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Short Communication

Zirconia–Calcium Phosphate Composites for Bone Replacement

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Abstract: Bioceramic composites utilizing the good mechanical properties of ZrO_2 and the biocompatibility of calcium phosphate have been developed. Sintered samples containing various proportions of yttria-stabilized zirconia and calcium phosphate powders have been produced. Optical and scanning electron microscopic techniques have been used to characterize the microstructural features. Diametral compression strengths of composites have been measured after various treatment times in Ringer's solution. The data indicate that the strength and toughness of calcium phosphates used in clinical applications may be improved through the addition of zirconia particles. © 1997 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Calcium phosphate ceramics have gained widespread attention due to their compositional and structural similarity to the mineralized constituent in hard tissues.[1] Hydroxyapatite is the main mineral constituent of natural bone, and thus synthetic calcium phosphate ceramics may create an excellent bond with natural tissue and can even stimulate new bone growth. These ceramics have been used extensively for dental applications, bone grafts, or as bioactive coatings. However, due to their relatively low strength and toughness, susceptibility to physiological attack, and poor fatigue properties, the biomedical uses of calcium phosphate ceramics are limited to non-load bearing applications.

One of the most promising approaches to increase the strength in ceramics is through transformation toughening based on the tetragonal–monoclinic transformation of zirconia.[2] In this case, a ceramic with dispersed tetragonal zirconia can be used to enhance the strength and toughness. In recent years, zirconia has received considerable attention as an orthopaedic material for several reasons, including: (a) high strength with low modulus, (b) low wear rate with polyethylene, (c) ability to polish the surface to achieve a fine surface finish, and (d) good biocompatibility.[3] In this investigation, yttria-stabilized zirconia and calcium phosphate powders were used to produce a biocomposite. The mechanical properties of the composite were measured and resorption behaviour in Ringer's solution was studied.

2 EXPERIMENTAL PROCEDURE

Calcined calcium phosphate powder (CaP) was obtained from Sigma Chemical Company (St. Louis, MO), while the zirconia powder was obtained from American Vermiculite (Marietta, GA). The zirconia powder was doped with 3 mol% Y_2O_3 as the stabilizing agent, and included polyvinyl alcohol as a binder. The as-received calcium phosphate powder was predominantly hydroxyapatite. X-ray sedigraph and SEM analyses of the calcium phosphate particles indicated that the powder was relatively fine, with particle sizes ranging from the sub-micron level to approximately 25 μm, with a median particle size of 1·66 μm. Zirconia powders were supplied as spray-dried agglomerates. According to the manufacturer, 32% of the agglomerates were finer than 38 μm, while 68% ranged from approximately 38 to 100 μm (Fig. 1).

Samples corresponding to the following nominal compositions (on a weight percent basis) were prepared: 100% CaP, 20% CaP–80% ZrO_2, 60% CaP–40% ZrO_2, 40% CaP–60% ZrO_2, 20% CaP–80% ZrO_2 and 100% ZrO_2. The powders were mixed with a binder (typically dextrin) and cold pressed uniaxially at a pressure of 38 kPa to produce a cylindrical disk about 3·2 cm in diameter and 1·3 cm in thickness. The pressed samples were sintered at 1300°C for about 4 h. The density of the samples was measured according to ASTM D3800. X-ray diffraction studies were conducted

