

Preparation of calcium–phosphate bioceramics from natural resources

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Abstract

In this study, calcium phosphate based bioceramics have been synthesised by using eggshell derived raw materials and phosphoric acid at different mixing ratios. Development of the elaboration processes has been conducted to gain mono phase hydroxyapatite (HAP). The processing route of calcium phosphate ceramics and the end product characteristics have been found to be influenced by acid/CaO mixing ratio, milling time and heat treatment applied. Calcium phosphate foams resulted at higher acid/CaO mixing ratio with high specific surface area. At higher sintering temperatures, calcium phosphate thin and thick film coatings have been produced by a condensation method. The films contained a mixture of micron size crystals and nanofibrous cover layer. The good adherence of films to the calcium phosphate substrate assured a higher strength for these samples.

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1. Introduction

This work is based on preparation processes of hydroxyapatite and other calcium phosphates from biogenic (natural) materials that are available in large quantities in nature.^{1,2} Hydroxyapatite (HAP) is known as a highly bioactive and biocompatible inorganic material. Therefore, it is widely used in tissue engineering and bone replacement.^{3,4} In this study, calcium phosphate based bioceramics were synthesised by using eggshell derived raw materials and phosphoric acid that was added to starting powders at different mixing ratios. In order to get the full use of the benefits provided by high percentage of calcium carbonate in eggshell, it is crucial to optimise the all synthesis processes. Because of unfavourable mechanical properties that were reported for porous HAP and calcium phosphate based ceramics⁵ importance was given to composite processing. Different methods are known for calcium–phosphate coating processing, such as electrophoretic deposition,⁶ sol–gel,⁷ sputtering⁸ or plasma spray.⁹ A specific biomimetic process for apatite coating was presented by Kokubo et al.¹⁰ In our study, first, the calcium–phosphate substrates were prepared. After that

an apatite coating was applied by a condensation method. In this paper, the preparation and coating processes as well as morphological, structural observations and characterisation of mechanical properties are presented.

2. Experimental procedure

2.1. Preparation of powders

Raw eggshells were calcinated at 900 °C. After a short time (30 min), the colour of eggshells turned to black, and after 3 h they became white. The colour change suggested that most of the organic materials were burnt out. As-obtained powders were crushed in an agate mortar and reacted by an exothermic reaction with phosphoric acid. The details of mixing procedure and powder preparation are presented in Table 1. Short (10 h) and long milling (24 h) periods were applied. For example, powder sample A resulted from short milling, whereas the powder sample B, which is a derivative product of sample A, was obtained from long milling. Sample B contains double amount of phosphoric acid. All of the products that derived from powder samples A and B have notations as “S” (A sintered, noted AS), “P” (contains polyethylenglycol) “PS” (contains PEG and sintered) or “BCPS” (powder B contains carbon, C”, PEG and sintered). After milling, polyethylenglycol (PEG) were added to some of the powder mixtures. The batches were sieved with

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Table 1
The details of mixing procedure and powder preparation

Samples	Starting powders (eggshell) (wt%)	H ₃ PO ₄ (wt%)	Carbon addition to batch (wt%)	PEG addition to batch (wt%)	Ball milling (in ethanol) (h)	Sintering conditions	
						Temp.(°C)	Holding time (h)
A	50	50	–	–	10	–	–
AS	50	50	–	–	10	900	2
APS	50	50	–	10	10	1000	2
Derivative to A							
B	50	50	–	–	24	–	–
BPS	50	50	–	10	24	900	2
BCP	50	50	1	10	24	–	–
BCPS	50	50	1	10	24	900/1000	2

100 µm mesh. Green samples were obtained by dry pressing at 220 MPa.

2.2. Sintering method

Sintering of samples was performed in air at 900 or 1000 °C for 2 h. The heating rate did not exceed over 2 °C/min. The dimensions of the as-sintered specimens were 3.5 mm × 5 mm × 50 mm or bigger (in the case of series of B).

