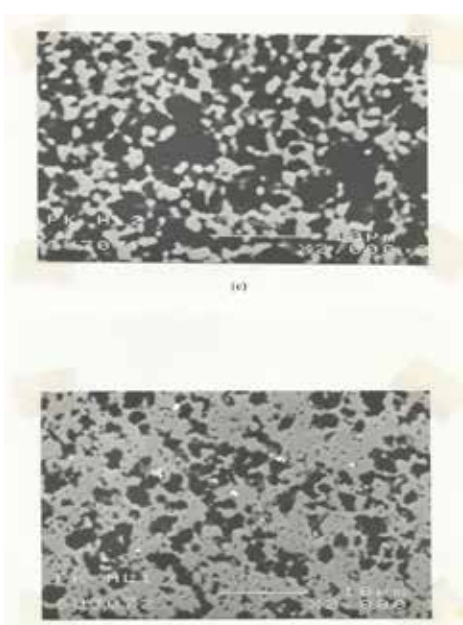


Figure 6: BSI for polished samples prepared from composite of (a) 10/90 wt% ZrO2/HAp and (b) 30/70 wt% ZrO2/HAp, fired at 1450 oC for 6 h in an air atmosphere. Original mag. 2000 (Scale bar = 10 m).



The theoretical density and linear firing shrinkage values are presented in Figure 9.7-9.10, as a function of sintering temperature and time for compacts formed from composition of 50/50 % HAp/ZrO_2 by weight. Both theoretical density and linear firing shrinkage values increased with increasing sintering temperature whereas sintering time has relatively little effect. All these variables are affected primarily by the densification behaviour of the zirconia powder which started to densify at 1400°C.

Small additions of zirconia powder to the HAp caused a increase in the true porosity values and consequent decrease in the theoretical density values as shown in Figure 9.11. With more zirconia addition the porosity reduced with a gradual increase in the density. The linear

shrinkage increased with zirconia content and showed at the highest value for composite containing 90 wt% zirconia as presented in Figure 9.12. The SEM micrographs (Figure 9.6) of the fired and polished microstructures of composite containing various amount of zirconia show a general agreement in the extent of porosity of the mixtures of hydroxyapatite and zirconia when compared with the calculated porosities.

Figur 9.11 also shows that small additions of zirconia to HAp caused a sharp drop in the % TD. Equally small addition of HAp to zirconia caused a larger than expected drop in % TD. Thus small additions of one powder to the other had a disproportionate effect. Also it can be noted that there is no benefit from the addition of zirconia until vol % > 50 % when a zirconia matrix is formed. Any potential benefit at lower vol % is lost due to increased porosity.

The biaxal flexural strength values for test-pieces prepared from a composition of 50/50 wt% HAp/ZrO_2 (Figure 9.13 and 9.14) increased when increasing both the sintering temperature and time. The addition of zirconia resulted in a considerable increase in the biaxial flexural strength when the zirconia content was greater than 70 wt% (i.e. 50 vol. %). This is believed to be due to a combination of achieving a high density and the formation of a zirconia matrix as can be seen in Figure 9.15 and 9.16.

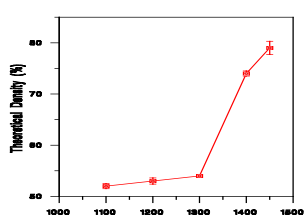


Figure. 7: Theoretical density (%) plotted as a function of sintering temperature for samples prepared from composition of 50/50 wt% HAp/ZrO2, fired for 6 h in an air atmosphere.

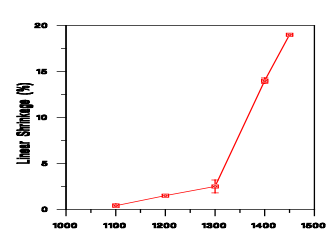


Figure 8: Linear shrinkage (%) plotted as a function of sintering temperature for samples prepared from composition of 50/50 wt% HAp/ZrO2, fired for 6 h in an air atmosphere.

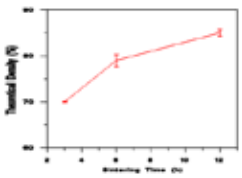


Figure 9: Theoretical density (%) plotted as a function of sintering time for samples prepared from composition of 50/50 wt% HAp/ZrO2, fired at 1450 oC, in an air atmosphere.

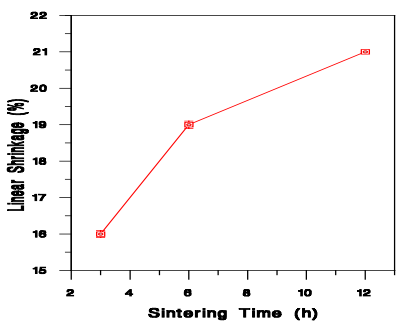


Figure.10: Linear shrinkage (%) plotted as a function of sintering time for samples prepared from composition of 50/50 wt% HAp/ZrO2, fired at 1450 oC, in an air atmosphere.

