J Mater Sci: Mater Med (2008) 19:197–201
DOI 10.1007/s10856-007-3120-8

Phase development and sintering behaviour of biphasic HA-TCP calcium phosphate materials prepared from hydroxyapatite and bioactive glass

A. Behnamghader · N. Bagheri · B. Raissi · F. Moztarzadeh

Received: 25 December 2005 / Accepted: 25 July 2006 / Published online: 28 June 2007

Abstract The composites of hydroxyapatite (HA) with 2.5 and 5 wt% of a double oxide (50 mol% CaO and 50 mol% P_2O_5) glass were prepared using the conventional powder mixing and sintering method. The addition of the glass significantly enhanced the decomposition process of HA into alpha tricalcium phosphate (α-TCP) for bodies sintered at 1,300 and 1,350 °C and β-TCP phases for the ones sintered at 1,200, 1,250 and 1,300 °C. Microstructural characteristics, phase development and thermal behaviour were studied by SEM, XRD and STA. The effects of TCP phase content and phase transformation from β-TCP to α-TCP on the sintering are discussed. The characterizations revealed considerable content of TCP in the form of large semi-islands due to important reactions between the fine HA and the glass mixed powders.

Introduction

During the last decade considerable attention has been directed towards the use of bioactive fixation of implants. Among the calcium phosphates, while hydroxyapatite is considered as most stable in contact with body fluids, calcium phosphate glass shows high bioactivity [1]. To combine the advantageous properties of hydroxyapatite (HA) and bioactive glass (BG), their composites have been developed to enhance mechanical properties and/or osseointegration depending on the BG/HA ratio [2, 3]. They have been used as coatings and small unloaded implants in middle ear surgery, precutaneous access devices and in spinal surgery. The calcium phosphate composites owe their use to the desired characteristics of the constituent phases; a stable phase (HA) and a resorbable phase (beta tricalcium phosphate). The presence of beta tricalcium phosphate (β-TCP) promotes a faster osseointegration of the calcium phosphate biomaterials [4–6].

In spite of the reports on the increasing of TCP phase content with addition of the BG [7–10], its extent (size) aspect is less studied [3, 8]. Taking into account the enhanced atomic diffusion due to presence of liquid phase among the HA particles through sintering, the constituent phases extents and contents are expected to be highly depended on the size distribution of mixed powder. The synthesis and microstructural analysis of the bodies prepared from fine mixed powders of HA and BG were the aim of this research.

Materials and methods

A double oxide calcium phosphate (50 mol% CaO and 50 mol% P_2O_5) glass was prepared from chemical grade precursors P_2O_5 (Merck #100540) and $CaCO_3$ (Merck #102069). The mixed powders were placed in an alumina crucible and melted in an electric furnace at 1,060 °C for 20 min. Once the glass was quenched in cold water, it was quickly dried at 120 °C and fast milled for 2 h with alumina balls in dry condition until 90% of the particles had an average size less than 7 μm.

A. Behnamghader (✉) · N. Bagheri · B. Raissi
Materials and Energy Research Centre (MERC), P.O. Box 14155-4777, Tehran, Iran
e-mail: a-behnamghader@merc.ac.ir

F. Moztarzadeh
Department of Biomedical Engineering, Amirkabir University of Technology, P.O. Box 15875-4413, Tehran, Iran

To prepare HA-2.5G and HA-5G composites (bodies), Hydroxyapetite powder (Merck #2196) was mixed with 2.5 and 5 wt% of the glass, respectively. The mixed and pure HA powders were separately ball milled in methanol media for 2 h followed by drying the slurries and screening through a 120-mesh screen. The powders were uniaxially pressed at 120 MPa in a metallic die to obtain samples with the dimensions of 54 × 52 × 5 mm. Resulting plates were finally sintered in air at the temperatures of 1,200, 1,250, 1,300 and 1,350 °C for 2 h with a heating rate of 5 °C/min and then cooled in furnace.

