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Short communication

Preparation of porous hydroxyapatite ceramics containing mullite by reaction sintering of clay, alumina and hydroxyapatite

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Abstract

Porous hydroxyapatite ceramics containing mullite have been obtained from reaction sintering at 1150° to 1350 °C of clay and alumina in the presence of pure hydroxyapatite. XRD results showed that hydroxyapatite decomposes to TCP by adding mullite. Hydroxyapatite, β-TCP and mullite were detected in samples containing 10 wt.% and more mullite, sintered at 1150° and 1250 °C for 2 h. Porosity amount increased by adding mullite and decreased by increasing sintering temperature. The highest porosity content was in samples containing 30 wt.% mullite at all sintering temperatures.

Keywords: Mullite; Hydroxyapatite; TCP; Composites; Porosity; Microstructure

1. Introduction

Hydroxyapatite (HAp) is known as a bioactive material widely used as bone substitute [1,2]. In order to minimize the brittle nature of bioactive ceramics especially HAp, biocomposite materials have been developed consisting of HAp and other bioceramic materials such as alumina, zirconia, TZP, Mg-PSZ, TiO_2 and bioglasses [3–8]. On the other hand, mullite has a high mechanical strength at both low and high temperature, a low thermal expansion, a high thermal shock resistance and good thermal and chemical stability. The transmission electron microscopy (TEM) study of HAp–mullite (10 and 30 wt.%) composites sintered at 1350 °C for 2 h was performed [9]. It was found that the decomposition of HAp to β-TCP is enhanced at higher mullite content through an intermediate stage of α-TCP with 10 wt.% mullite addition.

This work presents the preparation of porous hydroxyapatite ceramics by reaction sintering of clay, alumina and hydroxyapatite. Phase development, density, porosity and microstructure evolution were examined.

2. Experimental procedures

Hydroxyapatite [$Ca_{10}(PO_4)_6$ $(OH)_2$, MERK], clay (d_{50} = 1.8 μm) and alumina (d_{50} = 2.3 μm) were used as the starting materials (Table 1). XRD (Siemens, D500 system) of clay showed that it contains kaolin, quartz and muscovite as the crystalline phases. The hydroxyapatite, clay and alumina were mixed in a ball mill for 2 h, then pressed at 255 MPa in a 10 mm diameter die and sintered in an electrical furnace between 1150° and 1350 °C for 2 h. The bulk density and porosity of fired samples were measured according to ASTM-C373. The microstructure of sintered samples was observed on polished surface by SEM (Cambridge-360).

3. Results and discussion

XRD results showed that HAp was the only crystalline phase when pure HAp was sintered for 2 h at temperatures of 1150°, 1250° and 1350 °C. Samples containing the same mullite content obtained quite similar phases after sintering at 1150° and 1250 °C. In samples containing 5 wt.% mullite sintered at 1150° and 1250 °C, peaks corresponding to β-TCP appeared, while HAp peaks were still detectable. Mullite, HAp, β-TCP and gehlenite peaks were observed in 30 wt.% mullite-containing samples sintered at 1150° and 1250 °C. With increasing sintering temperature to 1350 °C, mullite and HAp peaks disappeared while β-TCP, α-TCP, CaO and gehlenite peaks remained.