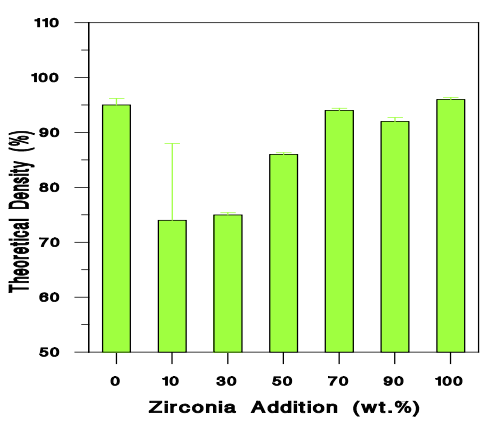


Figure.11: Theoretical density (%) plotted as a function of zirconia addition to hydroxyapatite, fired at 1450 oC for 6 h in an air atmosphere.

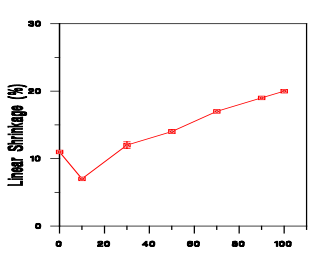


Figure.12: Linear shrinkage (%) as a function of zirconia addition to hydroxyapatite, fired at 1450oC for 6 h in an air atmosphere.

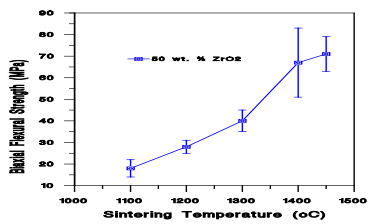


Figure.13: Biaxial flexural strength plotted as a function of sintering temperature for samples prepared from from composition of 50/50 wt% HAp/ZrO2, fired for 6 h, in an air atmosphere.

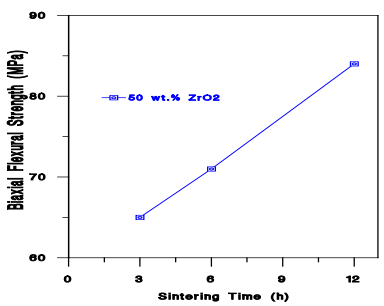
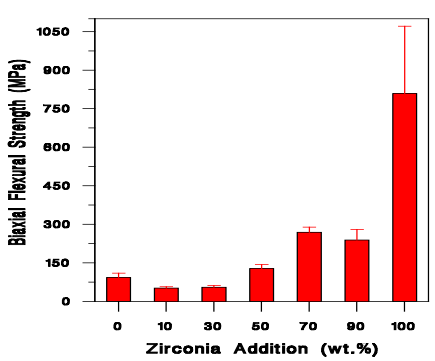


Figure.14: Biaxial flexural strength plotted as a function of sintering time for samples prepared from from composition of 50/50 wt% HAp/ZrO2, fired at 1450 oC, in an air atmosphere.



4- DISCUSSION

As shown in Figure 9.7, densification of the HAp/ZrO_2 composite does not begin to take place to any great degree until sintering temperatures in excess of 1350 ^{O}C are used, when employing a simple cold powder pressing and firing technique. Further increasing the sintering temperature resulted in an increase in the theoretical density and linear shrinkage values (Figure 9.8). The corresponding increase in biaxial flexural strength values is thus primarily due to the densification process (Figure 9.13).

This was also noted in our XRD and DTA data for the fired composite with the formation of a small amount of calcium zirconate. To minimise the diffusion of Ca, the sintering tem-

perature would have to be reduced. However, this is difficult because at lower sintering temperatures densification is compromised in the powder press technique.

The addition of zirconia resulted in a considerable increase in the biaxial flexural strength when the zirconia content was greater than 60 wt% (i.e. 50 vol%). This is believed to be due to a combination of achieving a high density and the formation of a zirconia matrix (Figure 9.11, 9.15 and 9.16).

In both mechanisms the increasing value in toughness is proportional to the volume fraction of dispersed particles of ZrO_2. Recently Takagi et al.[20] achieving considerable reduction of densification temperature in a composite ceramic containing zirconia particles dispersed in HAp using hot isostatic pressing.

5. CONCLUSIONS

1. Sintering temperature and addition of zirconia affected the densification behaviour of HAp/ZrO_2 composite, whereas the firing time had relatively little effect.

2. The biaxial flexural strength increased with an increase both in sintering temperature and addition of zirconia.

3. The XRD and DTA data suggested that there was interaction between zirconia and HAp, with formation of calcium zirconate.

4. Excessively high processing temperature are needed to densify the composite, resulting in breakdown of HAp.

5. There is considerable scope for improvement in the strength of calcium phosphate/zirconia composites by reducing the porosity.

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