2.3. Microstructure and mechanical properties

Phase compositions were determined by Philips PW 1050 diffractometer. Morphology of the solid products was studied by field emission scanning electron microscope, LEO 1540 XB. For sintered samples, the three point bending strength was determined by using spans of 20 mm.

3. Results and discussion

After calcination at 900 °C for 3 h the main lines of Ca(OH)₂ (JCPDS-PDF 78-0315) appeared, as can be observed in Fig. 1a. Presumably, the CaO phase was the calcination product, but as the powder sample was in contact with ambient atmosphere after firing the product turned to Ca(OH)₂ (as in Fig. 1a). Some small diffraction lines from CaO (JCPDS-PDF 82-1691) and MgO, JCPDS-PDF 78-0430 can be also observed. After a successive and intensive milling process, and by treating the powder with phosphoric acid, next to the main lines of Ca(OH)₂, new phases appeared (CaHPO₄, JCPDS-PDF 01-0653) that are characteristic for sample A (Fig. 1b). The morphological evolution of raw eggshell, calcinated at 900 °C for 3 h (Fig. 2a), followed by a mechanical activation (milling for 10 h, Fig. 2b, sample A) and milled for 24 h (Fig. 2c, sample B) are presented in Fig. 2.

A lamellar nanostructure can be observed (consisting of 10–20 nm columns) in the case Ca(OH)₂ as it was obtained after calcination (Fig. 2a). After mechanical activation for 10 h, this microstructure have been transformed to 1–20 µm grains which are consisting of Ca(OH)₂ and CaHPO₄ nanograins as resulted from XRD measurements (sample A). After 10 h, a small quantity (sample A) was collected from jars. The milling process has been continued by adding another amount of phos-

phoric acid (the same quantity as the powder sample). As can be observed from Figs. 1c and 2c, a totally new structure and morphology evolved after long milling. Micron size crystals of Ca(H₂PO₄)₂·H₂O (JCPDS-PDF 70-0090) with hexagonal shape are characterising the sample B.

A macroscopic view about calcium phosphate foams and testing bars realised by ball milling of eggshell and phosphoric acid at different mixing ratio and sintered at 900 °C for 2 h is shown in Fig. 3. As can be seen after sintering sample A (AS) was keeping the initial shape of a bar and transformed to hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂, JCPDS-PDF 74-0565, Fig. 4a). Characteristic morphology for AS samples is presented in Fig. 5a and b. A coarsening effect can be observed by applying a higher sintering temperature (900–1000 °C).

The samples, which resulted from a longer milling time (sample B) and with PEG (sample BPS) and carbon addition (BCPS), changed their morphology during sintering and resulted in calcium–phosphate foams (Figs. 3 and 5c and 5d). By carbon addition a more fine microstructure is obtained (Fig. 5d). X-ray diffraction analysis showed that the foams have β-Ca(PO₃)₂ structure (JCPDS-PDF 17-0500, Fig. 6a and b).

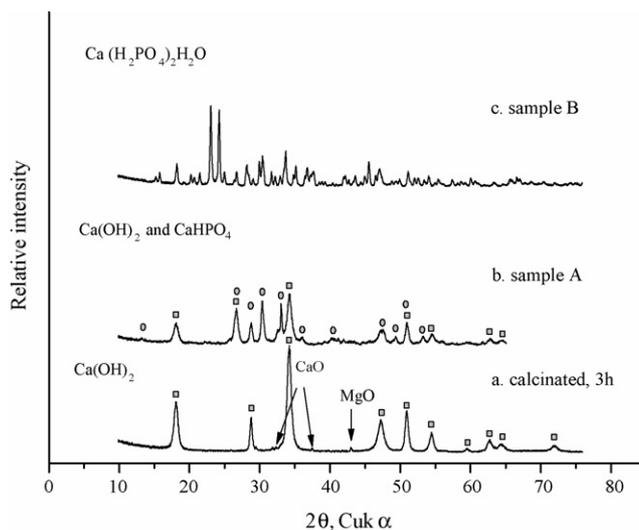


Fig. 1. X-ray diffractograms of powder samples. (a) Eggshell calcinated at 900 °C for 3 h, and exposed to ambient air after firing. (b) the product after calcination, low acid/CaO ratio and short milling time. (c) the product after calcination, high acid/CaO ratio and long milling time.

