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Effect of zirconia addition on the microstructural evolution of porous hydroxyapatite

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Abstract

In the present study, 0–5 vol.% of 230 nm zirconia particles was added into hydroxyapatite (HAp). Though the reaction between HAp and ZrO_2 has taken place, HAp remains after sintering at 1300 °C. The addition of zirconia reduces not only the sintering shrinkage, but also decreases the size of HAp grains. Both the strength and toughness of porous HAp decrease slightly due to the formation of $CaZrO_3$ phase.

Keywords: A. Sintering; B. Composites; C. Mechanical properties; D. Apatite

1. Introduction

Hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$), a calcium phosphate, is a bioactive ceramic. Its composition is similar to the mineral composition of bone and tooth; hence it has been used as the contact material of artificial components to human tissue [1]. However, the mechanical properties of HAp are poor, the application of bulk HAp as the replacement for bone is thus limited [2]. To improve the mechanical properties of HAp has thus attracted wide attention. One of the many approaches employs zirconia as the reinforcement to HAp [3–10]. If there is no reaction between HAp and ZrO_2, the strength and toughness of HAp are indeed improved significantly [5]. For example, the strength and toughness of a 50%HAp/50%ZrO_2 composite can reach 439 MPa and 2.5 MPa $m^{0.5}$, respectively. However, the HAp and ZrO_2 readily react with each other above 1000 °C [3–10]. Below the temperature, the densification is usually not possible unless very special processes, such as hot-isostatic pressing (HIP) [6], spark plasma sintering (SPS) [5,7], are employed. However, considerable cost is usually involved of applying these special processes.

The product of the reaction between HAp and ZrO_2 is a CaO-ZrO_2 compound, calcium zirconate ($CaZrO_3$), which is bio-inert to human tissue [11]. The penalty of such a reaction is the consumption of the Ca from HAp. As the amount of ZrO_2 is large, HAp would be consumed completely after sintering, and α- or β-tricalcium phosphate ($Ca_3(PO_4)_2$) formed [9]. Previous studies were mostly concentrate on the reaction between HAp and ZrO_2 [3,4,7–10]. However, the effect of such a reaction on the microstructure evolution of HAp during sintering has attracted relatively little attention. In the present study, a small amount, <5 vol.%, of ZrO_2, is added into HAp. The effect of the ZrO_2 addition on the microstructure evolution during sintering is investigated. The mechanical properties of the porous HAp-$CaZrO_3$ composites are also measured.

2. Experimental

The HAp powder used in the present study was prepared by using a solid-state reaction process with $Ca(OH)_2$ and $CaHPO_4$ as the starting materials. The amount of $Ca(OH)_2$ and $CaHPO_4$ was controlled such that a Ca/P ratio of 1.67 was achieved. These two powders were mixed together by ball milling in alcohol for 4 h. The grinding media used were Ø10 mm zirconia balls. The slurry of the powder mixtures was dried with a rotary evaporator. The calcination of the powder mixture was carried out at 1200 °C for 2 h. The calcined powder mixtures were crushed and sieved. The particle size of the HAp powder was determined with a laser particle size analyzer (Master 2000, Malvern Co., USA). The HAp powder was then mixed with 1, 3 or 5 vol.% of zirconia powder (ZrO_2 + 3 mol.% Y_2O_3, TZ-3Y, d_{50} = 230 nm, Tosoh Co., Japan) through ball milling.

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After drying and sieving, rectangular bars with the dimensions of 6 mm × 6 mm × 46 mm were formed by pressing uniaxially at 60 MPa. Sintering was performed at 1300 °C for 2 h in air.

Phase identification was determined using an X-ray diffractometer (XRD, Philips PW 1830, Netherlands) with Cu Kα radiation. Since most zirconia was reacted with HAp to form calcium zirconate, the relative density of the sintered HAp-$CaZrO_3$ composite was estimated by using the theoretical density of HAp (3.16 g/cm^3) and of $CaZrO_3$ (4.65 g/cm^3). The flexural strength of the composites was determined by 4-point bending technique. The loading rate was 0.5 mm/min. The fracture toughness was determined by single-edge notched beam (SENB) technique. The notch was generated by cutting with a diamond saw, its depth was 1/3–1/4 of the specimen thickness. The microstructure was observed by scanning electron microscopy (SEM, Philips XL30, Netherlands). The chemical composition of each phase during SEM observation was determined with the energy dispersive X-ray analysis (EDX). The size of HAp grains was estimated by using the linear intercept technique on the micrographs taken from the fracture surface. Due to the density of the sintered specimen was low, a relatively flat surface could be easily found and the morphology of each grain was distinguishable. More than 100 HAp grains for each composition were counted to obtain an average value and its standard deviation.

