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Microwave assisted-*in situ* synthesis of porous titanium/calcium phosphate composites and their *in vitro* apatite-forming capability

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ABSTRACT

Microwave irradiation has been proven to be an effective heating source in synthetic chemistry, and can accelerate the reaction rate, provide more uniform heating and help in developing better synthetic routes for the fabrication of bone-grafting implant materials. In this study, a new technique, which comprises microwave heating and powder metallurgy for *in situ* synthesis of Ti/CaP composites by using Ti powders, calcium carbonate ($CaCO_3$) powders and dicalcium phosphate dihydrate ($CaHPO_4 \cdot 2H_2O$) powders, has been developed. Three different compositions of Ti:$CaCO_3$:$CaHPO_4 \cdot 2H_2O$ powdered mixture were employed to investigate the effect of the starting atomic ratio of the $CaCO_3$ to $CaHPO_4 \cdot 2H_2O$ on the phase, microstructural formation and compressive properties of the microwave synthesized composites. When the starting atomic ratio reaches 1.67, composites containing mainly alpha-titanium (α-Ti), hydroxyapatite (HA), beta-tricalcium phosphate (β-TCP) and calcium titanate ($CaTiO_3$) with porosity of 26%, pore size up to 152 μm, compressive strength of 212 MPa and compressive modulus of 12 GPa were formed. The *in vitro* apatite-forming capability of the composite was evaluated by immersing the composite into a simulated body fluid (SBF) for up to 14 days. The results showed that biodissolution occurred, followed by apatite precipitation after immersion in the SBF, suggesting that the composites are suitable for bone implant applications as apatite is an essential intermediate layer for bone cells attachment. The quantity and size of the apatite globules increased over the immersion time. After 14 days of immersion, the composite surface was fully covered by an apatite layer with a Ca/P atomic ratio approximately of 1.68, which is similar to the bone-like apatite appearing in human hard tissue. The results suggested that the microwave assisted-*in situ* synthesis technique can be used as an alternative to traditional powder metallurgy for the fabrication of Ti/CaP biocomposites.

1. Introduction

Calcium phosphate (CaP) ceramics, especially hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) and tricalcium phosphate (TCP, $Ca_3(PO_4)_2$), are materials commonly used as bone substitutes in the biomedical industry [1,2]. HA, due to its chemical stability among all other CaP bioceramics under physiological environments, is clinically used as a coating material for metallic implants to enhance their osteoconductivity and osseointegration [3,4]. Meanwhile, TCP finds practical applications in temporary bone-grafting substitutes, where slowly resorbed TCP can facilitate bone formation [1]. However, the use of CaP for long term implantation is still limited in many load-bearing applications because of brittleness. Advances in the development of composite materials in recent years have enabled continuous improvements in the design of modern medical devices [5–12]. Therefore, incorporating CaP into a metallic implant as a composite can combine the good mechanical performance of the metal matrix with the good biocompatibility and bioactivity of CaP [13]. In this regard, many research studies have been dedicated in the development of titanium (Ti)/CaP composites, mainly due to the chemical stability, good biocompatibility and high corrosion resistance offered by Ti compared with various other metals [14,15].

Traditional powder metallurgy methods, such as isostatic pressing [16], plasma spraying [17] and metal injection molding [18,19], have been utilized to fabricate Ti/CaP composites, in which

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a mixture of Ti and HA powders was compressed into compact and high temperature was then applied directly for solidification. Although there are some advantages of the aforementioned methods, including the simple preparation procedures, obtaining a composite with a uniform microstructure and adequate mechanical properties often requires high temperature and long heat treatment, resulting in an increase in the production cost. Moreover, the high temperature processing condition may stimulate the dehydration and decomposition of CaP, compromising the biological compatibility.

Microwave heating is a process in which a material absorbs electromagnetic energy volumetrically and converts it into heat energy, depending on the dielectric nature of the material [20]. With high heating rates and reduced processing times, microwave heating is currently undergoing investigation for applications in ceramic and metal sintering. This technique has become a promising approach for *in situ* synthesis of Ti/CaP composites by using mixed powders of Ti, calcium carbonate ($CaCO_3$) and dicalcium phosphate dihydrate ($CaHPO_4 \cdot 2H_2O$). During microwave heating, $CaCO_3$ reacts with $CaHPO_4 \cdot 2H_2O$ and produces HA and TCP in the Ti matrix. Compared with traditional heating methods, microwave assisted-*in situ* synthesis offers the advantages of homogeneous heating, fast reaction rate and efficient energy transformation [20–22]. The microwave synthetic routes have been reported to fabricate HA and TCP in a short period of time with high thermal stability [23,24]. More importantly, no impurities or undesired phase transformations were found in the final products prepared by microwave heating [22,25,26]. In addition, the metal–ceramic adherence was enhanced by the chemical bonds formed between the as-synthesized CaP and the Ti matrix during the reaction [27].

