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The effect of low levels of zirconia addition on the mechanical properties of hydroxyapatite

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Calcium phosphate ceramics are popular materials for bone reconstruction and reinforcement. One of the calcium phosphate series of compositions, Hydroxyapatite, $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$, HA], exhibits excellent bio-activity, but its suitability for major load bearing applications is severely limited by its poor mechanical properties. While HA is strong in compression, it is extremely susceptible to tensile and fatigue failure [1].

Previous attempts have been made to improve the strength of HA by the incorporation of a ZrO_2 second phase. A range of HA/ ZrO_2 composites, produced using a variety of methods, zirconia compositions, reagent grades and mixing conditions, have been reported in the literature. While the HA phase was usually produced by the method of Hayek and Newesely [2], other processing conditions varied greatly. For example, Yamashita *et al.* [3] mixed a Ca-PSZ (partially stabilized zirconia) reinforcing phase with synthesized HA and Takagi *et al.* [4] performed similar experiments with 0–27 wt% fine commercial tetragonal zirconia polycrystals (TZP). Ioku *et al.* [5] dispersed fine yttria-stabilized ZrO_2 in di-ammonium hydrogen orthophosphate, then synthesized HA by the addition of calcium nitrate. Aoki [6] mixed HA with monoclinic ZrO_2 , at weight ratios of 3 : 1 and 1 : 1 and then sintered the green bodies. The lack of a standard methodology has made it difficult to determine the amount of a zirconia-based second phase required to reinforce the hydroxyapatite phase effectively. The objective of this work is to determine the ideal amount of ZrO_2 to add to the HA, which will be enough to reinforce the composite without being so much as to exacerbate the decomposition of the HA during sintering.

In this study, composites were produced by combining commercial HA and ZrO_2 grades. The HA powder, P120, was supplied by Plasma Biotol Ltd. (Tideswell, UK) and the ZrO_2 powder, Y_2O_3 -stabilized zirconia, termed Biograde 2 and described as ZrO_2 from here-with, was supplied by Morgan Matroc Ltd. (Rugby, UK).

The particle size, morphology and surface area of both powders were measured and the calcium to phosphorus ratio and the trace element impurity content of the HA were determined by X-ray fluorescence (Ceram

Research Ltd., Stoke on Trent, UK), prior to composite production.

Mixtures of P120 and 0 to 20 wt% Biograde 2, making up a dry powder weight of 50 g, were milled in a porcelain mill pot, using 200 ml of double distilled water and alumina balls as milling media for one hour. After milling, the resultant slurries were oven dried (85°C , 24 h).

Sintering was undertaken in a Carbolite STF 1600 $^\circ\text{C}$ furnace in an air atmosphere. Sintering commenced at room temperature, at a ramp rate of $2.5^\circ\text{C min}^{-1}$, dwelling at 400°C for 240 min, then ramping again to 1220°C , for a dwell of 800 min, before furnace cooling to room temperature.

The density of each sintered disc was determined using Archimedes' principle, as described elsewhere [7].

Samples of the composites and the pure HA control were analyzed using a Siemens D5000 X-ray diffractometer, with Cu K_α radiation at 30 mA, 40 kV. Scans were performed between 2θ values of 5° and 110° , with a step size of 0.02° . The diffraction lines from the scans were matched with the ASTM standards for HA and ZrO_2 and extraneous peaks were identified using ASTM and JCPDS standards. The ratio of the phases that were present in the as-sintered composites could be determined by employing the simple height law [8].

After chemical characterization, the mechanical properties of the samples were determined. The as-pressed surfaces of the sintered discs were analyzed by Vicker's micro-hardness indentation. A 500 g load was applied for 10 s and the height and width of the resultant diamond shaped indents were measured and averaged. This procedure was undertaken six times to determine a mean hardness value for each disc, calculated using the method described in ASTM E384-84. The flexural strengths of the sintered discs were measured using an Instron 4644 Universal Testing Machine with a 2 kN load cell. A concentric ring test, essentially a four point bend flexure test, involved the application of the load to a disc sample. The discs were placed on a support ring of 15 mm diameter, balanced on freely rotating ball bearings, and loaded at the center. Ten discs were tested for each condition.

