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Spark plasma sintered hydroxyapatite-yttria stabilized zirconia composites

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Abstract

Hydroxyapatite (HA) ceramics have been well known to have good bioactivity, i.e. bone bonding ability. However, their mechanical properties need to be improved for some biomedical applications. One of the commonly used methods to improve the mechanical properties has been the production of HA-based composites. Nevertheless, conventional pressure less sintering tends to result in poor densification and severe decomposition of the HA phase. In this study, hydroxyapatite-yttria stabilized zirconia (YSZ) composites were fabricated by means of spark plasma sintering (SPS) technique. A relative density of up to 93% theoretical density of the HA-YSZ composites was achieved after spark plasma sintering at 1200 °C for only 5 min. Only slight decomposition of HA to alpha-tricalcium phosphate (α-TCP) was observed at the sintering temperature of 1150 °C. Zirconia second phase remained to be tetragonal ZrO_2 phase even when the sintering temperature was as high as 1250 °C. It was also found that the equiaxial YSZ grains were uniformly dispersed in the HA matrices. The HA grain size in the HA-YSZ composites was much smaller than that in the pure hydroxyapatite monoliths. Furthermore, the HA-YSZ composites sintered at 1200 °C showed microhardness of about 9 GPa and Young's modulus of up to 160 GPa, considerably higher than those of the pure HA ceramics. The bending strength of the composites reached 200 MPa under the current sintering conditions, which was nearly one time higher than that of the pure HA ceramics.

Keywords: B. Composite; C. Mechanical properties; D. Zirconia; Hydroxyapatite; Spark plasma sintering

1. Introduction

Hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) is one of the most attractive bioceramic materials for human hard tissue implants because of its close resemblance to bones and teeth. However, hydroxyapatite possesses low mechanical strength and fracture toughness, which is an obstacle to its applications in load-bearing situations. The enhancement of mechanical properties of hydroxyapatite would extend its scope of applications compared to those biomert but strong ceramics currently used. A suitable method of improving the mechanical properties is based on the synthesis of composites made of HA and other second phases [1–4]. As the second phase, zirconia (ZrO_2) exhibits higher toughness than alumina and has wide applications in bone surgery [5]. Moreover HA-ZrO_2 composites showed improved fatigue resistance in addition to high strength [6].

The HA-ZrO_2 composites cannot be easily sintered without pressure [7] and the HA phase often decomposes into other phases during the conventional sintering. On the other hand, hot isostatic pressing (HIP) often results in grain coarsening or surface contamination due to the high temperatures and long sintering duration involved. Thus, a new sintering method for the HA-ZrO_2 composites was sought to get dense HA-ZrO_2 composites at relatively low temperatures. Spark plasma sintering (SPS) as an emerging densification process was thus tried for the HA-ZrO_2 composites in this study.

Spark plasma sintering is capable of sintering ceramic powders quickly to a high density at a relatively lower temperature, compared to the conventional sintering method [8]. The detailed configuration of the SPS process can be found in a previous report [9]. The SPS features a very high thermal efficiency because of the direct heating of the sintering graphite mold and stacked powder materials by the large

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spark pulse current. Although SPS has been used to produce metals and engineering ceramics, there are few reports on the application of this technique to produce dense bioceramic composites for biomedical applications. In this study, HA–40 wt.% ZrO_2 composites were sintered at different temperatures by spark plasma sintering. The microstructure and mechanical properties were investigated and discussed.

2. Experimental procedure

Hydroxyapatite and 3 mol% yttria stabilized zirconia (YSZ) were the two main starting materials used in the study. The HA powder (E. Merck, D-6100 Darmstadt, Germany) was in the form of micron-scale agglomerates of nano-scale primary particles. To modify the as-supplied HA powder, calcination at 900 °C for 1 h in air was carried out to obtain submicron sized particles. On the other hand, a commercial yttria stabilized zirconia (ZrO_2–3 mol% Y_2O_3) powder (FW: 123.22, Aldrich, USA) was used in the as-provided state with submicron-sized particles and 99.5% purity. The HA and YSZ powders were then mixed by ball milling for 4 h to obtain a homogenous mixture with a composition of 40 wt.% YSZ. The HA-YSZ mixtures were pressed in a steel die to produce green compacts. For comparison, pure HA green compacts were also prepared similarly. The HA-YSZ compacts were subsequently densified by the spark plasma sintering process on a Dr. Sinterer SPS-1050 system (Sumitomo Coal Mining Co., Japan). The sintering temperatures for the compacts were set at 1050, 1100, 1150, 1200, and 1250 °C, respectively, and the holding time at the sintering temperatures was 5 min. For comparison, some pure HA compacts were also produced by the spark plasma sintering at 900, 950, 1000, and 1050 °C for 5 min, respectively.