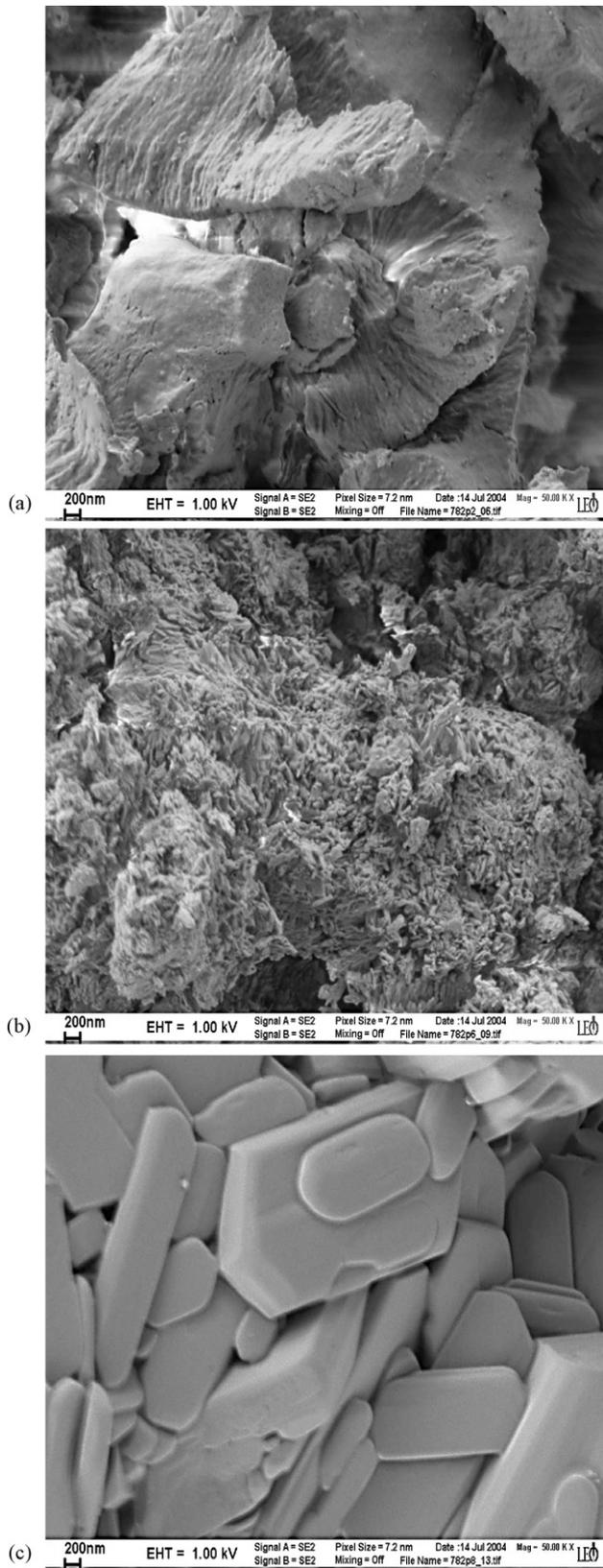


Fig. 2. Scanning electron micrographs of (a) eggshell calcinated at 900 °C for 3 h, (b) the product after calcination and 10 h milling time, low acid/CaO ratio, (c) the product after calcination and 24 h milling time, high acid/CaO ratio.