3. Results and discussion

XRD phase analysis reveals only HAp in the HAp starting powder prepared by the solid-state-reaction process at 1200 °C for 2 h. The average particle size (d_{50}) of the HAp particles after milling is 5.5 μm. The size distribution of the powder is wide, $d_{10} = 0.89$ μm and $d_{90} = 21$ μm. Though the solid-state-reaction process is a straightforward technique and its ability to control the Ca/P of the HAp powder is satisfactory, the technique is not able to produce a powder with small size and narrow size distribution.

Fig. 1 shows the XRD patterns of the sintered HAp and HAp-ZrO_2 specimens. No ZrO_2 peaks can be found in the patterns. Calcium zirconate is found instead in the sintered specimens, indicating that HAp is reacted with ZrO_2 to form $CaZrO_3$. These observations differ from previous studies on the HAp-ZrO_2 systems [3–10] in that the amount of ZrO_2 used in the present study is much lower. The HAp starting powder prepared in the present study is a stoichiometric one, namely, the Ca/P ratio of the HAp powder is 1.67. The Ca/P ratio of the HAp is reduced as the HAp and ZrO_2 are reacted to form $CaZrO_3$ during sintering. Due to the amount of ZrO_2 being low, the HAp remains after sintering with ZrO_2 at 1300 °C for 2 h. However, the HAp is no longer stoichiometric, it becomes Ca-deficit HAp instead. Taking the HAp-5 vol.% ZrO_2 as the example (corresponds to 9 wt.% ZrO_2), its Ca/P ratio reduces to 1.53 as the ZrO_2 is fully reacted with the HAp. This value is still higher than the Ca/P ratio of $Ca_3(PO_4)_2$, 1.5, the HAp thus remains stable after reaction with ZrO_2. The ceramic within human bone is a Ca-deficit HAp. The addition of ZrO_2 into stoichiometric HAp drives the HAp closer to the mineral composition of bone.

Fig. 2 shows the green and sintered densities of the HAP and HAp-ZrO_2 specimens. The addition of ZrO_2 particles has little influence on the green density, nevertheless reduces the sintered density. There is about 30% porosity in the sintered HAp-$CaZrO_3$ composites. The density of the specimens is low, which can partly be related to the large particle size and wide distribution of the HAp starting powder. Fig. 3 shows the sintering curve of a HAp-5%ZrO_2 specimen during heating from room temperature to 1300 °C. For the pure HAp specimen, the linear shrinkage after sintering is 2%. The total shrinkage for the composite after sintering is relatively small, indicating that the reaction between HAp and ZrO_2 induces a volume expansion that compensates the shrinkage resulted from the sintering. From the shrinkage curve, a small peak above 1200 °C can be found. The sudden drop of the dimension between 1050 and 1200 °C is contributed by the loss of OH^- [5]. The loss of OH^- can enhance the formation of $CaZrO_3$ [5]. The formation of $CaZrO_3$ is accompanied with a volume expansion; the resulting sintering shrinkage is therefore small.

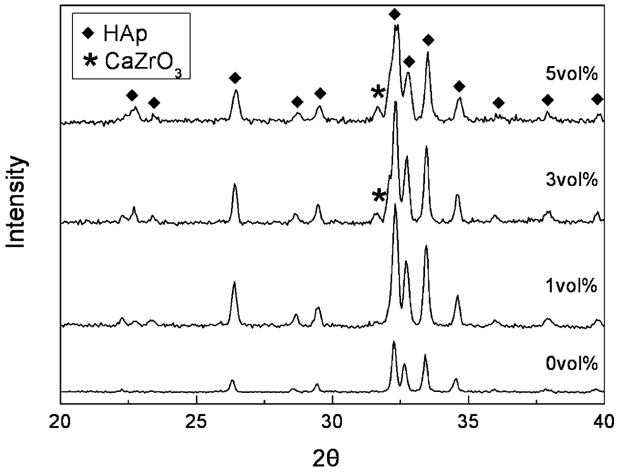

Fig. 1. XRD patterns for the HAp and HAp-ZrO_2 specimens after sintering at 1300 °C for 2 h.

