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Hot-pressed hydroxylapatite/monoclinic zirconia composites with improved mechanical properties

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Abstract Composites of hydroxylapatite (HA) and monoclinic zirconia were hot-pressed at 1100 °C and 1200 °C under vacuum to study the phase transformations and the mechanical properties. X-ray diffraction results showed a higher phase transformation from monoclinic-ZrO_2 to tetragonal-ZrO_2 when the sintering temperature increased from 1100 °C to 1200 °C. HA decomposed faster when the amount of ZrO_2 in the composites increased. Moreover, small amount of α-TCP and $CaZrO_3$ was observed in the composites hot-pressed at 1200 °C. Hot-pressing at 1100 °C resulted in better mechanical properties than the hot-pressing at 1200 °C because of less reaction between HA and zirconia at 1100 °C. 40 wt% monoclinic zirconia and HA composite hot-pressed at 1100 °C resulted in promising mechanical properties which are 6.5 GPa of Vickers μ-hardness, 2.23 MPa√m of fracture toughness, and 66 MPa of diametral strength.

Introduction

Hydroxylapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) has been widely used as a bulk implant in non-load bearing areas of the body and as coatings on implant metals. Although it has excellent biocompatibility in the human body, it is brittle [1–3]. HA and zirconia composites (or coatings) have been studied to combine the advantages of the HA's biocompatibility and high strength of zirconia [4, 5]. HA–zirconia composites can be produced by two methods. In the first, HA and zirconia powders are mixed, cold-pressed and then sintered at higher temperatures in different environments [5–10]. Pressure assisted sintering must be used to get high density and high strength composites [9, 10]. In the second, HA–zirconia composites are synthesized by the precipitation of $ZrOCl_2 \cdot 8H_2O$, calcium nitrate and ammonium phosphate chemicals [11, 12].

Although pure HA starts to decompose to tricalcium phosphate (TCP) at ~1300 °C; second phase formations start well below 1300 °C in the presence of ZrO_2 [5, 8, 13, 14]. It was suggested that the sintering temperature of HA and zirconia composites should be less than 1200 °C and the amount of zirconia must be less than 10 wt% to minimize the reactions between HA and zirconia [14]. Kim et al. [5] enhanced the sinterability of the partially stabilized zirconia (up to 40 vol%)-HA composites by increasing the green density of the composites by cold isostatic pressing and the addition of small amounts of CaF_2. In some of the composites, they observed the decomposition of HA first into β-TCP at a temperature of 1350 °C. Fracture toughness of the HA–ZrO_2 composites (1.7–2.3 MPa√m) is higher than that of pure HA (1 MPa√m) [5, 12, 15].

Phase transformations and mechanical properties of HA and partially stabilized zirconia composites have been studied extensively because of the high strength of partially stabilized zirconia [9–11]. However, HA and monoclinic zirconia composites have not been

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investigated enough especially for their mechanical properties.

In the present work, HA and monoclinic (m)-ZrO_2 composites were made by hot-pressing at 1100 °C and 1200 °C for 1 hr. Phase transformations in the composites were studied with X-ray diffraction (XRD). Vickers μ-hardness testing was used to determine the hardness and the fracture toughness of the composites and the diametral test was used to determine their tensile strength.

Experimental procedure

The materials used in this research were pure HA synthesized with a precipitation method and composites of HA with monoclinic zirconia made by hot-pressing of mixed powders.

HA was synthesized by mixing solutions of calcium nitrate and di-ammonium hydrogen phosphate in the alkaline pH region [16]. First, 0.5 M calcium nitrate ($Ca_3(NO_3)_2 \cdot 4H_2O$) and 0.3 M di-ammonium hydrogen phosphate ($(NH_4)_2HPO_4$) were prepared in distilled water separately. Ammonium hydroxide (NH_4OH) was added to both of these solutions to bring the pH level to 11–12. The calcium nitrate solution was added dropwise into the continuously stirred ammonium phosphate solution, producing a milky solution. After stirring the HA solution for 2–3 h, it was heated to 90 °C for 1 h during stirring to decrease the reaction time. Then, the HA solution was stirred for one day at room temperature. In the next step, the solution was washed repeatedly to remove the remaining ammonia and then filtered using a fine filter paper. The filtered wet cake was dried in an oven at 60–90 °C overnight to remove the excess water. Finally the dried cake was air sintered at 1100 °C to full density; it was heated and cooled in the furnace.