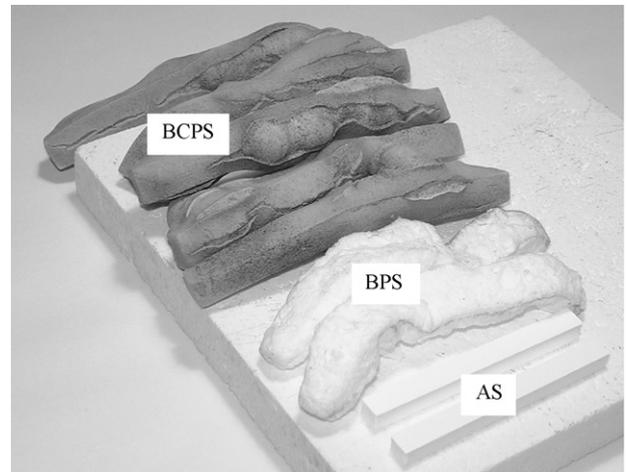


Fig. 3. Calcium phosphate foams and testing bars realised by ball milling of eggshell and phosphoric acid at different mixing ratio.

The sample A sintered at higher temperature (APS and APS-20, 1000 °C) resulted with the same crystal structure as sample AS (HAP, Fig. 4). The sample APS-20 was part of samples APS, but during sintering it was placed next to BCPS samples. The BCPS samples which have been sintered at 1000 °C, 2 h disappeared (burnt out) during sintering and they condensed to the surface of the neighbouring (APS-20) samples in form of micro- and nanocrystals (Fig. 7). A schematic view can be followed in Fig. 7 about the condensation process which took place in the presence of carbon. First, the BCPS samples have grown in dimension as presented in Fig. 3, after that a self-combustion process took place and all of the BCPS samples have been evaporated. The condensation might have occurred from saturated vapour phase during cooling step to the neighbouring surfaces. The as obtained layer is very inhomogeneous as shown in Fig. 8.

Large grains with dimensions of 20–60 μm have condensed next to fracture surface are shown in Fig. 8a. The surface of condensed grains is shown in Fig. 8b. As can be seen the big grains are consisting of small crystals with 1 μm length. Next

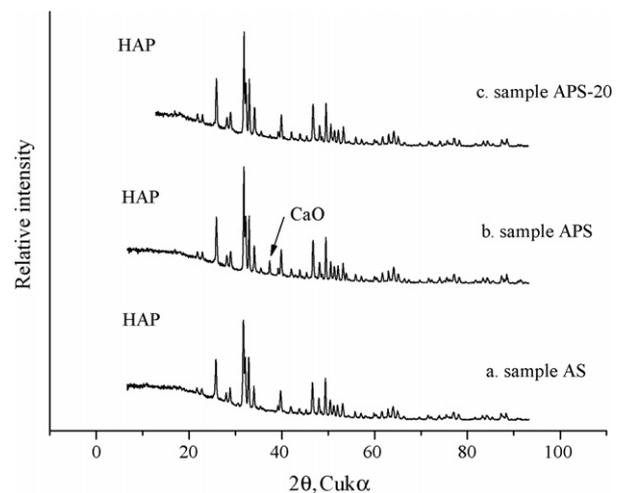


Fig. 4. X-ray diffractograms of sintered samples. (a) Sample AS, (b) sample APS, (c) sample APS-20. The main lines of hydroxyapatite (HAP) can be recognised in the case of all samples.