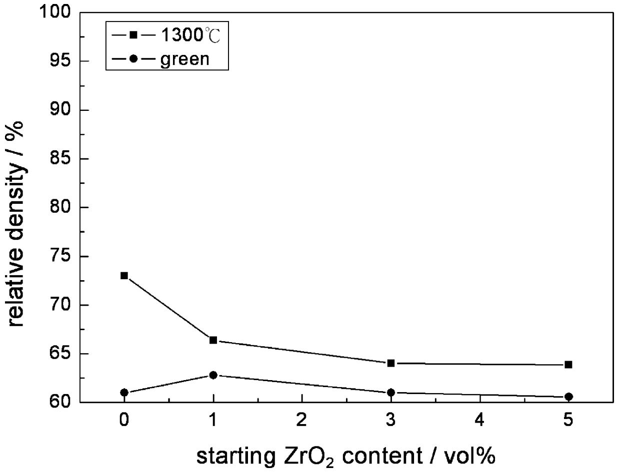

Fig. 2. Green and sintered densities of the HAp-ZrO_2 specimens as a function of starting ZrO_2 content.

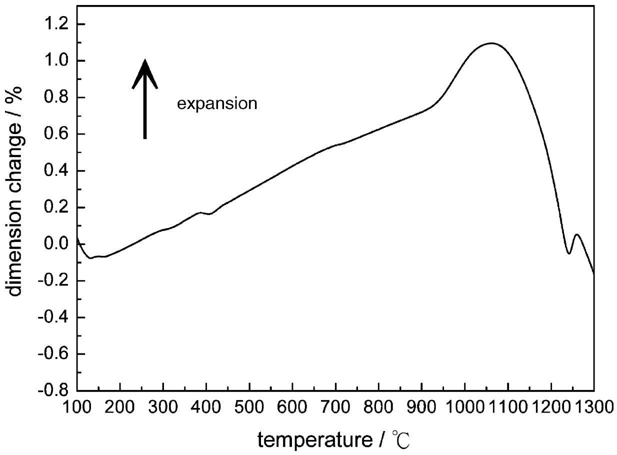

Fig. 3. Dimension change for the HAp-5%ZrO_2 specimen during sintering. Heating rate was 5 °C/min.

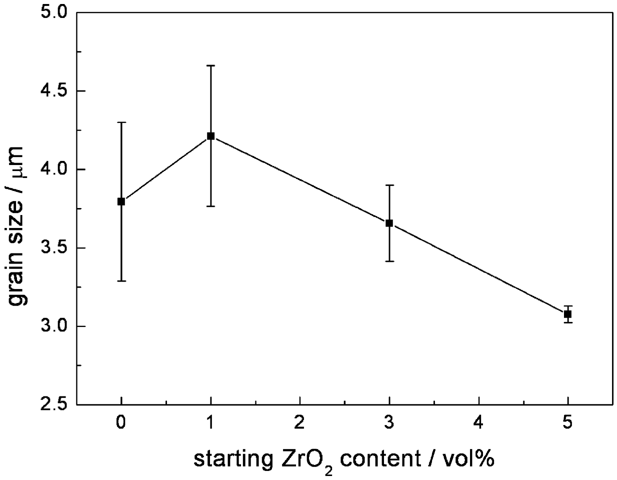

Fig. 5. Size of the HAp grains in the HAp-$CaZrO_3$ composites as a function of starting ZrO_2 content.

Fig. 4 shows the typical micrographs of HAp and HAp-$CaZrO_3$ specimens after sintering. The size of the starting ZrO_2 particles is one order smaller than that of the HAp particles; the resulting $CaZrO_3$ particles are therefore small. The distribution of fine $CaZrO_3$ particles is uniform, and they are mainly located at the grain boundary of HAp grains (Fig. 4b). The $CaZrO_3$ can thus act as an effective grain growth inhibitor to the HAp grains. Fig. 5 shows the average size of HAp grains in the sintered composites as a function of ZrO_2 content. The error bars show all the standard deviations. Exception being made for the specimen with 1 vol.% ZrO_2, the addition of ZrO_2 particles reduces the size of HAp grains. Furthermore, the pores are also smaller, indicating that the $CaZrO_3$ particles can act as microstructure refiner to HAp. A small amount of ZrO_2 addition, 1 vol.%, can increase the size of HAp grains, implying that some ZrO_2 may dissolve into HAp to enhance its growth. As the amount of ZrO_2 is higher than 3 vol.%, the grain growth of HAp is prohibited by the $CaZrO_3$ particles. The HAp grains of the composites become smaller.