The powders of m-ZrO_2 (2 μm powder size, Goodfellow, Cambridge, UK) were mixed with HA powder. First, dried HA particles were ground to –75 μm (–200 mesh) powder using a mortar and pestle. Second, they were calcined at 900 °C for 1 h and then mixed with zirconia powders by ball milling. The powders of the m-ZrO_2 were mixed with HA powders at weight ratios ranging from 10 to 40 wt%.

Mixed powders were hot-pressed at 1100 and 1200 °C using a high temperature – high vacuum furnace (Thermal Technology Inc., Concord, NH). Composite powders were put in a graphite mold and hot-pressed under 60 MPa in vacuum.

All the samples were characterized by XRD with a Scintag Inc., XDS–2000 diffractometer with Cu-Kα radiation at 50 kV/30 mA. Each sample was scanned from 20 ° to 50 ° in 2θ with a scanning speed of 1 degree/min.

The density of a hot-pressed disc was calculated by dividing the weight by its volume. The theoretical density of the composites (components a and b) was calculated from the known weights w and densities ρ by the following formula.

$$Density({}^{gm}/_{cm^3}) = \frac{W_a + W_b}{\left(\frac{W_a}{\rho_a} + \frac{W_b}{\rho_b}\right)} \tag{1}$$

Component ‘‘a’’ is ZrO_2 and component ‘‘b’’ is HA and/or TCP. Density of HA and TCP was assumed to be same for the simplicity of composite density calculation.

Micro (μ)-hardness of the hot-pressed samples was measured with a Vickers μ-hardness tester with a diamond indenter at 200 gm (or 300 gm) load for 10 s. Approximately 20 measurements were performed on each sample. The hardness value for each sample was calculated by:

$$HV = 0.001854 * \frac{P}{d^2} \tag{2}$$

where HV: Vickers hardness, P: Applied load, d: diagonal indent length

The fracture toughness (K_{1c}) of the composites was determined from cracks formed in the Vickers μ-hardness test. The Palmqvist equation for the fracture toughness of the composites is [17]:

$$K_{1c} = 0.035 * \left(\frac{H^{0.6} * E^{0.4}}{\phi^{0.6}}\right) * \left(\frac{a}{(c-a)^{0.5}}\right) \tag{3}$$

where, H: Hardness, E: Young's Modulus, ϕ: a dimensionless coefficient related to the material constraint ($\phi \cong 3$).

In diametral testing, a disk shaped sample is compressed diametrically between two parallel plates. The maximum tensile strength is developed normal to the applied load direction across the disk diameter. A thin steel sheet was placed between sample and the plates to minimize friction crushing of the contact points [18]. An INSTRON Universal Testing Machine was used for diametral testing. A speed of 0.4 mm/min was applied during the test. Tensile strength (S) of the samples was calculated by:

$$S = \frac{2F}{(\pi * D * T)} \tag{4}$$

where *F*: failure force, *D*: sample diameter, *T*: sample thickness

Results

After the HA was precipitated and dried in the oven, it was sintered at 1100 °C for 1 h. XRD results of dried and sintered HA are presented in Fig. 1. Dry HA shows very wide and low intensity peaks, which is due its small particle size. X-ray diffraction peaks for the HA sintered at 1100 °C are sharp and narrow showing that the HA grain size was greater than 100 nm after sintering. Air sintering of precipitated HA at 1100 °C for 1 h resulted in a fully dense material (3.14 gm/cm^3).

The HA sintered at 1100 °C–1hr had an average Vickers μ-hardness of 4.7 ± 0.35 GPa. A fracture toughness of 0.95 ± 0.05 MPa√m was calculated.

