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Toughening mechanisms in iron-containing hydroxyapatite/titanium composites

Q. Chang [a,b], D.L. Chen [a,*], H.Q. Ru [b], X.Y. Yue [b], L. Yu [b], C.P. Zhang [b]

[a] Department of Mechanical and Industrial Engineering, Ryerson University, 350 Victoria Street, Toronto, Ontario M5B 2K3, Canada
[b] Department of Materials Science and Engineering, School of Materials and Metallurgy, Northeastern University, Wenhua Road 3-11, Shenyang 110004, China

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ABSTRACT

Pure hydroxyapatite (HA) is brittle and it cannot be directly used for the load-bearing biomedical applications. The purpose of this investigation was to develop a new iron-containing HA/titanium composite via pressureless sintering at a relatively low temperature with particular emphasis on identifying the underlying toughening mechanisms. The addition of iron to HA/titanium composites led to a unique and favorable core/shell microstructure of Ti–Fe particles that consisted of outer titanium and inner iron, and good interfacial bonding with HA matrix. While the relative density, hardness and Young's modulus reduced, the flexural strength, fracture toughness, fatigue resistance, and the related fracture surface roughness increased significantly with increasing amount of Ti–Fe particles. Different toughening mechanisms including crack bridging, branching and deflection were observed in the composites, thus effectively increasing the crack propagation resistance and resulting in a substantial improvement in the mechanical properties of the composites.

1. Introduction

The important role of bioceramics in the application of human hard tissue repair and reconstruction has been highlighted in many reports, and it has been extensively studied in the past 30–40 years, as documented recently by Best et al. [1]. Synthetic hydroxyapatite (HA), due to its excellent bioactivity and biocompatibility [2,3], is a widely used biomaterial in clinical applications to repair human hard tissue bone and dentin. As toughness is crucial to the structural function of bone and dentin [4–8], the study on improving the mechanical properties of HA is a critically important topic due to its far-reaching applications in the field of bioceramics, since pure HA has its own weakness of low toughness and fatigue resistance.

The reinforcement of HA with a ductile metallic phase is a promising method to enhance the mechanical properties and expand the application of HA-based bioceramics. Several potential toughening mechanisms, including crack bridging and crack deflection, could effectively improve the mechanical properties [9]. Along with this line titanium (Ti) and its alloy, with high strength and toughness as well as bioactivity, have the potential to accomplish this requirement [10]. There have been considerable efforts to improve the mechanical properties of HA by the incorporation of Ti or its alloy [11–14]. The good bioactivity of such Ti-containing bioceramic composites has been demonstrated as well [15]. Despite the success of existing materials and technologies, these materials still have some serious shortcomings. First, decomposition of HA phases induced by the existence of Ti occurred [16,17]. The decomposition products, such as tricalcium phosphate (TCP) and tetracalcium phosphate (TTCP), could hinder the sintering process [18], which led to a weak interface bonding between HA and Ti. The weakly bonded interfaces would debond rapidly, resulting in a limited strength and toughness improvement. Second, the degradation of Ti phases could take place because of the decomposition of HA. Ti phase would react with the decomposition products, resulting in the desirable Ti phase rarely remained in the matrix after sintering. The presence of these issues led to only a limited improvement of mechanical properties of composites. So far the best way of suppressing the decomposition and reaction is to introduce the external pressure like hot pressing [11,15]. However, such processing methods have only limited use based on the technical and economical considerations. Therefore, it is necessary to develop a cost-effective route of fabricating HA/Ti composites with improved strength and fracture toughness.

Recently, iron, as an indispensable element in the human body [19], has been reported to promote effectively the sinterability of titanium with a small amount of addition [20,21]. It is

* Corresponding author. Tel.: +1 416 979 5000x6487; fax: +1 416 979 5265.
E-mail address: dchen@ryerson.ca (D.L. Chen).

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worthwhile to mention that iron is also effective in reducing the solubility of hydroxyapatite by incorporating into the apatite structure [22]. Besides, if a composition of Ti-33wt%Fe is selected, the alloy has a relatively low melting point since it is positioned around the eutectic composition in the Ti–Fe phase diagram. The addition of such Ti-33wt%Fe particles to HA would offer a potential to lower the sintering temperature. It is also known that liquid phase formed during the sintering process can promote densification. However, it is unclear what will happen in the microstructure provided that iron is added into the HA/Ti composite; if the Ti-33wt%Fe particles can improve the strength and toughness of HA; and if the pressureless sintering, a conventional and flexible processing technique, can be utilized at a relatively low sintering temperature since, to the authors' knowledge, iron-containing HA/Ti composites have not been reported in the literature. The purpose of this investigation was, therefore, to synthesize iron-containing HA/titanium composites in an attempt to develop HA-based composites with improved strength and toughness via low-temperature pressureless sintering, evaluate the microstructure and mechanical properties of the composites, and especially identify the underlying strengthening and toughening mechanisms.

2. Materials and methods

2.1. Synthesis of HA

The starting HA powder was synthesized using wet-chemical precipitation by reacting calcium hydroxide ($Ca(OH)_2$) with orthophosphoric acid H_3PO_4 [23]. The calcium solution and phosphate solution were prepared separately. The calcium hydroxide suspension was vigorously stirred in a water bath at a temperature of 40°C for 30 min, and orthophosphoric acid solution was added dropwise to produce a milky, gelatinous precipitate. A proper amount of ammonia was added during the precipitation process to adjust the pH value of the solution to 10.5. The stirring of the mixed solution was continued for another 6 h at 40°C. Then the solution was aged for 24 h at room temperature. After aging, supernatant was removed from the top of the sediment. The sediment was washed by distilled water and filtered by centrifuging and the same processing was repeated 3 times. The resulting sludge was dried at 80°C. The dried powders were further calcined at 750°C. After calcination, the powders were then ball-milled for 12 h to break down agglomerates. The average size of the obtained HA powders was less than 100 nm.