In order to evaluate the apatite-forming capability of an implant, a simulated body fluid (SBF) with similar ion concentration and pH value as in human blood plasma has been widely used [28]. This is a well-known *in vitro* assessment to mimic the *in vivo* surface changes, such as the composition and morphology changes, for testing various kinds of biomaterials [29]. The biological performance of a biomaterial obtained in the SBF measurement can thus be used to predict its bioactivity *in vivo* for the case of hard tissue repair.

In this study, the preparation of Ti/CaP composites through the microwave assisted-*in situ* synthesis method is presented. We found that the starting atomic ratios of $CaCO_3$ and $CaHPO_4 \cdot 2H_2O$ (Ca/P atomic ratio) play a significant role to determine the microstructure and bioactivity of the composites, which can be due to the fact that the phases in the composites are mainly produced from the chemical reactions among Ti, $CaCO_3$ and $CaHPO_4 \cdot 2H_2O$. In our research, composites were fabricated by microwave assisted-*in situ* synthesis using mixed powders of Ti, $CaCO_3$ and $CaHPO_4 \cdot 2H_2O$ with different mass ratios, and the correlations of Ca/P ratio and the phases and microstructure formation of the composites were studied. *In vitro* bioactivity of the composites was investigated by examining the apatite formation on the surface after incubation in SBF for different immersion periods.

2. Materials and methods

2.1. Materials

Commercially pure Ti powder with average particle size of 44 μm (purity > 99.5%, International Laboratory, USA), analytical grade $CaCO_3$ powder (purity > 98%, Wako Pure Chemical Industries Ltd., Japan) and $CaHPO_4 \cdot 2H_2O$ powder (purity > 98%, Yueqiao Reagent Plastic Co. Ltd., China) were used as the starting materials. The Ca/P atomic ratio and the mass ratio of the mixed starting powders are listed in Table 1. Samples with different Ca/P atomic ratio, i.e. $C_{1.33}$, $C_{1.67}$ and $C_{2.00}$ were prepared, and unfilled-Ti prepared by only Ti served as a control.

2.2. Powder mixing and compaction

Before microwave synthesis, approximately 100 g of the starting powders were mechanically mixed in a 500 ml alumina jar fillied with yttria-stabilized zirconia beads (~50 vol.% of jar) by a planetary ball mill pulverizer (QM-3SP2, Nanjing University Instrument Plant, China). Mixing was conducted at a rotational speed of 100 rpm for 1 h. A cylindrical green compact (diameter 15 mm and height 10 mm) was subsequently prepared using a hardened steel die by applying a peak load of 40 kN, i.e., 226 MPa, for 120 s.

2.3. Microwave assisted-in situ synthesis

Microwave synthesis of the green compact was conducted in a microwave heating furnace recently developed by our research team and was built by Kailing Industrial Microwave Equipment Ltd., China. Fig. 1 displays the schematic diagram of the experimental microwave setup. The furnace consists of three pairs of magnetrons operating on the left, right and back of a 2.45 GHz multimode cavity with chamber dimension of 0.45 m × 0.4 m × 0.3 m. The green compact was microwave heated in air without any special protective atmosphere, other than placing it in an alumina heat insulating crucible (diameter of 65 mm, height of 75 mm and wall thickness of 15 mm) filled with beta-silicon carbide (β-SiC) powders (99% purity, International Laboratory, USA) with particle size ranging from 2 to 5 μm, as shown in Fig. 1. The SiC powders are known to be good microwave absorbers and they served as microwave susceptors in order to obtain better electromagnetic field homogenization and more uniform temperature distribution in the compact during microwave synthesis [26,30]. The volume ratio of the green compact to the SiC susceptors was about 1:3.

All composite samples were synthesized by a two-step heating approach. Firstly, the green compact was heated at a microwave power of 1 kW for 10 min to ensure a complete reaction between $CaCO_3$ powders and $CaHPO_4 \cdot 2H_2O$ powders for the synthesis of the CaP ceramics. Then, increasing the microwave power from 1 kW to 2 kW for another 5 min heating allowed completion of the sintering. Finally, the samples cooled down naturally to room temperature inside the furnace for 10 min, followed by rinsing with distilled water.

2.4. Compositional and microstructural characterization

To study the crystalline phases of the composites, the synthesized composite samples were grounded into fine powders in a mortar and pestle for powder X-ray diffraction (XRD, Rigaku SmartLab 9 kW) with CuKα radiation ($\lambda = 1.54059$ Å) operating at 45 kV and 200 mA. The spectra were recorded in the 2θ range of 20–80° at a scanning speed of 2°/min. The phases were determined by comparing the experimental X-ray diffractograms to standards complied by the Joint Committee on Powder Diffraction Standards (JCPDS). Energy dispersive spectrometry (EDS) was used for the analysis of elemental composition.

To study the microstructure of the composites, the synthesized composite samples were cut into square pieces (8 mm × 8 mm × 4 mm) and then polished in turn with 120–800 grit abrasive paper, followed by ultrasonically cleaning in 70% ethanol and drying in ambient air. The surface morphology of the polished specimens was observed by scanning electron microscopy (SEM, JEOL JSM-6490). The accelerating voltage was 20 kV. The surface of the specimens was coated with a thin layer of gold to enhance their conductivity. The porosity and pore size of the