XRD patterns of the m-ZrO_2 and other phases are presented in Fig. 2. ZrO_2 (as received) had a monoclinic structure with a negligible amount of tetragonal (t) ZrO_2 phase. When the m-ZrO_2 powders were sintered at 1100 °C for 1 h, no phase change in the m-ZrO_2 was observed (Fig. 2e).

XRD results of HA–m-ZrO_2 composites, which were hot-pressed at 1100 °C and 1200 °C, are presented in Fig. 3. Although m-ZrO_2 did not transform to t-ZrO_2 when it was sintered at 1100 °C as a monolithic phase (Fig. 2e), m-ZrO_2 partially transformed to t-ZrO_2 in the composites after sintering at 1100 °C and 1200 °C because of the presence of HA (Fig. 3). Formation of α-TCP was observed after the hot-pressing at 1200 °C. From the comparison of the m-ZrO_2 and t-ZrO_2 XRD peak heights, phase transformation from m-ZrO_2 to t-ZrO_2 was increased when the sintering temperature increased from 1100 °C to 1200 °C. HA started to decompose faster when the amount of ZrO_2 in the composites increased (Fig. 3). Small amount of $CaZrO_3$ formation was observed in the composites hot-pressed at 1200 °C.

Vickers μ-hardness results of the 10, 25 and 40 wt% m-ZrO_2–HA composites are presented in Fig. 4. The μ-hardness of the composites decreased when the sintering temperature was increased from 1100 °C to 1200 °C. Porosity in the composites is presented in Fig. 5. The amount of the porosity in the composites increased (except 10 wt% ZrO_2 composites) when the sintering temperature was increased from 1100 °C to 1200 °C, which resulted in poor μ-hardness values. Although densification was improved for 10 wt% ZrO_2–HA composite when the sintering temperature was increased from 1100 °C to 1200 °C, it was

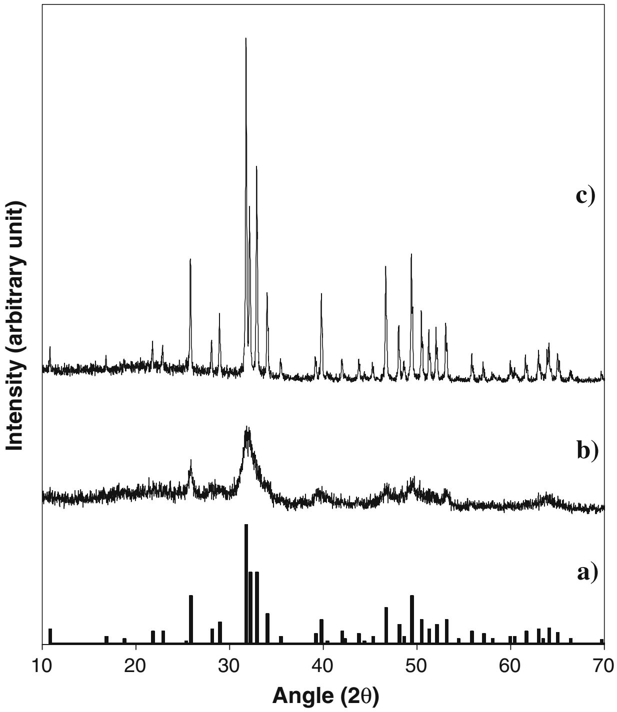

Fig. 1 X-ray diffraction spectra of (a) Standard HA (JCPDS # 9–432); (b) HA dried at 90 °C; (c) HA sintered at 1100 °C–1 hr. All peaks correspond to hydroxylapatite