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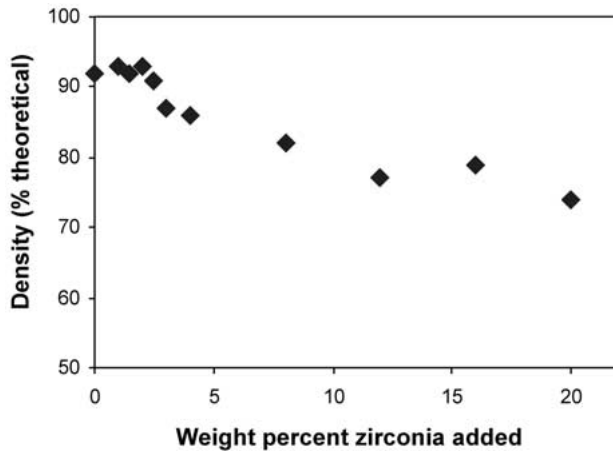


Figure 1 Density vs. wt% reinforcement for the HA/ZrO₂ composites.

The HA contained the expected low levels of impurities [9, 10], although large amounts of these were removed by washing and filtering, so it is unlikely that they had any adverse effects upon mechanical performance. It is likely that manganese was present in trace quantities since the unfilled specimens turned blue after sintering.

The mean particle size of the spherical P120 HA powder particles was $D_{0.5} = 2.89 \mu\text{m}$, the specific surface area was $13 \text{ m}^2 \text{ g}^{-1}$ and the Ca : P ratio was 1.70. The particle size of the spheroid Biograde 2 ZrO₂ powder particles was $D_{0.5} = 15.51 \mu\text{m}$ and the specific surface area was $3.7 \text{ m}^2 \text{ g}^{-1}$.

The sintered densities of the P120/Biograde2 HA/ZrO₂ composites were constant for up to 2.5 wt% ZrO₂ additions, at approximately 92% of the theoretical density. When the level of zirconia addition was greater than 2.5 wt%, the sintered density decreased with increasing amounts of ZrO₂ (see Fig. 1), decreasing down to a value of 74% for the sample containing 20 wt% ZrO₂.

After sintering, a selection of composites across the range of additions were analyzed by X-ray diffraction to determine their phase compositions, Table I.

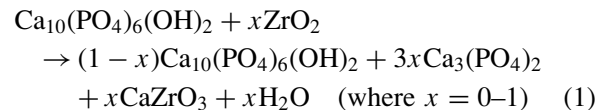
It has been reported that HA can decompose to TCP (tricalcium phosphate) and TeCP (tetra calcium phosphate) at temperatures in excess of 1000 °C and that the TeCP further decomposes to TCP and CaO at yet higher temperatures [11–13]. It is accepted that the level of decomposition increases for lower Ca : P ratios, as the material is then calcium deficient. The Ca : P ratio of the HA in this study is 1.70, implying that the level of inherent decomposition during sintering at tempera-

TABLE I Phases present in a selection of the composites, as determined by X-ray diffraction

wt% ZrO ₂	Phases
0	100%HA
2	80%HA, 10%CZO, 5% α -TCP, 5% β -TCP
16	20%CZO, 38% <i>c</i> -Z, 7% α -TCP, 35% β -TCP

where HA hydroxyapatite Ca₅(PO₄)₃(OH), TCP tricalcium phosphate Ca₃(PO₄)₂, CZO calcium zirconate CaZrO₃, *c*-Z cubic zirconia ZrO₂.

tures greater than 1000 °C will be minimal. The literature shows that when HA is mixed with 20 wt% ZrO₂, phase transformation occurs extensively [14] and is exacerbated with increasing temperature. ZrO₂ acts as a phase impurity much in the way that MgO acts in Al₂O₃ [15], in that it enhances the densification rate and reduces grain boundary mobility, restricting the time for abnormal grain growth. This research agrees with the literature in that the HA without any ZrO₂ addition did not exhibit any phase decomposition when sintered at 1220 °C, but when mixed with ZrO₂, it reacted to form TCP and calcium zirconate, Table I.