Particle size distribution of the powders was evaluated by laser particle size analyser (Fritsch Analysete 22) in ethanol media. Microstructural characterization, phase investigation and observation of powder specimens were carried out using powder X-ray diffractometer (Siemens D-500) and SEM (Cambridge Streoscan 360). The amounts of TCP phase was determined using semi-quantitative XRD by comparing the peak of HA (211), β-TCP (0210) and α-TCP (034) from XRD patterns.

$$\mathrm{TCP} = (\mathrm{I}_{\mathrm{TCP}})/(\mathrm{I}_{\mathrm{TCP}} + \mathrm{I}_{\mathrm{HA}})$$

The TG/DTA curves were recorded in air with a heating rate of 10 °C/min using an simultaneous thermal analyzer, STA/1640 of Polymer Laboratories. The Ca/P ratio was measured by ICP (ARL 3410 Switzerland) analysis. The density of the sintered bodies was measured through Archimedes method (ASTM C373-88).

Results and discussion

Material characterization

XRD patterns show that the as-received HA powder was pure hydroxyapatite. The Ca/P atomic ratios of the calcium phosphate glass and the as-received HA powders were 0.51 and 1.66 and their average sizes before mixing reached to 3.38 and 0.9 µm, respectively. SEM observations showed while the glass powder was more irregularly-shaped, HA powder had a tendency to remain agglomerated (Fig. 1). The average particle size of the mixed powder used in pressing reached to 0.75 µm after 2 h ball milling in methanol media (Fig. 2).

At 1,200 °C for all the time of sintering or for 1 h at the higher temperatures, sintering of both HA and composite specimens is already in development (Fig. 3). XRD patterns show that all sintered pure HA samples and HA-based composites were crystalline (Figs. 4, 5).

The only crystalline phase present in the pure HA samples was HA while the composites were composed of HA and TCP phases at all four test temperatures. This agrees with the other reports [8, 11, 12] in which it is reported that Ca-deficient HA can transform to TCP at temperatures above 800 °C.

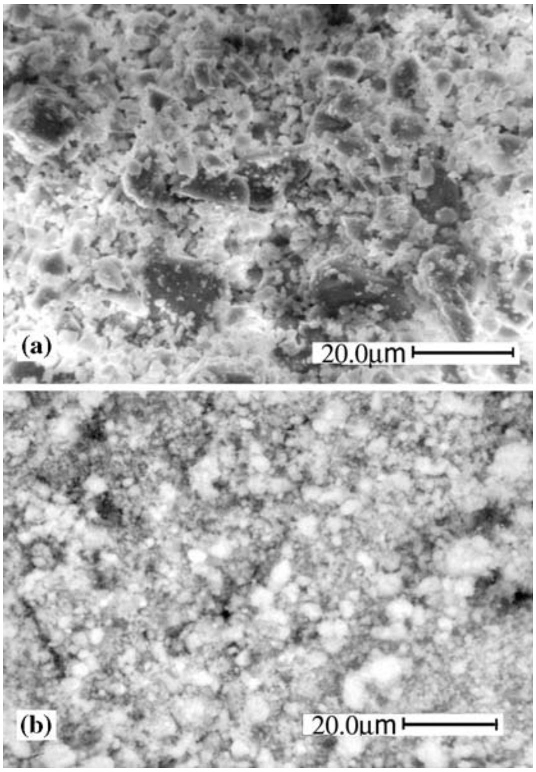

Fig. 1 SEM photographs of (**a**) prepared glass and (**b**) as-received hydroxyapatite (HA) powders

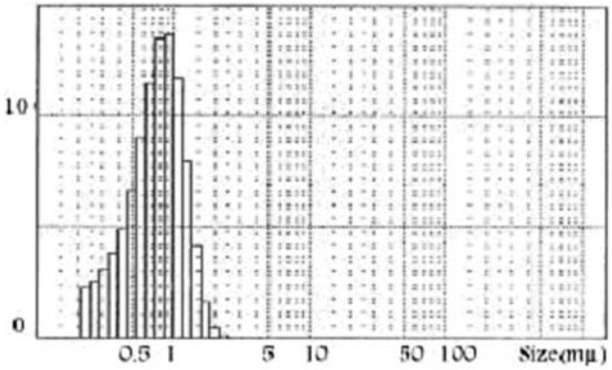

Fig. 2 Particle size distributions of mixed powder used for preparation of HA-5G composite

Differential thermal analysis of glass powders showed two distinct thermal events attributed to crystallization (at 634 °Cand melting (at 960 °C) of Calcium metaphosphate $Ca(PO_3)_2$. Differential thermal analysis of HA-5G composites showed only a sharp variation at about 1,300 °C (Fig. 6). Based on the results obtained from XRD, this exothermic reaction can be related to the