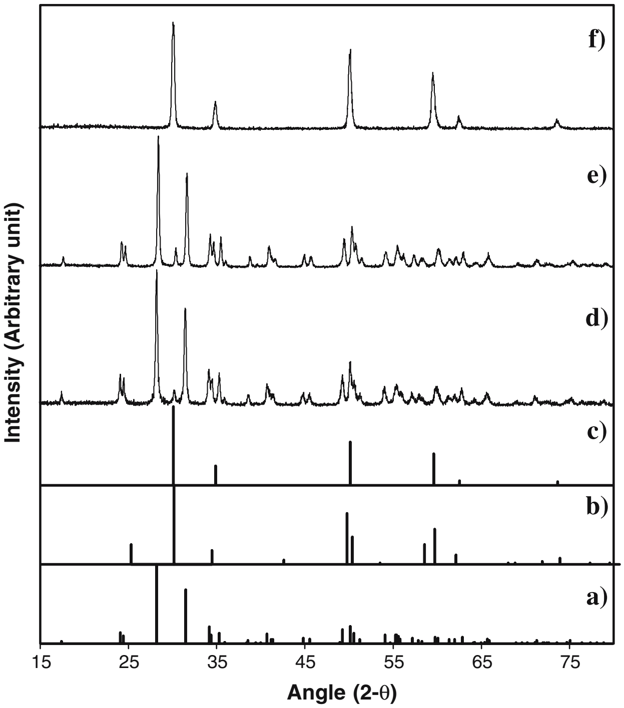

Fig. 2 XRD spectra of (a) m-ZrO_2 (JCPDS # 37–1484); (b) t-ZrO_2 (JCPDS # 17–0923); (c) c-ZrO_2, 8% Y_2O_3 (JCPDS # 30–1468); (d) Pure ZrO_2 as received; (e) ZrO_2, sintered at 1100 °C–1hr; (f) ZrO_2, 8%Y_2O_3

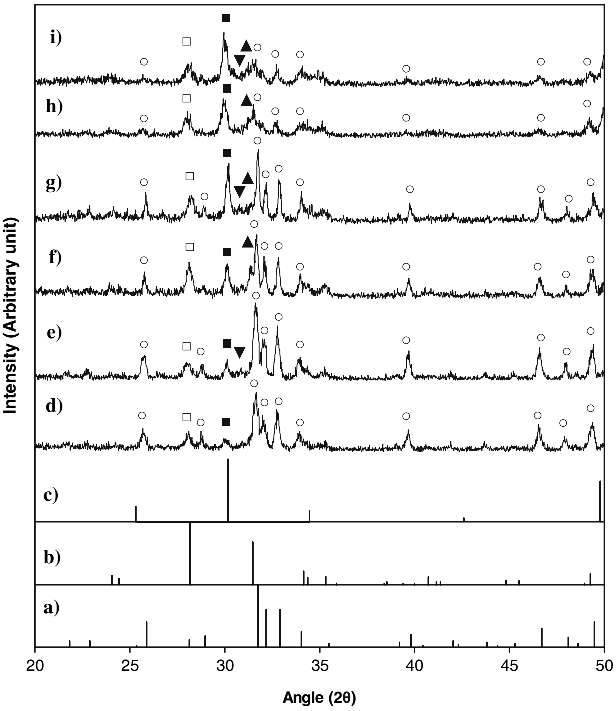

Fig. 3 XRD-ray diffraction spectra of the hot-pressed composites: (a) HA (JCPDS # 9–432); (b) m-ZrO_2 (JCPDS # 37–1484); (c) t-ZrO_2 (JCPDS # 17–0923); (d) 10 wt% m-ZrO_2, 1100 °C–1hr; (e) 10 wt% m-ZrO_2, 1200 °C–1hr; (f) 25 wt% m-ZrO_2, 1100 °C–1hr; (g) 25 wt% m-ZrO_2, 1200 °C–1hr; (h) 40 wt% m-ZrO_2, 1100 °C–1hr; (i) 40 wt% m-ZrO_2, 1200 °C–1hr. (Phases: ○: HA; □: m-ZrO_2; ■: t-ZrO_2; ▼: α-TCP; ▲: $CaZrO_3$

