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Novel processing of hydroxyapatite-zirconia composites using nano-sized particles

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Hydroxyapatite, HA, is employed in the repair of skeletal defects, because it closely resembles the mineral phase in bone and is bioactive. However, its relatively poor strength has limited its use in major load-bearing applications. Attempts have been made to improve the strength of HA by the incorporation of a second ceramic phase, such as ZrO₂ phases (e.g. yttria-doped tetragonal zirconia polycrystals, Y-TZP), but the addition of a second phase can have inherent disadvantages.

Sintering HA {Ca₁₀(PO₄)₆(OH)₂} at high temperatures can result in the formation of decomposition products such as tri-calcium phosphate, TCP {Ca₃(PO₄)₂} and tetracalcium phosphate, TeCP {Ca₄(P₂O₉)} [1, 2]. TeCP can decompose further to TCP and calcium oxide [CaO] at higher temperatures. These secondary phases have, in certain instances, been reported to adversely affect the biological response [3, 4].

When a ZrO₂ phase, such as Y-TZP, is added to HA, high temperatures of 1200–1400 °C are commonly required to sinter these composites to high density, but HA has been reported to be thermally unstable above 1300–1400 °C [5, 6]. It has commonly been observed that phase transformations/decompositions occur extensively during sintering of these composites at temperatures even below 1200 °C. For example, at 1150 °C, HA will react with the ZrO₂ phase, with the formation of cubic calcia-stabilized ZrO₂, and subsequently calcium zirconate (CaZrO₃) [7]. Increasing the sinter temperature further increases the amounts of β-TCP and CaZrO₃. At a sinter temperature of 1400 °C, virtually no HA remains and some α-TCP forms from β-TCP. This phase decomposition means that the advantage of combining a low-strength bioactive ceramic (HA) with a high-strength, bioinert ceramic (Y-TZP) is lost. This problem of decomposition reactions between the HA and the ZrO₂ phases during sintering have limited the applications of this composite, as the mechanical and biological properties are compromised by the formation of undesirable secondary phases.

In this study, a novel approach has been used to produce composites of HA with ZrO₂ (Y-TZP) additions between 0 and 10 wt % at a low sinter temperature (750 °C), in order to limit the amount of reaction between the HA and ZrO₂. The aim was to find a

ZrO₂ loading level that would be expected to improve strength while limiting the decomposition of the HA.

Samples of pure HA were produced at a synthesis temperature of 45 °C by a simple precipitation method [2]. A dilute solution containing 78.72 g Analar (analytical reagent) grade diammonium hydrogen orthophosphate (BDH supplies, Leicestershire, UK), made basic by the addition of 10 ml of Analar grade ammonium hydroxide (BDH supplies, Leicestershire, UK), was added to a dilute solution containing 26.41 g Analar grade calcium nitrate (BDH supplies, Leicestershire, UK), also made basic by the addition of 25 ml of Analar grade ammonium. Addition was by a dropping funnel, taking one hour for completion, and the sample was then left to stand (24 h; 45 °C).

After 24 h, the suspension had separated, and the clear aqueous layer was decanted, then the remaining slurry was washed with de-ionized water, re-stirred and left to stand again. This procedure was undertaken three times, to remove any unwanted residue from the sample. The suspension was then filtered and the filtercake was washed and filtered again until most of the water had been removed. This method precipitated 28 g of HA.

The composites were produced by adding 1, 2, 3, 4, 6 and 10 wt% Y₂O₃-ZrO₂ sol (Tioxide Ltd, Billingham, UK) to the HA during precipitation. The appropriate weight of sol for a given wt% addition was diluted in 100 ml of distilled water, stirred and then added to the calcium nitrate solution, prior to the addition of the ammonium phosphate solution. The precipitation was then conducted as for the pure HA.

The particle morphology of the precipitated mixture was studied by placing a drop of the HA/ZrO₂ suspension onto a 3 mm diameter copper grid, fitted with a carbon support film. Any excess solution was removed using absorbent paper. The sample was then inserted into a Jeol TEM 2010. The TEM was evacuated and the filament saturated (accelerating voltage, 200 keV). The objective aperture was inserted and corrections were made for astigmatism.

The HA particles synthesized at 45 °C were elliptical in nature, with particle lengths of approximately 50–300 nm and widths of approximately 3 nm, Fig. 1. The

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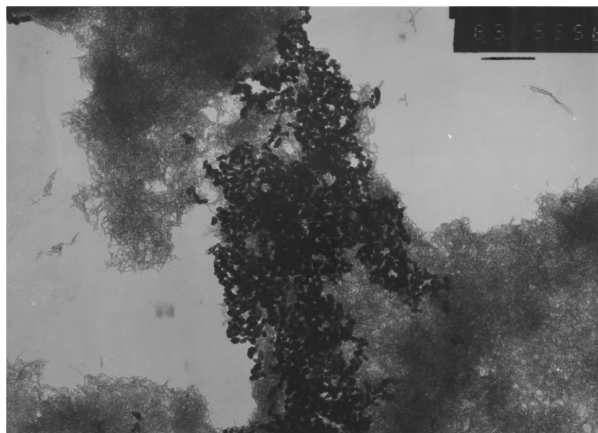


Figure 1 TEM micrograph of HA-ZrO₂ composite, synthesized at 45 °C (+/-3 °C). The marker indicates 200 nm.

ZrO₂ sol particles were spherical in morphology and approximately 50 nm in diameter.