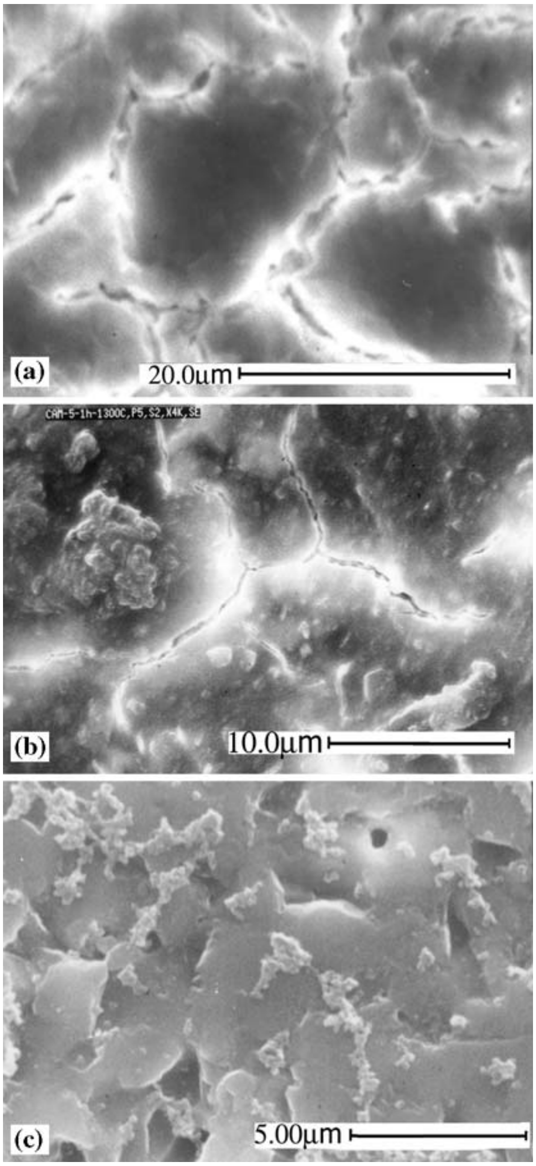

Fig. 3 SEM photographs of HA-5G sintered (**a**) at 1,200 °C for 2 h, (**b**) at 1,300 °C for 1 h and (**c**) at 1,300 °C for 2 h

phase transformation of β-TCP to α-TCP. The difference observed between our result (Table 1) and the prediction of CaO–P$_2$O$_5$ phase diagram (thermodynamically 1,120 °C) is also reported elsewhere [3, 7, 8, 13].

The phase contents estimated by semi-quantitative XRD (without calibration) are shown in Fig. 7. As shown in this figure, the TCP phase contents in all temperatures are almost the same with the average values of 35% and 61% for HA-2.5G and HA-5G composites, respectively. Taking into account the stoichiometric composition of hydroxyapatite and tricalcium phosphate phases, the TCP phase contents of 26% and 56% corresponding to the Ca/P atomic ratios of 1.62 and 1.57 measured by ICP are calculated for HA-2.5 G and HA-5 G composites, respectively.

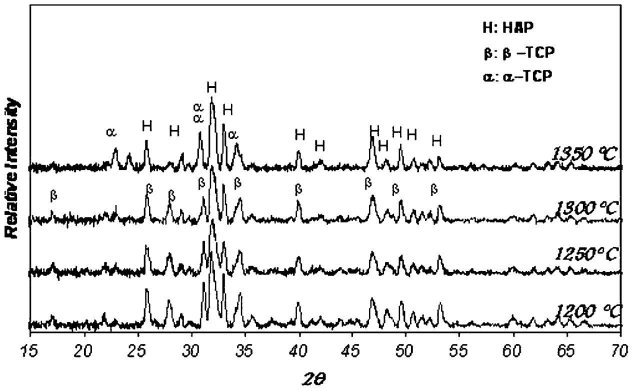

Fig. 4 X-ray diffraction patterns of HA-2.5G composite sintered at different temperatures