The extent of the decomposition reaction increased with increasing ZrO₂. The molecular weights of ZrO₂ and HA, 123 and 1005, respectively, imply that greater than approximately 10 wt% ZrO₂ ($x = 1$ in Equation 1) is required for all the HA to decompose fully to form TCP. The results from this work agree with the theory. The addition of 2 wt% ZrO₂ ($x = 0.17$) resulted in some HA reacting with the ZrO₂, but the sintered material was still 80% HA. The addition of 16 wt% ZrO₂ ($x = 1.55$ in Equation 1) caused all the HA to react to TCP and CaZrO₃. The excess ZrO₂ was transformed to its cubic polymorph, suggesting some incorporation of Ca into the tetragonal structure. Less CaZrO₃ was observed for this composition than would be expected from Equation 1, but it is possible that some of the CaZrO₃ reacted with the ZrO₂ to stabilize the tetragonal ZrO₂ to the cubic form by the incorporation of Ca ions.

The microhardness of the samples was measured and plotted against the weight percent ZrO₂ addition (see Fig. 2). The micro-hardness peaked at around 1.5 wt% ZrO₂ addition, followed by a gradual decrease.

The flexural strength of the samples was also plotted against weight percent ZrO₂ addition (see Fig. 3). A maximum in flexural strength (averaging 46 MPa)

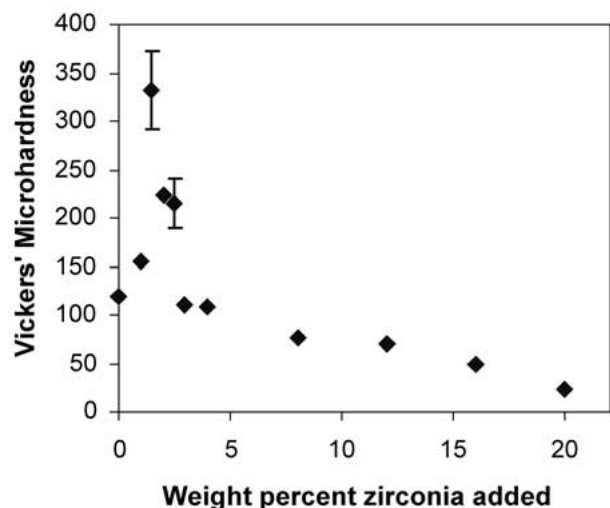


Figure 2 Microhardness vs. wt% reinforcement for the HA/ZrO₂ composites.

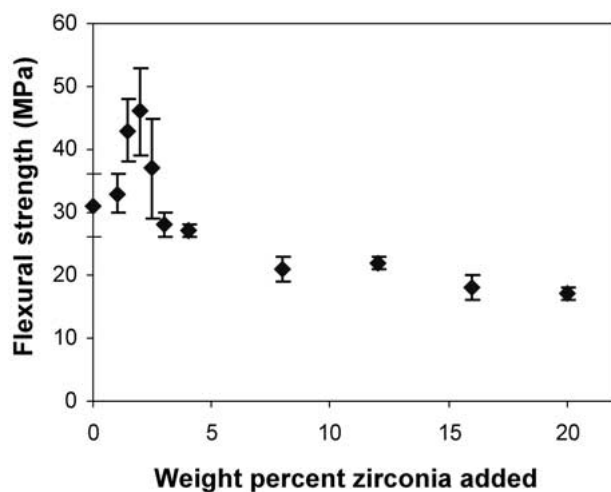


Figure 3 Flexural strength vs. wt% reinforcement for the HA/ZrO₂ composites.

occurred at approximately 2 wt% ZrO₂ addition, close to the peak in micro-hardness results (1.5 wt% ZrO₂, Fig. 2).