The microstructure of the spark plasma sintered composites was inspected by JEOL JSM-5410 scanning electron microscope (SEM). Phase analysis on a Shimadzu X-ray diffractometer (XRD) with Cu Kα radiation generated at 50 kV and 20 mA was carried out to determine the phase stability of the HA and the YSZ phases in the composites. The density of the samples was determined on a densometer based on the Archimed's principle. The microhardness of the composites was tested by a Shimadzu HMV-2000 Knoop microhardness tester with an applied load of 300 g and a holding time of 15 s. The Knoop hardness H_K is expressed as

$$H_K = 14229\frac{L}{d^2} \quad (1)$$

where L is the load (N) and d is the longer diagonal of the indentation impression (μm).

The Knoop hardness tester was also used to determine the Young's modulus (E) of the composites. The Young's modulus can be calculated using the following equation [10]

$$\frac{b'}{a'} = \frac{b}{a} - \alpha\frac{E}{H_K} \quad (2)$$

where b'/a' is the indent diagonal ratio after elastic recovery, i.e. after indentation, b/a is the ratio of the Knoop indenter dimensions (=1/7.11) and α is a constant with a value of 0.45. Finally, the three-point bending strength of the composites was determined on an Instron 4206 tensile tester using a cross-head speed of 0.5 mm/min. The bending strength was finally calculated based on the following equation

$$\sigma = \frac{3PL}{2bd^2} \quad (3)$$

where σ denotes the bending strength; P, applied load and L, b, and d are the span length, the width and thickness of the test specimen, respectively.

3. Results and discussion

3.1. Thermal stability of HA-YSZ composite

Fig. 1 compares the XRD patterns of a green compact of HA-YSZ mixture, and the HA-YSZ composites spark plasma sintered at 1150 and 1200 °C for 5 min, respectively. Tetragonal zirconia (t-ZrO_2) phase and HA phase were the main constituent phases in the green compact.

There was no phase change for the composite sintered at 1150 °C. However, when sintered at 1200 °C, HA started to discompose since small peaks corresponding to the tricalcium phosphate (TCP) phase were observed. Meanwhile, the t-ZrO_2 phase did not change into other phases at this sintering temperature. Previous studies showed that HA decomposed into tricalcium phosphate and tetracalcium phosphate 1000 °C in vacuum [11]. In this study, the HA phase was stable up to 1150 °C, and even at the sintering temperature of 1200 °C, only small amount of HA was decomposed. The limited decomposition could be contributed to the pressure, the short duration, and the low sintering temperature used in the spark plasma sintering for the densification of the HA-YSZ powder compacts.

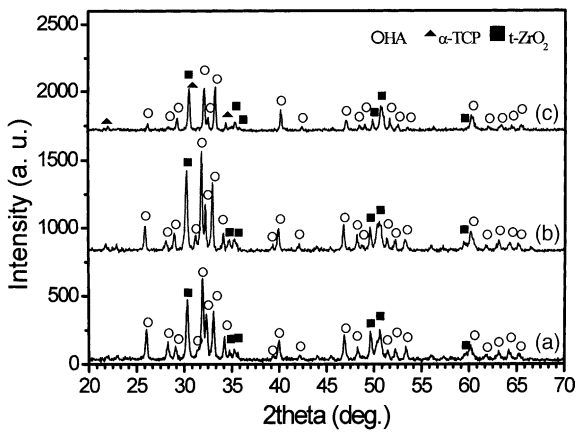

Fig. 1. XRD patterns from the green compact of the HA-YSZ mixture: (a) the HA-YSZ composites spark plasma sintered at 1150 °C, (b) 1200 °C, (c) for 5 min.

