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Reinforcement of hydroxyapatite by adding P_2O_5–CaO glasses with Na_2O, K_2O and MgO

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Commercial hydroxyapatite was reinforced by adding small amounts (2 and 4 wt%) of P_2O_5-based glasses during its sintering process. The composites prepared had a chemical composition closely related to the mineral part of bone tissues in terms of trace elements usually detected, such as Na, K and Mg. X-ray diffraction analysis (XRD) showed that the glass reinforced-HA composites were composed of a HA matrix and variable amounts of tricalcium phosphate phase, depending on sintering temperature and glass composition. These composites were shown to have much higher biaxial bending strength than sintered HA, 107 MPa for Ha/2% of $35P_2O_5$–35CaO–$10Na_2O$–$10K_2O$–10MgO glass composite and 28 MPa for sintered HA. The presence of β-tricalcium phosphate in the microstructure of the composites is an important factor in the reinforcement process.

1. Introduction

A number of attempts have been made to reproduce the inorganic part of bone, and synthetic hydroxyapatite and other calcium phosphate materials have increasingly been used in biomedical applications, such as dental, orthopedic or maxillofacial [1–4]. However, natural apatite in bone and synthetic apatite, while having a related crystallography, have fundamental atomic differences [5–7]. Furthermore, the inorganic part of bone does not consist entirely of apatite but also contains traces of beta tricalcium phosphate (β-TCP), β-$Ca_3(PO_4)_2$ [8].

In bone tissues the exact composition and relative proportions of collagen fibres, mineral part and ground substance, depend upon the location and loading requirements of bone [3, 9, 10]. The chemical and structural analysis of the inorganic part of bone has been complicated by the effect of ionic substitutions which may occur within the hydroxyapatite lattice, where CO_3^{2-} is a common substitute for OH^- or PO_4^{3-}, Mg^{2+} and Na^+ for Ca^{2+}, and F^- for PO_4^{3-} [9]. However, it is well accepted that the inorganic part of bone contains several trace ions, particularly Na^+, Mg^{2+}, K^+ and F^- [3]. Therefore, there is a need to incorporate these trace elements in the hydroxyapatite used for implants and prosthesis since the biological behaviour of apatites is closely dependent on their composition [11]. On the other hand, the mechanical properties of sintered hydroxyapatite are inadequate for load-bearing applications when compared to bone [12, 13], and stronger implant materials should be produced.

Using glasses within the P_2O_5–CaO system with additions of Na, Mg and K oxides, glass reinforced hydroxyapatite composites were prepared by a liquid phase sintering process, with much higher biaxial bending strength than commercial sintered hydroxyapatite. In addition, the nominal elemental compositions of Na, Mg and K in the composites are similar to that found in bone tissues. The P_2O_5–CaO based glasses used in the reinforcement process react with hydroxyapatite particles and different amounts of β-$Ca_3(PO_4)_2$ are formed depending upon the sintering temperature.

2. Materials and methods

Two P_2O_5-based glasses were prepared from reagent grade chemicals as shown in Table I.

Each glass was wet-mixed and milled with the hydroxyapatite powder using methanol in a ball mill pot for 12 h. Glass additions of 2 and 4 wt % were used.

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TABLE I Chemical composition of the glasses (mol %)

Sample	P_2O_5	CaO	Na_2O	K_2O	MgO
G1	35	35	20	10	–
G4	35	35	10	10	10

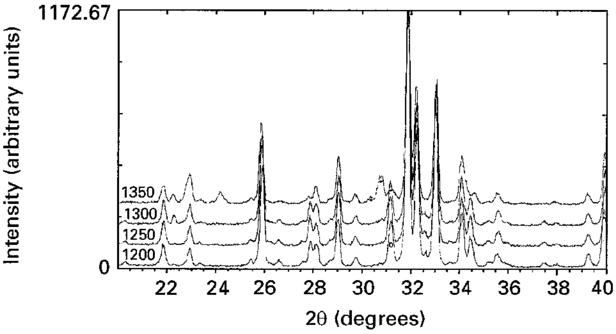

Figure 1 X-ray diffraction analysis for HA/4%G4 (+ , α-TCP; 0, β-TCP).