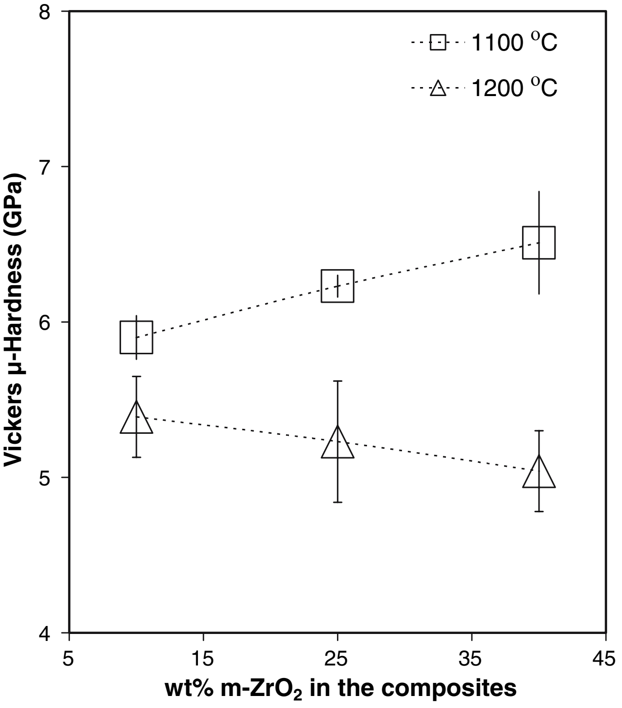

Fig. 4 Vickers μ-hardness of 10, 25, and 40 wt% m-ZrO_2–HA composites hot-pressed at 1100 °C and 1200 °C

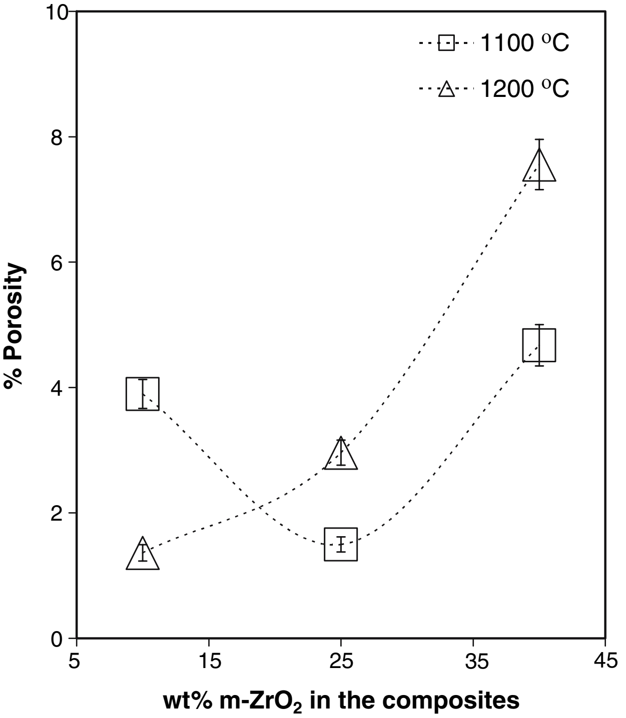

Fig. 5 %Porosity amounts in 10, 25, and 40 wt% m-ZrO_2–HA composites hot-pressed at 1100 °C and 1200 °C

diminished for 25 wt% and 40 wt% ZrO_2 composites. This showed that there was less reaction in the 10 wt% ZrO_2 composite during the hot-pressing because there was only 10 wt% ZrO_2 present in HA matrix.

SEM micrograph of 25 wt% m-ZrO_2–HA composite hot-pressed at 1200 °C is presented in Fig. 6. Cracks often formed along grain boundaries. The fracture toughness of the 10, 25 and 40 wt% m-ZrO_2–HA composites is presented in Fig. 7. Increasing the sintering temperature from 1100 °C to 1200 °C decreased the fracture toughness of the composites similar to μ-hardness results. The tensile strength of the composites was determined by diametral testing as shown in Fig. 8. The tensile strength of the 40 wt% m-ZrO_2 composite was double that of pure HA.