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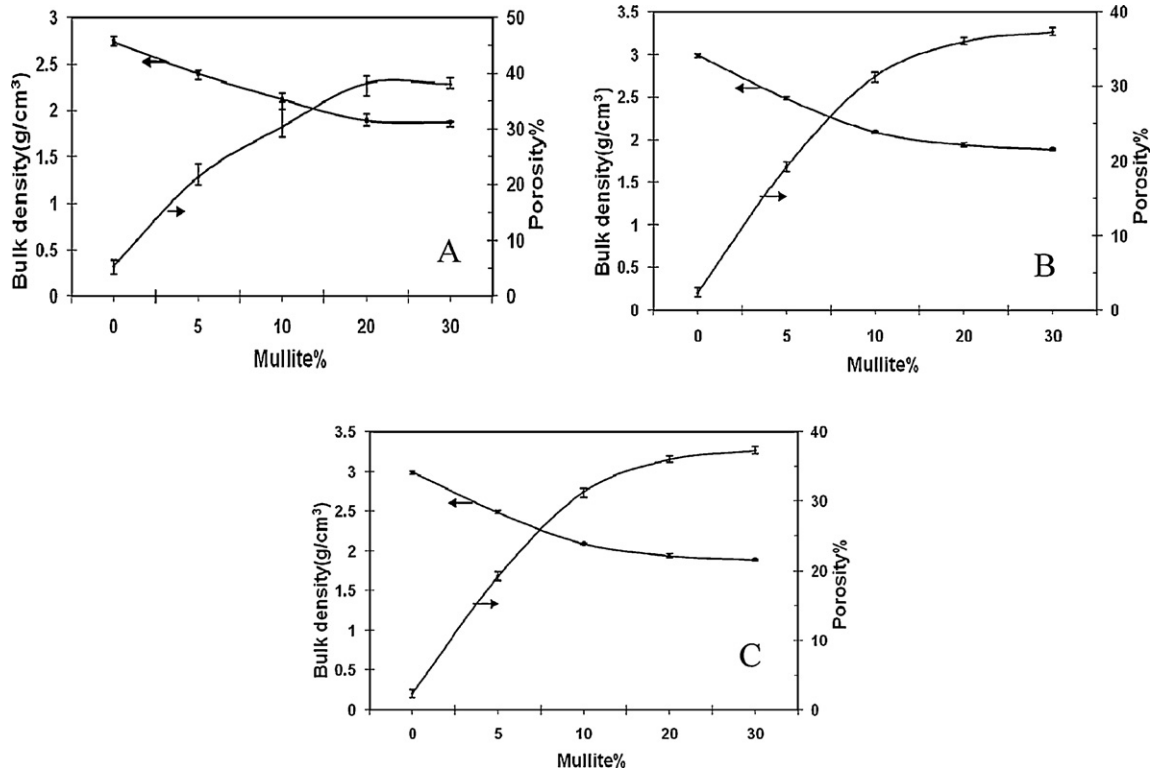

Fig. 1. Density and porosity of samples containing different weight fractions of mullite sintered at (A) 1150°, (B) 1250° and (C) 1350 °C for 2 h.

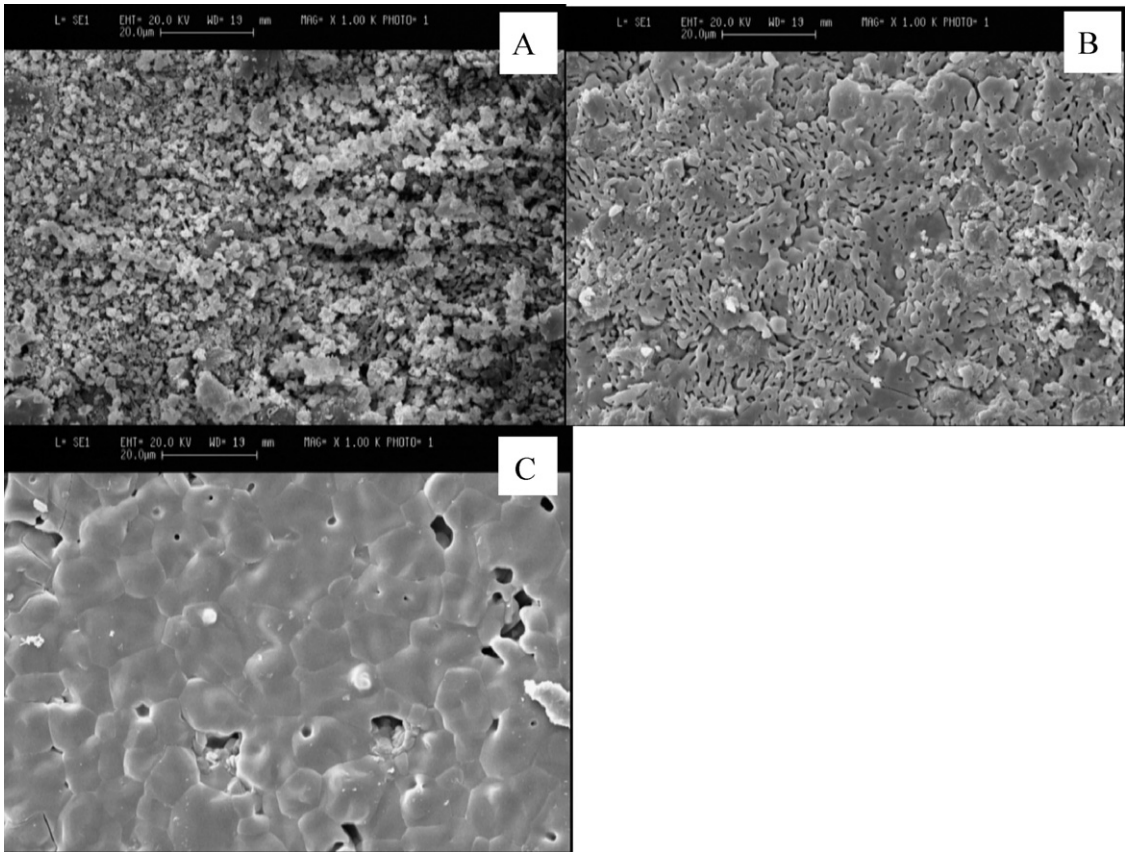

Fig. 2. SEM images of 30 wt.% mullite-containing samples sintered at (A) 1150°, (B) 1250° and (C) 1350 °C for 2 h.