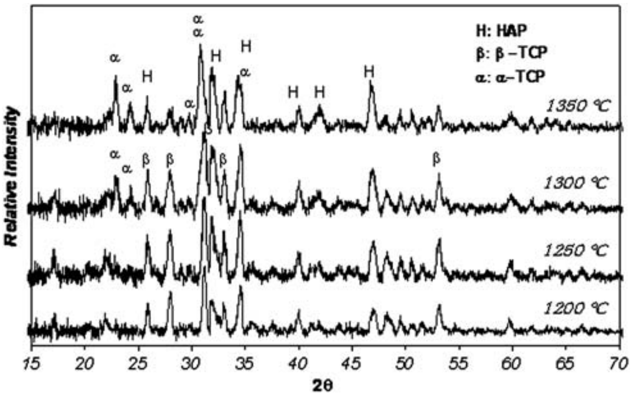

Fig. 5 X-ray diffraction patterns of HA-5G composite sintered at different temperatures

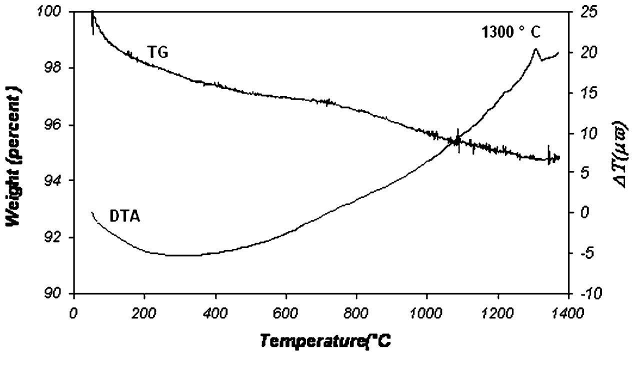

Fig. 6 Differential thermal analysis of HA-5G composite

In spite of the lower effect of the sintering temperature, the addition of glass has significantly increased the TCP content. The glass dependency of TCP content is also reported elsewhere [2, 3, 7–10].

Of special interest here is the appearance of HA, beta TCP and alpha TCP phases in images taken by SEM which

Table 1 Identified phases in pure HA and HA-based composites sintered at different temperatures

Glass percentage (%)	Sintering temperature (°C)			
	1,200	1,250	1,300	1,350
0	Hydroxyapatite (HA)			
2.5	HA + β-tricalcium phosphate (TCP)			HA + α-TCP
5	HA + β-TCP		HA + α and β-TCP	

is insufficiently studied in the literature [8, 14]. Despite its difficulty, distinguishing TCP from HA regions was done from phase contrast development of SEM images, aided by compositional analysis (EDS) of calcium and phosphorus. The phase contrast was developed electronically. As shown in Fig. 8 taken in the BSE mode without any etching, the HA and β-TCP phases appeared as bright areas and light gray semi-islands, respectively. The composites exhibited homogeneous microstructures suggesting uniform distribution of mixed powders. These finely distributed particles seem to promote a close contact between HA and BG powders, leading the formation of high contents of TCP phase extended throughout the microstructure.

Sintering behaviour

The sintered bodies consisted of micropores that can be associated to OH^- Release from HA during sintering [3, 8, 15]. However, it is also probable that they have been originated from local shrinkage of glassy phase through liquid-phase sintering, taking into account the distribution and size of pores (typically less than 2 μm). Theoretical density percentage of composites increased from 89% to 95% with the increase of the sintering temperature from 1,250 to 1,350 °C. It was higher for the composite containing 2.5% glass than that contained 5% glass (Fig. 9).

The decrease of the density with the addition of glass could be attributed principally to the increasing of TCP phase content. The TCP is considered as a poor sinterable phase [11, 12]. Because of the only small variation of TCP content (Fig. 7) and eventual grain growth at temperatures ranging from 1,250 to 1,350 °C, the increasing of density can be attributed to better sintering in the presence of liquid phase. Fanovich et al. [12] reported a decrease in the density due to an extraordinary grain growth, leaving many trapped pores.

SEM and optical microscopy evaluation of samples sintered at 1,300 and 1,350 °C revealed a microstructure without any microcrack. Volume increasing due to β-TCP to α-TCP transformation is considered as an undesirable phenomenon because of its effect on HA/TCP phase boundary cracking of bodies sintered at temperatures higher than β-TCP to α-TCP transition point [1, 16, 17]. Tancred et al. [8] have also reported that the expansion associated with phase transformation of HA to β-TCP and of β-TCP to α-TCP could not be so high to cause important microstructural defects. According to other reports [10] this volume increase produces compressive stresses that could strengthen the composite structure.