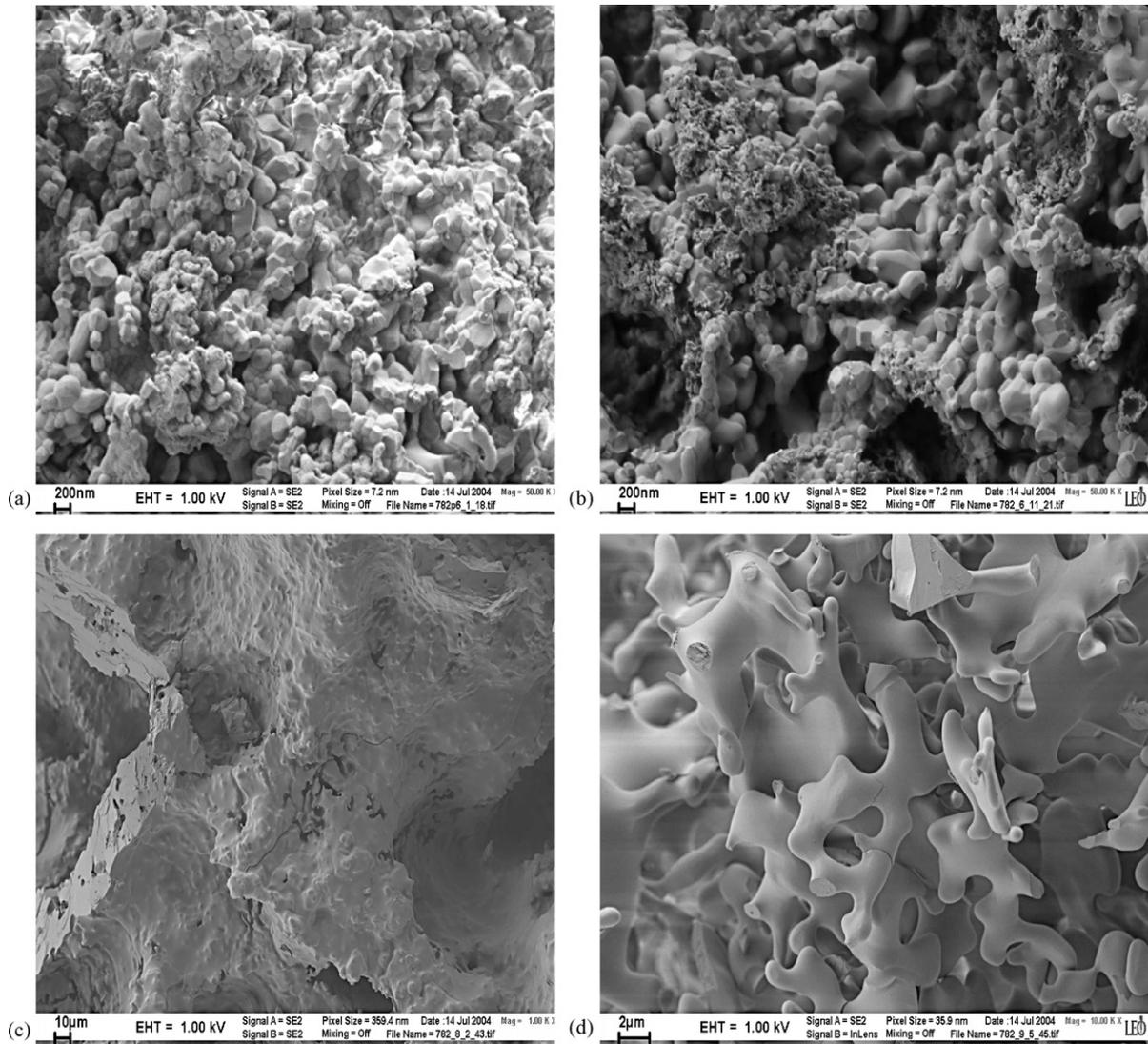


Fig. 5. Scanning electron micrographs of sintered samples. (a) Nanocrystalline structure of sample AS (900 °C, 2 h). (b) Sample APS (1000 °C, 2 h). (c) Foam structure with 10–50 μm pores of sample BPS (900 °C, 2 h) and (d) sample BCPS (900 °C, 2 h). Note the formation of foam structures in case of (c and d).