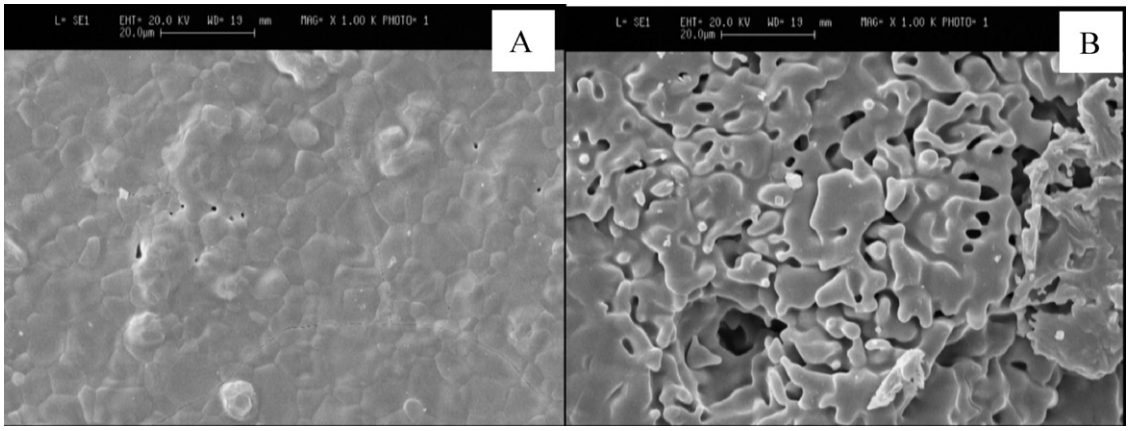

Fig. 3. SEM images of samples sintered at 1350 °C for 2 h, containing (A) 5 and (B) 10 wt.% mullite.

Table 1
Chemical composition of raw materials

Oxide	Al_2O_3 SiO_2 Fe_2O_3 TiO_2 MgO CaO NaO_2 K_2O L.O.I
Clay	39.22 48.46 0.2 0.25 0.3 0.5 - 1.1 9.97
Alumina	98.7 0.07 0.035 0.015 - 0.04 0.43 - 0.7

The maximum density with the lowest porosity was achieved in pure HAp samples (Fig. 1). Moreover, increasing the sintering temperature leads to a decrease of density and increase of porosity. Figure 2A presents the porous microstructure (38% porosity) of 30 wt.% mullite-containing sample sintered at 1150 °C. No considerable grain growth is observed and almost all spherical grains are fine. By increasing the sintering temperature to 1250 °C, the microstructure changes drastically (Fig. 2B) and grain growth is accelerated, leading to the development of a prevalent vermicular microstructure of elongated pores 0.6-2.5 μm in size and minor aggregates of nearly equiaxed grains. No significant reduction (1.8%) of porosity is observed in 30 wt.% mullite-containing samples sintered at 1250 °C compared to those sintered at 1150 °C. The microstructure of 30 wt.% mullite-containing sample sintered at 1350 °C (Fig. 2C) experienced pore coalescence 24% porosity and pore sizes in the range of 2.2-6.7 μm. In most cases, the grains are nearly equiaxed within the range between 5.2 and 8.7 μm. Sample containing 5 wt.% mullite sintered at 1350 °C (Fig. 3A) exhibits a dense microstructure (6.8% porosity). SEM micrograph of 10 wt.% mullite-containing sample sintered at 1350 °C (Fig. 3B) consists of a highly porous structure (21.3% porosity) with grains embedded in a glassy phase.

4. Conclusions

Porous hydroxyapatite ceramics were prepared by reaction sintering of clay, alumina and pure hydroxyapatite powders. Phase changes of sintered samples showed mullite to decompose hydroxyapatite at a sintering temperature as low as 1150 °C. Hydroxyapatite was completely decomposed by adding 10 wt% mullite after sintering at 1350 °C. Porosity increased by increasing mullite content and decreasing the sintering temperature. The microstructure uniformity decreased by increasing mullite content after sintering at high temperatures.

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