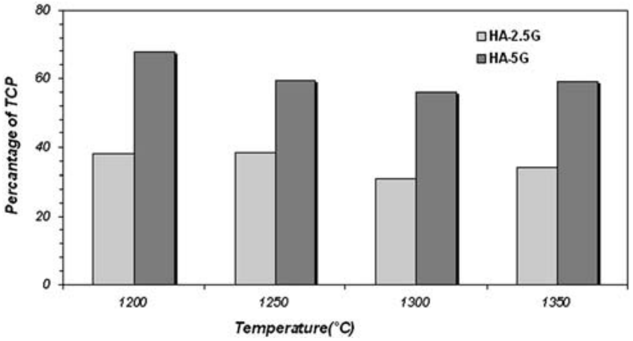

Fig. 7 Relative amounts of tricalcium phosphate (TCP) deduced from the XRD patterns

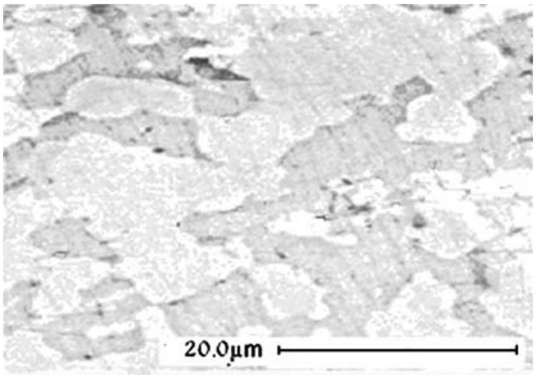

Fig. 8 SEM photograph taken in BSE mode of HA-2.5G sintered at 1,300 °C

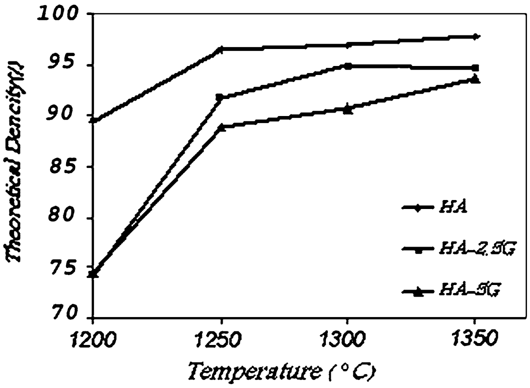

Fig. 9 Theoretical density versus temperature curves for pure hydroxyapatite (HA) and HA-glass composites

It seems that the slightly different results reported by authors may be explained by the presence of the liquid phase and grain growth. The fact that α-TCP has been maintained in room temperature reveals no transformation was occurred through cooling period. Liquid phase could compensate partially the stresses caused by volume increasing upon β-TCP to α-TCP transformation during heating.

Conclusion

HA-calcium phosphate glass bodies seem to have a great potential in the biomedical field as bone substitute. According to the results obtained in this study, addition of the glass enhances significantly the decomposition process of HA into tricalcium phosphate phase (TCP). The biphasic HA/β-TCP calcium phosphate (BCP) materials particularly made of large quantities of bioactive glass, should not be essentially designed to improve mechanical reliability but to control the biological performance of HA ceramics. The latter is functional and highly demanded in hard tissue applications.

Tissue engineering in vitro and in vivo involves the interaction of cells with a material surface. It is now known that minor variations in the nature of the surface and surface texture and topography can directly influence cellular response, ultimately affecting the rate and quality of new tissue formation [18–20]. The osseointegration time of these calcium phosphate materials could therefore be affected by the presence of TCP phase. The considerable content and extent of TCP phase found in this work can be related to high chemical activity within bioglass and HA powders resulted from the uniformly distributed fine mixed powders.

Acknowledgements The authors are grateful for the financial and material support provided by the MERC. We thank the laboratory managers and technicians at the Ceramic, Semiconductor and Renewable energy Departments of the MERC. We thank especially Mr. E. Djabbari, M. Hasanzadeh, M. Kabiri and A. Keshavarz for excellent technical help and Mr. A. Rajabi for language assistance.

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