Mixed powders were then dried and uniaxially pressed at 288 MPa. The composite preparation method has been fully described elsewhere [14]. Disc samples were sintered at temperatures ranging from 1200 to 1350 °C with 1 h dwell time, and naturally cooled inside the furnace. Control sintered hydroxyapatite samples were also prepared using the same process.

Phase identification was performed using X-ray diffraction analysis (XRD) in a Siemens D 5000 diffractometer. Scanning electron microscopy (SEM) equipped with energy dispersive X-ray analysis (EDXA) was used for microstructural analysis.

A concentric-ring testing with a 20 mm supporting span and 10 mm loading span at a crosshead speed of 5 mm/min was used to determine the biaxial bending strength [15].

Grain size measurements were carried out on SEM photomicrographs using the equations $d_m = 1/\sqrt{m}$ and $a = 1/m$, where d_m is average diameter of the grain, m is the number of grains/mm^2 and a is the average area of the grain, according to Euronorm 103-71 standard [16].

3. Results

Using XRD analysis no phase changes were found for the HA compacts at all studied sintering temperatures. Fig. 1 shows the XRD results for HA/4%G4 composite. Below 1300 °C besides the HA matrix only β-TCP could be detected. Above 1300 °C β-TCP transformed into α-TCP which became the main TCP phase present in the microstructure.

Although a similar behaviour was detected for the other composites, smaller percentages of TCP were found, and peaks were detected in the microstructure only for samples sintered at 1350 °C, as shown in Fig. 2 for HA/2%G1 composite.

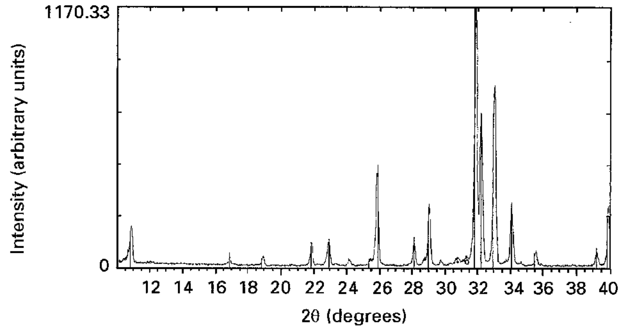

Figure 2 X-ray diffraction analysis for HA/4%G1 sintered at 1350 °C, (+ , α-TCP; 0, β-TCP).

TABLE II Biaxial bending strength results (MPa)

Sample	Temperature (°C)			
	1200	1250	1300	1350
HA	24 ± 4	26 ± 5	28 ± 7	28 ± 7
HA/2%G1	20 ± 8	38 ± 10	74 ± 12	73 ± 23
HA/4%G1	38 ± 7	42 ± 9	44 ± 12	57 ± 14
HA/2%G4	19 ± 7	47 ± 15	60 ± 15	107 ± 21
HA/4%G4	54 ± 10	87 ± 20	87 ± 23	93 ± 27

Each result is the average of 10 samples

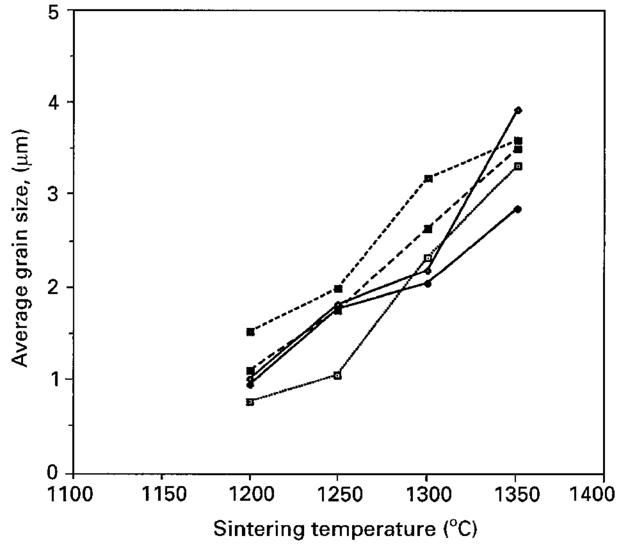

Figure 3 Grain size measurements: (--⊟--) HA; -◆- HA/2%G1; -□- HA/4%G1; -◇- HA/2%G4; -■- HA/4%G4.