The flexural strength and micro-hardness values of the different compositions were plotted against their sintered densities to illustrate if a relationship existed, Fig. 4. If the data points corresponding to the HA/ZrO₂ compositions containing 1.5–2.5 wt% ZrO₂ (with densities between 91 and 93%) were ignored there was a reasonable linear relationship between the mechanical properties and sintered densities. The flexural strength and microhardness values of the compositions containing 1.5–2.5 wt% ZrO₂ were significantly larger than such a linear relationship would suggest. Indeed, extrapolating the linear relationship described above to a value of 100% sintered density would yield approximate flexural strength and microhardness values of 35 MPa and 150 H_v, respectively. In contrast, the values obtained for the composite with a 1.5 wt% ZrO₂ addition had flexural strength and microhardness values of 43 MPa and 330 H_v. The results presented in Fig. 4 suggest that the enhanced mechanical properties observed for compositions containing 1.5–2.5 wt% ZrO₂ were not due directly to their sintered densities.

Some ceramics retain residual porosity as a consequence of the fabrication process, normally as small

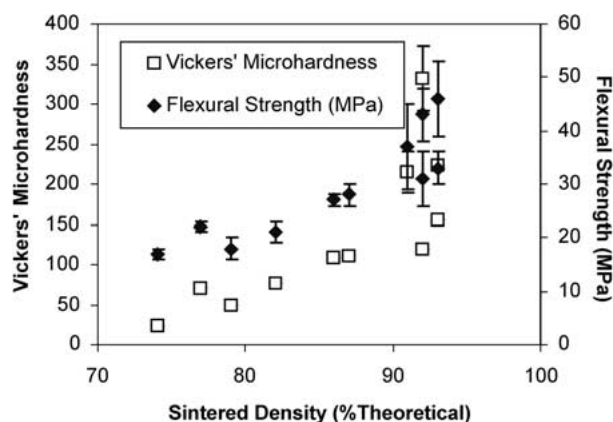


Figure 4 Microhardness vs. flexural strength for the HA/ZrO₂ composites.

isolated pores, which reduce the cross-sectional area across which the load is applied. As a consequence of its design, the concentric ring test employed to measure flexural strength exposes a relatively large volume of material to stress, in comparison to conventional 3 and 4-point bend tests. The larger the stressed area, the higher the possibility of a flaw being present. Thus strength measured by more conventional means would be expected to be higher than that measured by the concentric ring test. This was confirmed when comparing the flexural strength of HA synthesized in this work with corresponding results from the literature [16–18]. It is difficult to directly compare the strengths of the composites recorded in this work with those in the literature, as previous work has concentrated on composites with higher levels of addition of ZrO₂.

The hardness of HA with no ZrO₂ added was 120 Hv; lower than the values reported in the literature [4, 19], but higher than the hardness of bone [20]. From this study it may be deduced that the amount of ZrO₂ required to increase significantly both the hardness and flexural strength of HA was approximately 2 wt%. Higher flexural strength values were found in samples with lower intergranular porosity, agreeing with the literature [16].

This work has determined that, when producing composites for load bearing applications, the low level addition of ZrO₂ to HA (2 wt%) results in a composite with better mechanical properties than pure HA but with minimum levels of decomposition to less bioactive products such as β -TCP, a phase which often forms during the sintering of HA, and is more soluble, less bioactive and weaker than HA [21]. The enhanced mechanical properties observed for compositions containing 1.5–2.5 wt% ZrO₂ were probably due to either a smaller grain size or an optimum phase composition.

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