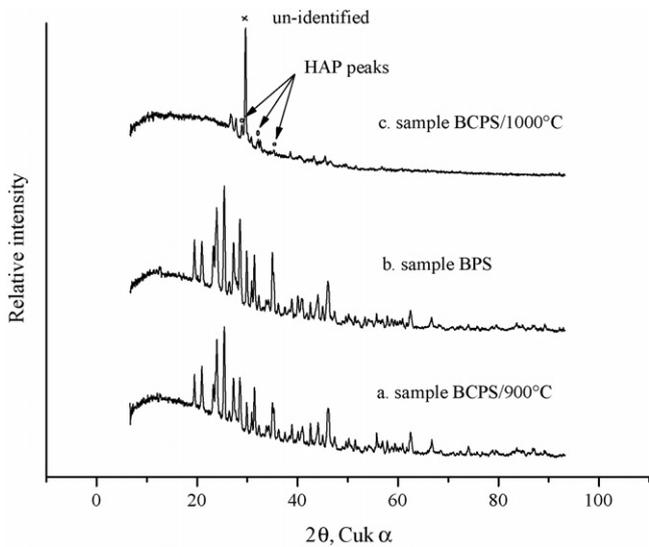


Fig. 6. X-ray diffractograms of sintered samples. (a) Sample BCPS/900 °C, (b) sample BPS. (c) sample BCPS/1000 °C.

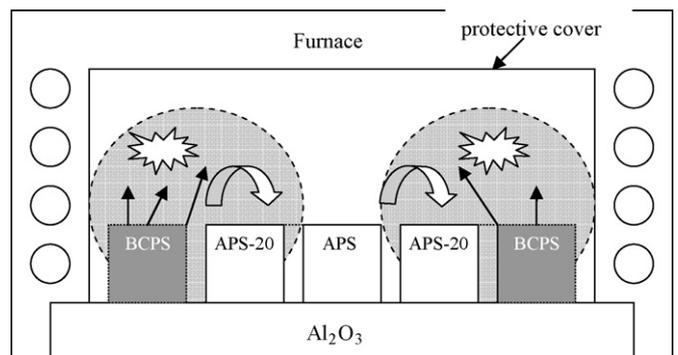


Fig. 7. A schematic view of condensation process.