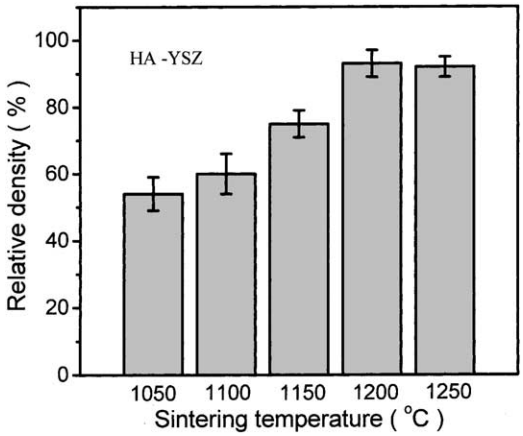

Fig. 2. Relative density of the HA-YSZ composites vs. sintering temperature.

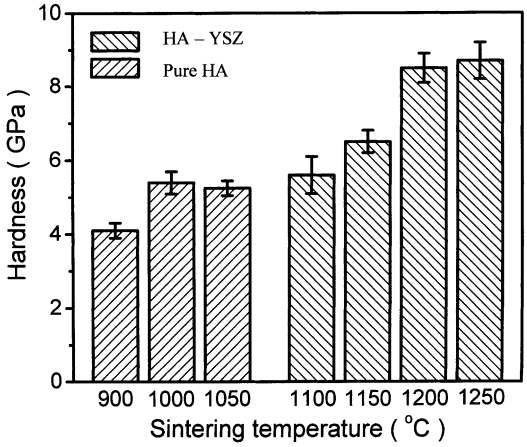

Fig. 4. The hardness of the HA-YSZ composites vs. sintering temperature.

3.2. Densification and microstructure of HA-YSZ composite

The relative density of the HA-YSZ composites as a function of sintering temperature is shown in Fig. 2. The measured density increased rapidly with the increase of the sintering temperature up to 1200 °C. Specifically, after sintering at 1200 °C for 5 min, the relative density of the composite increased up to 93%. Further increase of the sintering temperature up to 1250 °C, resulted in a small decrease in the density, due to the decomposition of HA into TCP. It is well known that TCP has a density of 3.0 g/cm^3, which is a little lower than that of HA (3.16 g/cm^3).

Fig. 3 is an SEM micrograph of the HA-YSZ composite sintered at 1200 °C. From the micrograph one can see that the t-ZrO_2 phase (white spots) is uniformly dispersed in the HA matrix, and the composite is also very dense, since large pores are not found on the finely polished surface of the composite. The HA grains grew up to more than 1 μm after spark plasma sintering at 1200 °C for 5 min. The average size of the YSZ grains was much smaller than that of HA grains. The YSZ grains were mostly located on the grain boundaries of HA matrix, with a small amount of the YSZ grains dispersed within the HA grains. In addition, some microcracks can be observed along the HA/HA and the HA/YSZ grain boundaries. The microcracks along the HA/HA boundaries were mainly due to the anisotropic thermal expansion coefficients of the HA single crystals, which caused the thermal stresses. As to the microcracks along the HA/ZrO_2 phase boundaries, they were mainly caused by the difference in thermal expansion coefficient of the different phases ($\alpha_{HA} \approx 16.9 \times 10^{-6}\,°C^{-1}$ and $\alpha_{ysz} \approx 10 \times 10\,°C^{-1}$ [3]).

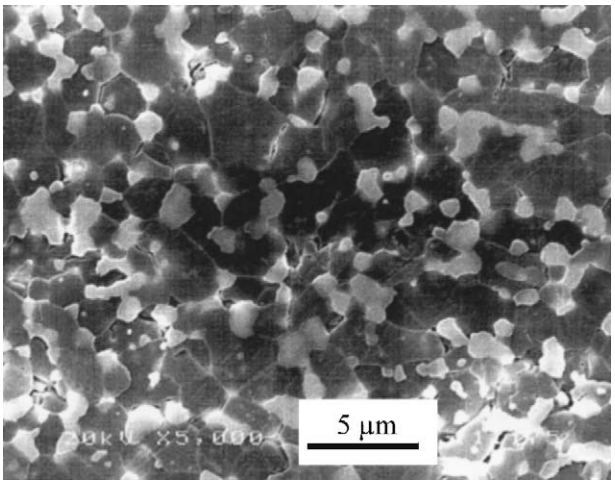

Fig. 3. SEM micrograph of the HA-YSZ composite prepared by spark plasma sintering at 1200 °C for 5 min.