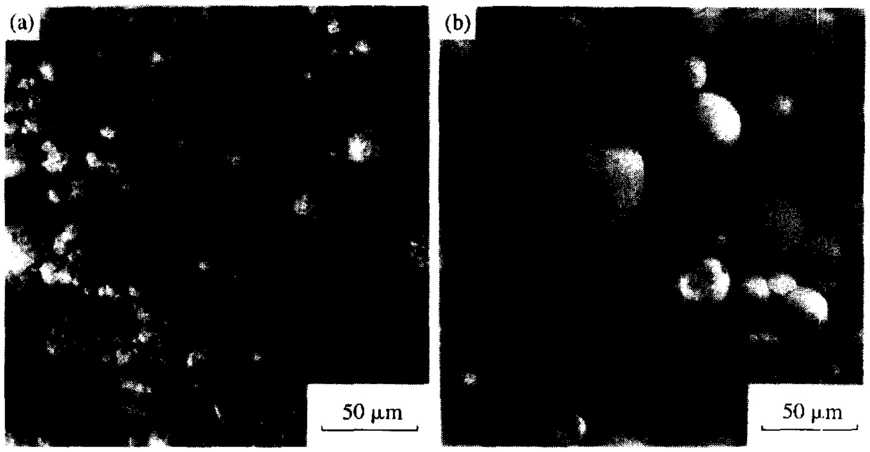

Fig. 1. SEM photographs showing the distribution of particles in (a) calcium phosphate and (b) zirconia powders.

on as-received powders and crushed powders obtained from sintered specimens. All specimens were scanned using CuKα radiation over a 2θ range between 5° and 110°. The microstructure of the samples was characterized by scanning electron microscopy. Diametral compression tests were conducted on sintered disks, approximately 2·5 cm in diameter and 0·5 cm in thickness, at a cross-head speed of 1·5 mm/min. The effect of Ringer's solution treatment on the structure and properties of the sintered samples was determined. Additional details pertaining to the experimental procedure have been published elsewhere.[4]

3 RESULTS AND DISCUSSION

X-ray diffraction analysis did not indicate any chemical reactions between the calcium phosphate and zirconia during the sintering process. Several phases of calcium phosphate, including β-TCP and/or α-TCP, were present in the sintered specimens. Similar results have been obtained by Yamashita *et al.*,[5] who have shown that the apatitic phase of a HA–ZrO_2 composite decomposes to TCP during sintering in air at 1300°C. A SEM photograph of the composite containing 80% CaP–20% ZrO_2 is shown in Fig. 2. It is clear that the calcium phosphate and zirconia phases did not fuse together completely during the sintering process. Archimedes density measurements yielded densities between 85% and 95% of theoretical.

The compressive strength of calcium phosphates increased steadily with the addition of zirconia as shown in Table 1. Analysis of the fracture surface of a 100% ZrO_2 sample indicates that the fracture occurs through the spray-dried agglomerates. In composite samples, fracture generally occurs through the weaker calcium phosphate phase, or along the interface between the calcium phosphate and zirconia (Fig. 3). These results indicate that improved powder mixing methods and modified densification techniques, such as hot pressing, may be necessary to produce a dense composite. Hermansson and Soremark[6] produced an 85% ZrO_2–15% HA composite that was densified at 1225°C by glass-encapsulated HIPing. Prior to densification, uniform powder dispersion was achieved by ball milling in light benzene for 48 h. Nearly 100% theoretical density was achieved, as well as a three-

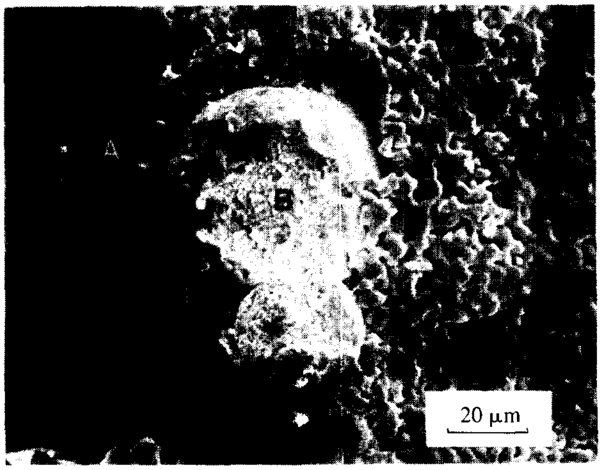

Fig. 2. SEM photograph showing the microstructure in a composite containing 80% calcium phosphate and 20% zirconia. Note the lack of fusion between the calcium phosphate (A) and zirconia (B) particles.