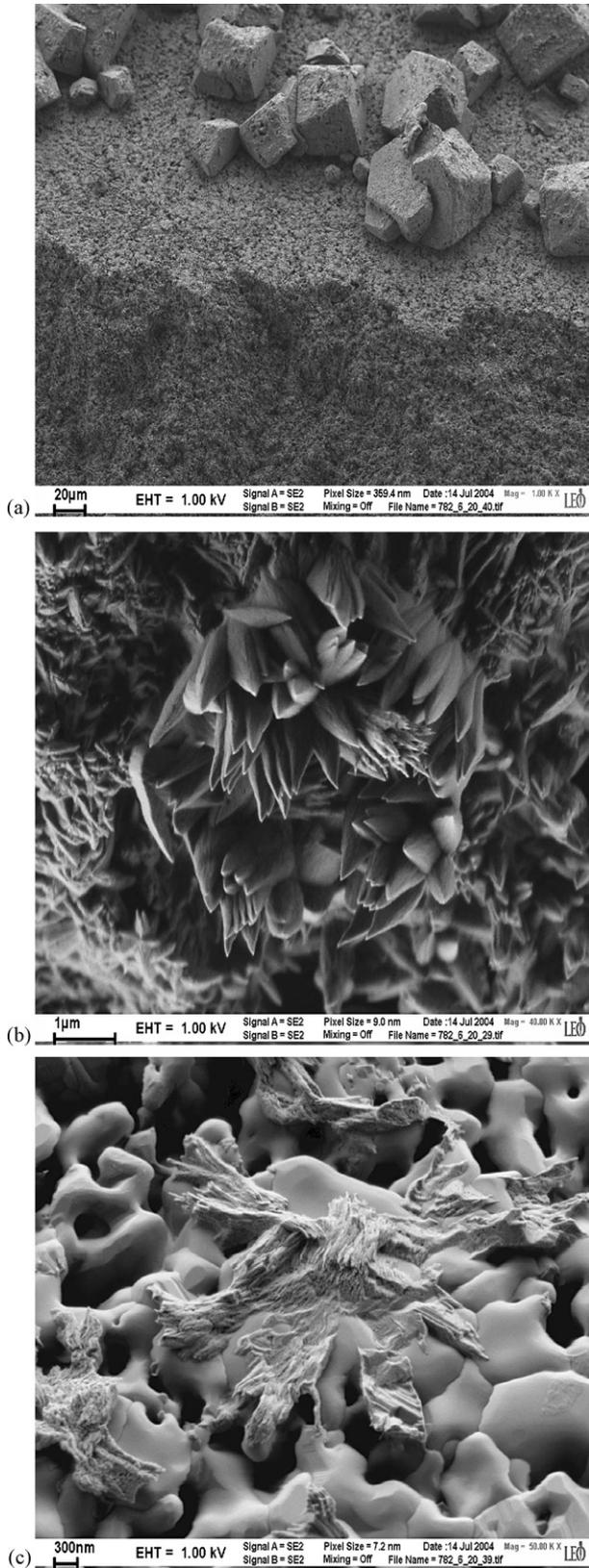


Fig. 8. Scanning electron micrographs of sintered BCPS sample. (a) Large grains at fracture surface, (b) the surface of grains, (c) condensed spots connecting the grains of HAP surface.

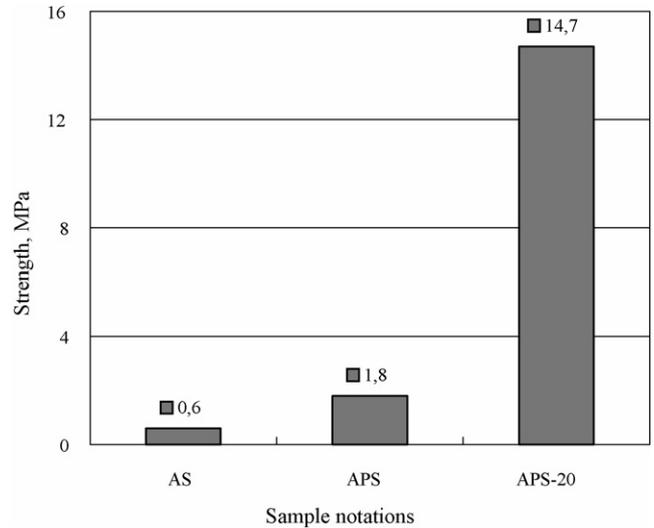


Fig. 9. The comparison of three point strength of the samples AS (sintered 900 °C, 2 h), APS (sintered 1000 °C, 2 h) and APS-20 (sintered and coated at 1000 °C, 2 h).

to the bigger grains “small spots” with nanometer thickness can be observed which are well attached to the surface of sample APS-20 (as shown in Fig. 8c).

For a set of samples, three point bending strength have been measured (Fig. 9). As can be observed, the HAP sample, APS-20, which is covered with a thin calcium–phosphate layer is showing a remarkable increase in strength in comparison to other HAP samples (AS and APS). Although the condensed layer is not homogeneous, the calcium–phosphate spots are well attached to (one of) the surface of HAP, and locally they can act as reinforcing elements.

4. Conclusions

The processing route of calcium phosphate ceramics and the end product characteristics have been found to be influenced by acid/CaO mixing ratio, milling time and temperature of heat treatment applied. Calcium phosphate foams resulted at higher acid/CaO mixing ratio, longer milling time with high specific surface area. Samples with mono phase HAP have been obtained at lower acid/CaO mixing ratio and shorter milling. At higher sintering temperatures calcium phosphate thin coatings have been realised with good adherence to HAP substrate. The good adherence of films to the HAP substrate assured a higher strength for these samples.

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