Discussion

Green densities of the composites were about 54% of the theoretical density. After the sintering, composites had densities between 92% and 99% of the theoretical density (Fig. 5). Sintering of the ceramics in the solid state happens in three steps:

(1) Neck formation
(2) Removal of the intermediate—open porosities
(3) Removal of isolated pores—usually on grain boundaries

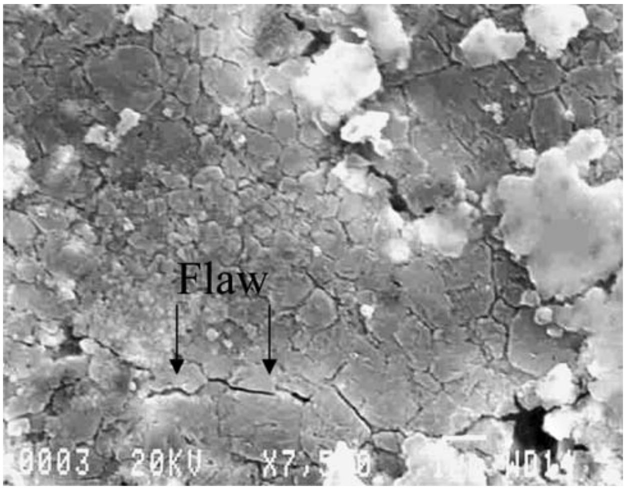

Fig. 6 SEM micrograph of 25 wt% m-ZrO_2 composite hot-pressed at 1200 °C–1hr, x7500

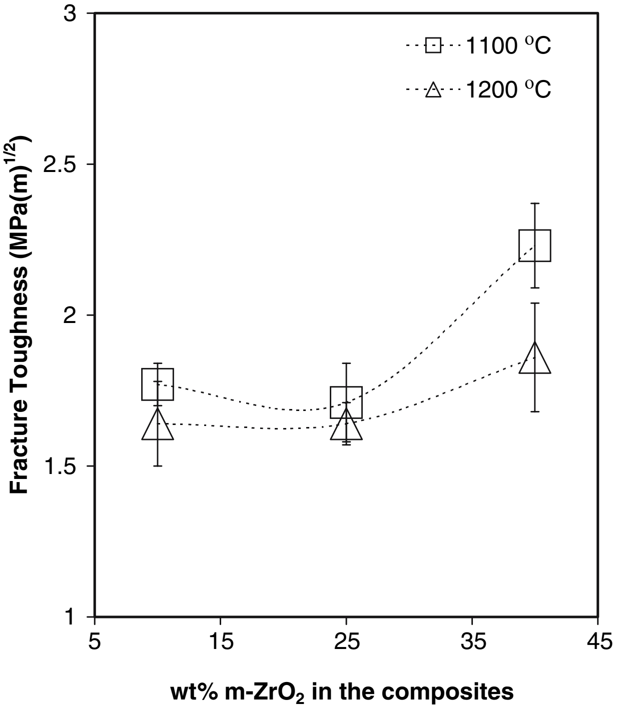

Fig. 7 Fracture toughness of 10, 25, and 40 wt% m-ZrO_2–HA composites hot-pressed at 1100 °C and 1200 °C

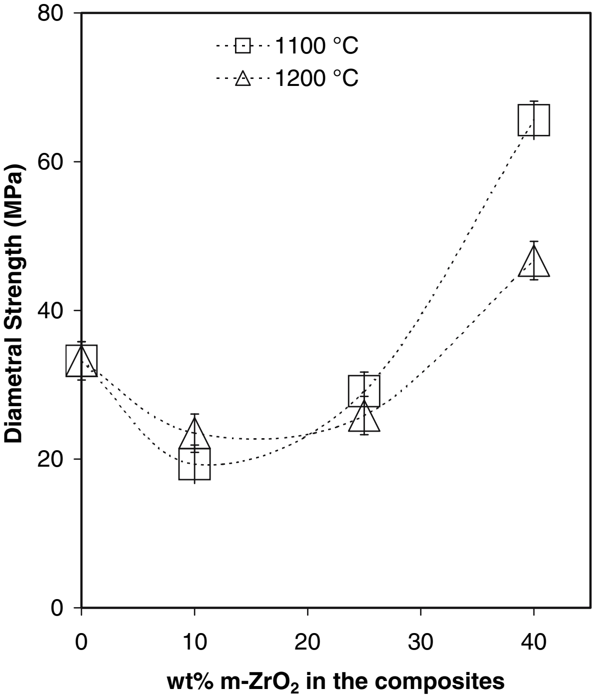

Fig. 8 Diametral tensile strengths of the HA–m-ZrO_2 composites hot-pressed at 1100 °C and 1200 °C