Table 1. Characteristic strength (MPa) obtained from Weibull plots after sintering and after treatment in Ringer's solution

Composition	After sintering	After 10 weeks in Ringer's solution
100% CaP	7.7	4.6
80% CaP–20% zirconia	9.1	6.4
60% CaP–40% zirconia	10.9	9.0
40% CaP–60% zirconia	17.2	16.3
20% CaP–80% zirconia	37.2	39.5
100% zirconia	136.3	136.8

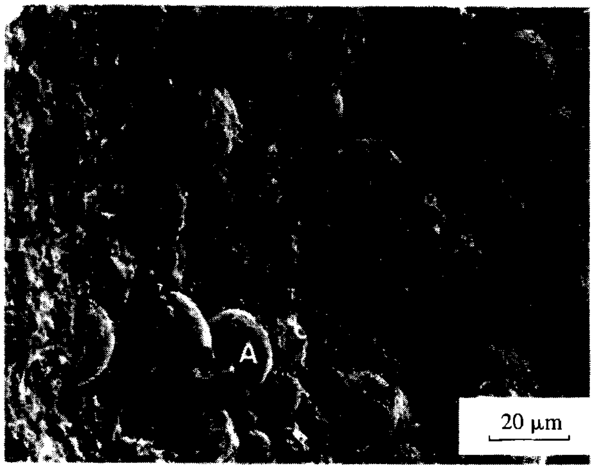

Fig. 3. SEM photograph of the fracture surface in a sample containing 40% CaP–60% ZrO_2. Note that the ZrO_2 agglomerates (A) are intact, indicating that fracture is occurring at the interface or in the CaP phase.

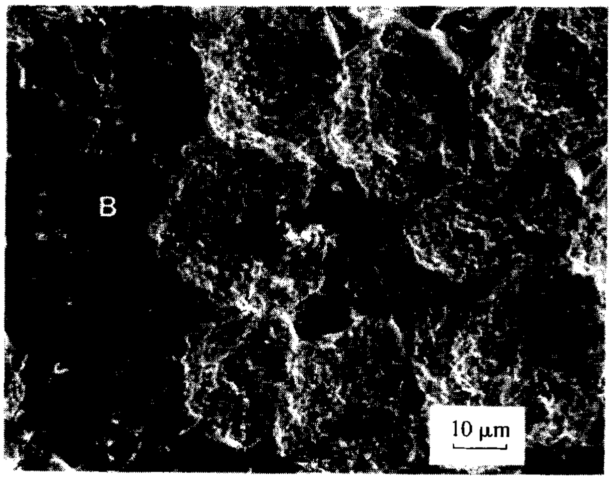

Fig. 4. SEM photograph showing the surface of a composite containing 40% CaP and 60% ZrO_2 after 10 weeks in Ringer's solution. Note that the resorption of the calcium phosphate phase (B) in the Ringer's solution may increase the apparent concentration of zirconia particles (A).

point bending strength of 860 MPa. The mechanical strength of the composite was almost as high as that of pure zirconia.

The compressive strength of samples containing calcium phosphate did not change significantly after 2 weeks in Ringer's solution. However, the strength of calcium phosphate-rich samples decreased significantly after 10 weeks in the solution (Table 1). This reduction in strength may be due to the resorption of the calcium phosphate phase in Ringer's solution (Fig. 4). The strength of the sample containing 100% ZrO_2 did not change considerably, even after relatively long times in Ringer's solution.

4 CONCLUSIONS

Toughening agents, such as zirconia, may be added to improve the mechanical properties of calcium phosphates. Preliminary X-ray diffraction data do not indicate any surface reaction between the zirconia and the calcium phosphate during the sintering process. Sintering the samples at 1300°C produces a calcium phosphate phase that undergoes significant resorption. The addition of zirconia to calcium phosphates improves the diametral compression strength. The addition of calcium phosphate to zirconia lowers the strength considerably. This reduction in strength may be minimized through improved processing techniques. Calcium phosphate-rich composites show an appreciable reduction in strength after 10 weeks of immersion in Ringer's solution. By comparison, the compressive strength of zirconia-rich composites did not change significantly after the Ringer's solution treatment. The toughness and other mechanical properties of the composites are currently being evaluated.

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