Fig. 6 shows the strength and toughness of the sintered HAp-$CaZrO_3$ composites as a function of ZrO_2 content. Both the strength and toughness decrease with the increase of ZrO_2 content, which corresponds to the increase of porosity in the composites (see Fig. 2). It indicates that the amount of porosity plays an important role on the mechanical performance of the present system.

There are several benefits of adding a small amount of ZrO_2 particles into porous HAp; there are

1. the HAp grains and pores are reduced in size;
2. the sintering shrinkage is also reduced;

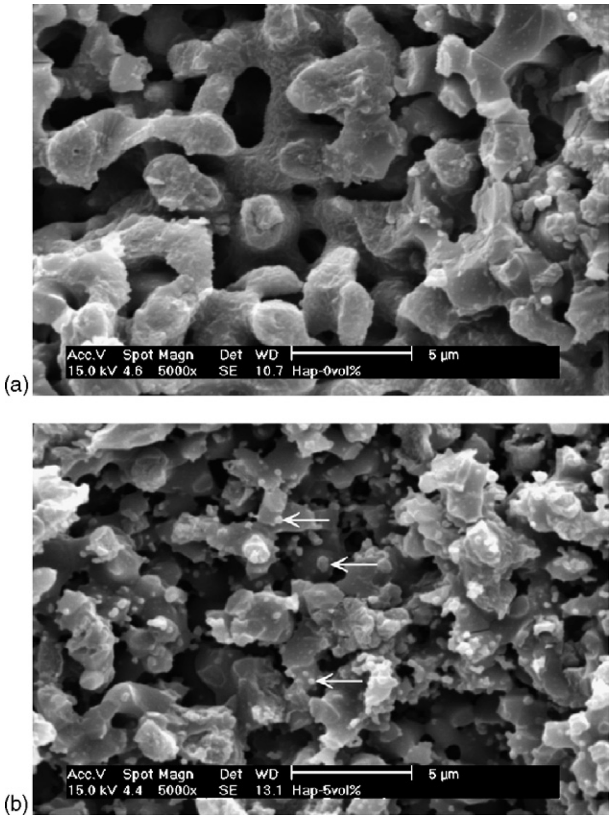

Fig. 4. Typical micrographs of HAp (a) and HAp-5%ZrO_2 (b) specimens after sintering at 1300 °C for 2 h. Several $CaZrO_3$ particles in (b) are indicated.

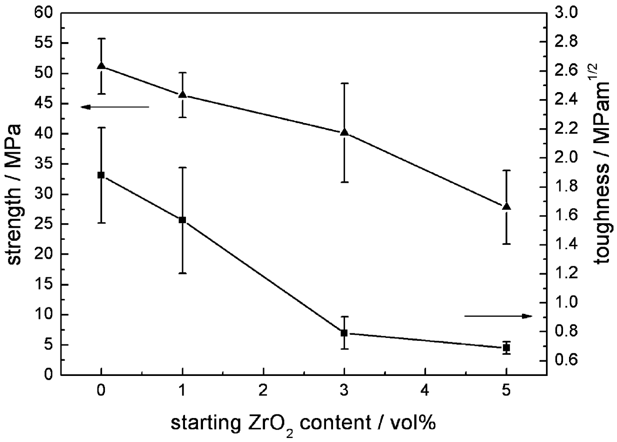

Fig. 6. Strength and toughness of the HAp-$CaZrO_3$ composites as a function of starting ZrO_2 content.

3. the HAp phase remains after part of its Ca is reacted with ZrO_2 to form $CaZrO_3$.

The major drawback is the decrease of strength and toughness due to the reaction between HAp and ZrO_2. To avoid such reaction seems to be the key to improve the mechanical properties of porous HAp.

4. Conclusions

As far as the preparation of porous HAp is concerned, the addition of a small amount of fine ZrO_2 particles can refine its microstructure. Furthermore, the addition of ZrO_2 can reduce the sintering shrinkage; it would be beneficial for the near-net shaping for the porous HAp materials. However, the volume expansion which accompanies the reaction between the HAp and ZrO_2 may also reduce the final density of the composites. The strength and toughness are consequently traded off slightly.

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