Biaxial bending strength for the HA/phosphate glass composites showed a tendency to increase with increasing sintering temperature as may be seen in Table II. The most significant increase was obtained for the HA/G4 glass composite, which reached values of the order of 100 MPa for the 1350 °C sintering temperature, i.e. three times those determined for HA.

Grain size increased with sintering temperature for both sintered hydroxyapatite and glass reinforced hydroxyapatite composites, as may be seen in Figs 3 and 4. There is no evidence that for glasses with such chemical compositions grain size affects the bending strength nor that the glassy phase might control grain size.

4. Discussion

In previous works it was shown that sintered hydroxyapatite could be reinforced through both SiO_2 and P_2O_5 based glass additions [14]. In this work it

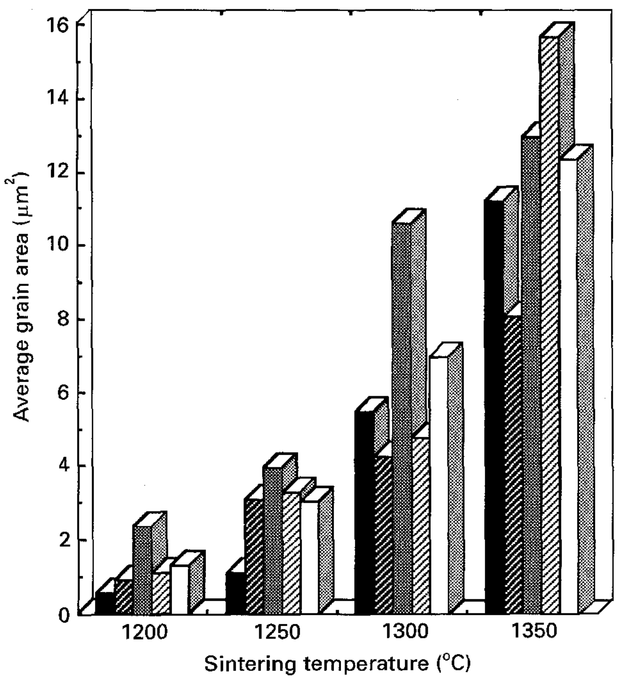

Figure 4 Average grain area: ■ HA; ▨HA/2%G1; ▦ HA/4%G1; ▨HA/2%G4; □ HA/4%G4.

has been demonstrated that this hydroxyapatite reinforcement process could also lead to composite materials with a chemical composition that approaches the inorganic part of bone. The chosen elements incorporated into the glassy phase were therefore those commonly found in bone tissues in higher percentages, i.e. Na, Mg and K. The possibility of having composites with a biphasic structure of hydroxyapatite and β-TCP was also achieved, particularly for sintering temperatures lower than 1300 °C. Above 1300 °C a highly soluble α-tricalcium phosphate appeared in the microstructure.

Biphasic hydroxyapatite/β-tricalcium phosphate structures are being considered for filling periodontal osseous defects; substituting, with advantage, simple hydroxyapatite implants [17]. The presence of a more bioactive phase (β-tricalcium phosphate) in the biphasic composite promotes a much faster osseointegration without complete implant resorption, since there is a relatively stable phase, i.e. hydroxyapatite [2]. Therefore, glass reinforced hydroxyapatite composites seem to be very promising materials for those applications requiring better mechanical properties, when compared to sintered hydroxyapatite.

The improvement in the mechanical properties of hydroxyapatite seems to be related to the presence of β-tricalcium phosphate in the composites microstructure. The highest bending strength results were achieved for samples sintered above 1300 °C, where the relative amount of β-tricalcium phosphate was significant and clearly detected using XRD analysis. This effect was confirmed by the fact that G4/HA composites showed the highest bending strength. Due to the chemical similarity of the P_2O_5–CaO glassy phase with HA, the former acts as sintering agent and enhances the sintering process.

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