3.3. Mechanical properties of HA-YSZ composite

The Knoop microhardness and the Young's modulus of the pure HA ceramics and the HA-YSZ composites sintered at different sintering temperatures are shown in Figs. 4 and 5, respectively. For the pure HA ceramics, the hardness and the Young's modulus increased rapidly with the sintering temperature, and reached the maximum values of 5.5

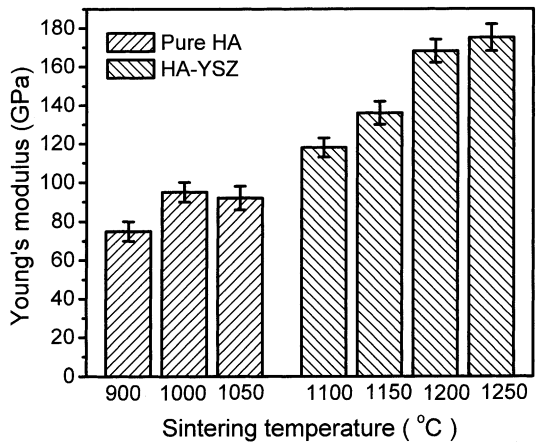

Fig. 5. Young's modulus of the HA-YSZ composites vs. sintering temperature.

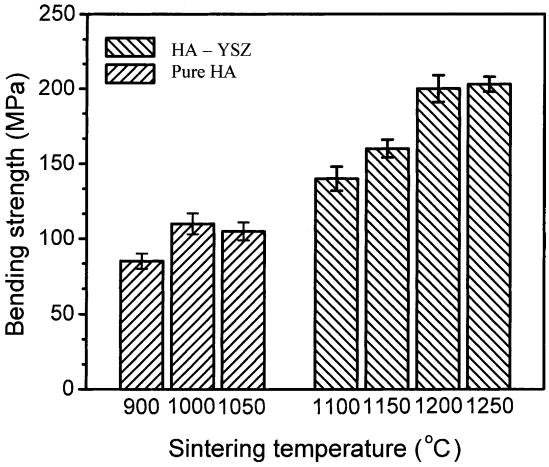

Fig. 6. Bending strength of pure HA ceramics and the HA-YSZ composites sintered at different temperatures for 5 min.

and 95 GPa at 1000 °C, respectively. The slight decrease in the mechanical properties at 1050 °C may be due to the decomposition of HA [11]. The HA-YSZ composites sintered at 1200 °C showed the microhardness of about 9 GPa and the Young's modulus of up to 160 GPa, respectively, which were much higher than those of the pure HA ceramics. It is clear that the addition of YSZ to HA could remarkably enhance the mechanical properties of the pure HA ceramics.

Fig. 6 is a comparison of the bending strengths of the pure HA ceramics and the HA-YSZ composites spark plasma sintered at different temperatures. The pure HA ceramics sintered at 950–1050 °C exhibited bending strengths of 85–110 MPa. In contrast, the HA-YSZ composites sintered at 1200 °C showed bending strengths of up to 200 MPa, which were considerably higher than the bending strengths of the pure HA ceramics.

4. Conclusions

1. Hydroxyapatite–40 wt.% yttria stabilized zirconia powder compacts were densified to up to 93% theoretical density by spark plasma sintering at 1200 °C and for 5 min. The sintering temperature showed significant effect on the densification of the HA-YSZ composites.
2. The HA phase in the composites was stable up to 1150 °C, above which the HA phase started to discompose into α-TCP. The zirconia phase in the composites remained t-ZrO_2 phase even when the sintering temperature increased to 1250 °C. The YSZ grains were dispersed uniformly among the HA matrix, and were mostly located on the boundaries of the HA grains. Meanwhile, the HA grains grew up to more than 1 μm after spark plasma sintering at 1200 °C for 5 min.
3. The HA-YSZ composites sintered at 1200 °C for 5 min showed microhardness, Young's modulus, and bending strength values of up to 9 GPa, 160 GPa, and 200 MPa, respectively, which were significantly higher than those of the pure HA ceramics.

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