Following filtration, the residue was transferred into cotton wool for drying. This cotton wool was 25 cm thick in order to approximate to an infinite layer of insulating still gas. The residue was dried slowly in air and the samples were weighed every day until constant weights were obtained. The dried composites were then removed from the cotton wool. This method has been used previously to produce HA and carbonate-substituted HA ceramics with high densities at low sintering temperatures [8]. Sintering was undertaken in a Carbolite STF 1600 °C furnace in an air atmosphere. Sintering commenced at room temperature, at a ramp rate of 1 °C min⁻¹, dwelling at 400 °C (240 minutes), then ramping again at 2.5 °C min⁻¹ to 950 °C (800 min), before furnace cooling to room temperature.

The density of each sintered disc was determined by Archimedes' principle. The discs were first weighed in air and then their buoyancy in water was determined. Sample density was then calculated by the formula:

$$\text{Sample density} = \left(\frac{\text{sample weight}}{\text{sample buoyancy}} \right) \times \text{density of test liquid}$$

The percentage density was calculated using:

$$\% \text{ Density} = \left(\frac{\text{sample density}}{\text{HA fully sintered density}} \right) \times 100$$

for the HA control and

$$\% \text{ Density} = \left(\frac{\text{sample density}}{\{ \text{HA fully sintered density} \times \text{wt\% HA} \} + \{ \text{ZrO}_2 \text{ fully sintered density} \times \text{wt\% ZrO}_2 \}} \right)$$

for the composites where:

$$\begin{aligned} \text{Density of water} &= 0.998 \text{ Mg m}^{-3} \text{ (at 20 C)} \\ \text{Density of fully sintered HA} &= 3.156 \text{ Mg m}^{-3} \\ \text{Density of fully sintered ZrO}_2 &= 5.7 \text{ Mg m}^{-3} \end{aligned}$$

The density data were collected from only one sample per composition, due to the long drying times required to produce each composite.

TABLE I Level of phase transformation of HA as a result of ZrO₂ addition, for the HA/Y₂O₃-ZrO₂ sol, synthesized at 45 °C, sintered at 950 °C

wt% sol	0	1	2	3	4	6	10
Percentage phase transformation as a result of ZrO ₂ addition.	—	0	0	0	0	2	16

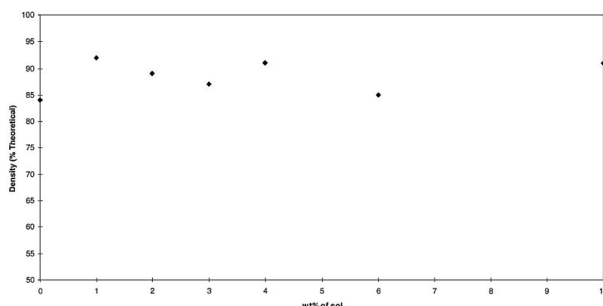


Figure 2 Sintered density of the HA/ZrO₂ composites sintered at 950 °C.

The sintered samples all had densities greater than 85% of theoretical density, with the HA control being the least dense, Fig. 2. This suggests that using reagents with small particle sizes coupled with a low sintering temperature will result in the production of relatively dense sintered bodies.

Samples of the composites and the pure HA control were analyzed using a Siemens D5000 goniometer, with a 710 X-ray generator (Cu K_α radiation at 40 mA, 40 kV). Scans were performed between 2θ values of 5° and 110°, with a step size of 0.02°. The peaks from the scans were matched with the ASTM standards for HA, TCP and ZrO₂ phases 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 [9]. The *a* and *c* lattice parameters of the HA crystal structure in the pure HA and the composites were determined by Rietveld analysis of the diffraction profiles.

The phases evident in the XRD traces were identified and are shown in Table I as a percentage of phase transformation relative to the HA with no zirconia addition. The ZrO₂ additions up to 6 wt% did not affect the phase composition of HA, and only additions of 6 and 10 wt% ZrO₂ resulted in an increase in the amount of β-TCP formed. However, calculations using the simple height law may only be accurate to 10% [9].

There was no variation in the *a* and *c* axes of the samples with increasing amounts of ZrO₂, suggesting that solid state ionic substitution did not occur during the heat treatment. Lattice parameter *a* was consistently measured as 0.9418 nm and *c* was measured as 0.6878 nm, within a range of ±0.0001 nm, Table II.

Agreeing with the literature [5, 10], the presence of ZrO₂ did affect the TCP content, although this was only

TABLE II Lattice parameters of the HA/Y₂O₃-ZrO₂ sol, synthesized at 45 °C, sintered at 950 °C

wt% sol	0	1	2	3	4	6	10
<i>a</i> (nm)	0.9148	0.9419	0.9149	0.9418	0.9418	0.9417	0.9419
<i>c</i> (nm)	0.6879	0.6878	0.6878	0.6879	0.6877	0.6878	0.6879

observed in this study at higher ZrO₂ levels, with a threshold level of 6 wt% additions. Increasing the ZrO₂ content beyond 4 wt% has a similar effect to increasing the sintering temperature, in that HA decomposition is encouraged.

This novel processing route, employing starting materials of nano sized particles and a low sinter temperature, produces high-density HA-ZrO₂ composites. The small ZrO₂ loadings and sintering temperature used ensured that the HA did not decompose at the levels that have been observed with conventional processing routes, which require high (> 1200 °C) sintering temperatures. The formation of dense composite specimens that still retain the primary phases of hydroxyapatite and Y-TZP implies that the mechanical properties of these materials may be improved compared to HA alone.

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