The main factor affecting the sintering process is the third step. The surface free energy of the powder is the driving force for sintering. In response to the surface free energy of the powder, mass transport will occur from the high chemical potential region to the low, which results in lowering the total free energy of the system [19]. To get the full densification of the composites after the sintering, removal of the pores via grain boundary diffusion (3rd step) must be completed during the sintering. It is believed that the sintering process finished between the 2nd and the 3rd steps for the composites investigated in this study. This resulted in porosities in the composites.

Ca^{2+} ions in HA helped m-ZrO_2 to transform partially to the tetragonal phase by the diffusion of Ca^{2+} ions from HA into ZrO_2. Moreover OH^- ions were also removed from the HA because HA decomposed faster in the presence of ZrO_2 during sintering.

Ca^{2+} ions were transported from HA to the contact surface of ZrO_2 particles to react with them to form the reaction 5. Moreover, reactions can also be assisted by polymorphic reactions, which involve bond breakage and structural reformation [20]. In this study, m-ZrO_2 transformed into t-ZrO_2 partially after the sintering at either at 1100 °C or 1200 °C. Moreover, this transformation increased when the sintering temperature was increased from 1100 °C to 1200 °C.

$$CaO + ZrO_2 \rightarrow CaZrO_3 \qquad (5)$$

At temperatures above about 1150 °C in ambient atmosphere, HA begins to decompose by the following reaction:

$$Ca_{10}(PO_4)_6(OH)_2 \rightarrow 3Ca_3(PO_4)_2 + CaO + H_2O \qquad (6)$$

Water caused the formation of the porosity in the system. The reaction between HA and ZrO_2 increased when the sintering temperature increased from 1100 °C to 1200 °C. ZrO_2 in the composites with HA appears to catalyze the decomposition of HA. One reason might be the reaction of CaO formed in reaction 6 with the oxides, removing the CaO and driving reaction 5 to the right. X-ray evidence for $CaZrO_3$ was found (Fig. 3).

Tetragonal ZrO_2 has a distorted fluorite structure [21], in which oxides such as calcium, magnesium and yttrium show considerable solid solubility. Removal of some calcium from the HA must be compensated by the formation of oxygen vacancies; the resultant relaxation of the apatite structure apparently causes it to decompose slightly. There was also evidence that some CaO dissolved in the ZrO_2, stabilizing the tetragonal form of zirconia (Fig. 3).

All of the m-ZrO_2–HA composites showed a densification better than 90% of the theoretical density. Finally there was not a wide range of porosity present in the composites to observe the effect of porosity or densification. Micro-cracking could be the reason for toughening because micro-cracks were observed in the matrix along the HA grain boundaries as seen in Fig. 6 because of the difference in thermal expansion coefficients of HA and m-ZrO_2. Micro-cracking happens when the thermal expansion coefficient of the matrix is bigger than that of particle. This resulted in the formation of tensile stresses on the HA matrix causing cracking. Decomposition of HA (Eq. 6) leads to the formation of additional phases and water vapor, which cause additional porosity and reduce hardness.

Because of the improved mechanical properties, 40 wt% zirconia composite could be used as a hard tissue replacement material in orthopaedic applications. It showed highest μ-hardness, fracture toughness and diametral strength when compared with other compositions.

Conclusion

The effects of monoclinic zirconia on the phase transformations and the mechanical properties of HA and monoclinic zirconia composites were studied. The main phases were HA and a mixture of monoclinic and tetragonal zirconia after the sintering at 1100 °C. In addition to these phases, formation of α-TCP and $CaZrO_3$ was observed when the composites were sintered at 1200 °C. This study suggests that 40 wt% monoclinic zirconia and HA composite hot-pressed at 1100 °C should be examined for orthopedic applications because it showed promising mechanical properties.

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