2.2. Preparation of HA/Ti-33%Fe composites

Commercially pure Ti and Fe powders with a ratio of Ti-33wt%Fe were mixed by ball-milling to obtain ultra-fine mixed powders. The powders consisting of pure HA and 5 wt% or 15 wt% (Ti-33wt%Fe) were further mechanically mixed using ball-mill rollers for 12 h, then dried at 80°C. The dry mixed powders were crushed using mortar and then sieved through a 200 μm sieve. The mixed powders as well as pure HA powders were uniaxially pressed at 50 MPa, followed by cold-isostatic pressing at 200 MPa. The green compacts were subsequently pressureless sintered in vacuum at 1000°C for 2 h using a heating rate of 3.33°C/min and cooling rate of 5°C/min.

2.3. Microstructure and mechanical properties

The density of sintered samples was measured via Archimedes principle using distilled water, and the relative density and porosity were computed. The microstructure was examined using a scanning electron microscope (SEM). The phase and crystallinity were analyzed via X-ray diffraction (XRD) using CuK_α radiation at 40 kV and 30 mA. The dimensions of *a*- and *c*-axes were calculated from (300) and (002) reflections, respectively. The elemental concentration profile of the microstructure was determined using energy dispersive X-ray spectroscopy (EDS). The Vickers microhardness was tested on the polished surfaces using a computerized microhardness tester at a load of 500 g for a dwell time of 15 s. Eleven indentations were made on each sample and the averaged values were reported.

The three-point bending (TPB) and fatigue test samples, with a dimension of 25 mm × 2 mm × 2 mm, were prepared and polished to a surface finish using 1 μm diamond paste. The TPB and fatigue tests were performed using a three-point bending stage with a span of 20 mm attached to a computerized Instron 8801 fatigue testing system. In the TPB tests the cross-head speed was set at a rate of 0.2 mm/min in accordance with ASTM C1161. The values for bending strength σ, Young's modulus E, and strain ε at failure were calculated according to the following equations [24]:

$$\sigma = \frac{3PL}{2bh^2}, \tag{1}$$

$$E = \frac{\sigma}{\varepsilon}, \tag{2}$$

$$\varepsilon = \frac{6h\delta}{L^2}, \tag{3}$$

where P is the load at failure (N), L is the span (mm), δ is the displacement in the middle of the sample (mm), b is the sample width (mm) and h is the thickness (mm).

In the cyclic fatigue tests the samples were tested at a frequency of 10 Hz and a load ratio (R) of 0.1 using a sinusoidal waveform. Three levels of maximum stresses were applied. The tests were continued up to 10^6 cycles if no failure occurred. The fracture surfaces of the failed TPB and fatigue samples were examined via SEM after coating with a thin film of gold to enhance the resolution.

Fracture toughness was determined using a Vickers indentation technique [25].

$$K_C = \chi\left(\frac{E}{H}\right)^{1/2}\frac{P}{a^{3/2}} \tag{4}$$

where P is the applied load, E is Young's modulus, H is Vickers hardness, a is the radial crack length measured from the center of indent and χ is an empirically determined "calibration" constant taken to be 0.016 ± 0.004 [26].

3. Results

3.1. Microstructure and density

Fig. 1 shows the microstructure of composites of HA with Ti-33%Fe particles. It can be seen that the Ti–Fe particles were uniformly distributed in the HA matrix (Fig. 1(a)). In particular, a unique feature – the formation of a core/shell microstructure represented by a white core and a gray shell was observed at higher magnifications, as shown in Fig. 1(b). Fig. 1(c) shows a typical EDS line scan across the core/shell particle, where A and B denoted the shell and core areas, respectively. It is seen that Ti content rose in area A and dropped down in area B, whereas Fe content dropped down in area A and rose in area B. Obviously, the core had a high iron content, while the shell contained a high titanium content. Besides, it was observed from the microstructure that the composite with 15% of Ti-33%Fe particles had higher porosity than that of composite with 5% of Ti-33%Fe particles (Fig. 1(d)).

Fig. 2 shows the relative density of the composites as a function of Ti-33%Fe content. It is seen that high densification was almost achieved for pure HA, reaching about 99% theoretical density. However, with the addition of Ti-33%Fe particles the relative density decreased. It became about 94.8% for the HA/5%(Ti-33%Fe) and approximately 85.4% for the HA/15%(Ti-33%Fe) composites. It appeared that the following linear relationship could be used to describe the variation of the relative density with the amount of Ti-33%Fe particles:

$$\rho_R = \alpha + \beta W, \tag{5}$$

where ρ_R is the relative density, W is the weight percent of Ti-33%Fe particles, and α and β are two constants, which are 99.05 and −0.90 in the present study. With a lower value of relative density, the porosity became higher, which could also be seen in Fig. 1(d).

3.2. X-ray diffraction analysis

Fig. 3 shows the XRD patterns of pure HA, HA/5%(Ti-33%Fe) and HA/15%(Ti-33%Fe). It is seen that the obtained HA exhibited a typical XRD pattern of HA (JCPDS, 009-0432) without decomposition (as seen in Fig. 3(a)), suggesting the HA structure obtained in this study was thermally stable enough while sintering at 1000°C in vacuum. It was observed that HA composites with 5% of Ti–33%Fe particles consisted mainly of HA, Ti and Fe, together with intermetallic phase TiFe and traces of calcium titanate ($CaTiO_3$) (Fig. 3(b)). With increasing content of Ti–33%Fe to 15%, β-TCP and