Mechanical and in vitro degradation behavior of ultrafine calcium polyphosphate reinforced magnesium-alloy composites

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ABSTRACT

Magnesium alloy (ZK60A) matrix composites reinforced with 2.5, 5, 7.5 and 10 wt.% calcium polyphosphate particles, which were sphere-like in shape with average size of about 750 nm, were fabricated by powder metallurgy. The microstructure, mechanical properties and degradation behavior in physiological saline of the composites were investigated. The obtained results show that ultrafine calcium polyphosphate particles uniformly distribute in the ZK60A matrices without voids for the composites containing 2.5 and 5 wt.% calcium polyphosphate. For the composites containing 7.5 and 10 wt.% calcium polyphosphate, however, calcium polyphosphate particles agglomerate in the ZK60A matrices, and some obvious voids appear. The ultimate tensile strengths, yield strengths and elastic moduli of the composites tend to increase when the calcium polyphosphate contents increase from 0 to 5 wt.%, however, appear to decrease with the further increase of calcium polyphosphate from 5 to 10 wt.%. The weight losses of the composites, pH values and Mg ion concentrations of the solutions immersing the composites gradually decrease with increase of calcium polyphosphate content, which indicates that the addition of more calcium polyphosphate into ZK60A alloy results in significant degradation slow-up of the composites. This can be attributed to the formation of dense corrosion product layers on the composites. The composites have good mechanical properties and controllable degradation rates and thereby have potential to be used as load-bearing bone implants.

1. Introduction

Traditional biomedical metal alloys such as Co–Cr–Mo, stainless steel, and titanium alloy have played an essential role in load-bearing implants for the repair or replacement of diseased or damaged bone [1,2]. However, the elastic modulus of these metal alloys is much higher than that of bone, leading to stress shielding and bone absorption [1]. Compared with the traditional metals alloys, a biodegradable material will not cause permanent physical irritation, avoiding the secondary surgery to remove implants [3].

In recent years, magnesium and its alloys have attracted great attention for orthopedic applications due to their biodegradable nature [4]. Moreover, the Young's modulus of Mg and its alloys is about 45 GPa, much close to that of the human bone (10–15 GPa [5]), which will minimize stress shielding effects [1,6]. Magnesium and its alloys also exhibit non-toxicity and good biocompatibility. For example, the presence of Mg enhances bone cell adhesion and has no inhibitory effect on cell growth [7]. Witte et al. indicated that high magnesium ion concentration even could lead to bone cell activation [8]. AZ91D alloy caused no significant harm

to their neighboring tissues, could react *in vivo* with an appropriate inflammatory host response in a rabbit model and promoted both bone formation and resorption [9]. Li et al. reported that high activities of osteoblast and osteocytes were observed around the Mg–1Ca alloy pin for 1, 2 and 3 months [10]. However, the major drawbacks of magnesium and its alloys are their fast degradation rate in the physiological environment. The fast degradation of magnesium alloys not only results in losing their mechanical integrity before the injured tissues have sufficient time to heal [11], but also leads to serious hydrogen evolution and alkalization of body fluid [12].

Up till now, three routines have been developed to solve the fast degradation rate of magnesium and its alloys. One is alloying magnesium with non-toxic elements such as Ca [10], Zn and Zr [13] to form novel magnesium alloys. The second is surface modification of traditional magnesium alloys, such as coating Ca–P [14], bone-like apatite [1], brushite [15], hydroxyapatite [6,16] layers on the alloys. An alternative routine is to form magnesium-matrix composite reinforced with bioactive ceramic. Recently, Witte et al. [17] reported a potential of AZ91D magnesium-matrix composites reinforced with hydroxyapatite (HA) particles for load-bearing applications. In this magnesium-matrix composites, however, the AZ91D matrix contains toxic element Al which appears to be the impairment of phosphorous metabolism and its resultant adverse

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effects [18]; and also HA is a bioceramic with slow degradation rate, there being a risk that the HA particles remained from the completely degraded matrix could react with macrophages resulting in bone osteolysis [19].

To be suitable implant materials, Mg-alloys based composites should possess certain properties [3]: appropriate mechanical characteristics to offer adequate mechanical support to the injured tissue; a moderate degradation to effectively assist the healing process and to prevent from early destabilization; released ions during degradation need to be biocompatible. As known, ZK60A is a magnesium alloy containing non-toxic elements of Zn and Zr [20,21]. Calcium polyphosphate (CPP) is a polymeritic ceramic with good biocompatibility and osteoconductivity, exhibiting a stoichiometry of $Ca(PO_3)_2$ and a linear regular tetrahedral polymer structure based of PO_4 units [22–25]. It seems to promote rapid bone growth and can be tailored to degrade at a given rate *in vivo* to some degree through appropriate selection of the starting particle size [26], and degradation products are Ca^{2+}, HPO_4^{2-}, PO_4^{3-} [27,28]. This paper reports our effort to prepare novel magnesium-matrix composites, composed of ZK60A matrix reinforced with CPP particles, focusing on the microstructure, mechanical and degradation properties of the CPP_p/ZK60A composites.

2. Experimental procedures

The composites of ZK60A reinforced with four different percentage (2.5, 5, 7.5 and 10 wt.%) of CPP particles were synthesized by a powder metallurgy process as follows. The used ZK60A powder (WeiHao Corporation of China) were less than 50 μm in size, and had a composition of 5.21 wt.% Zn, 0.34 wt.% Zr and balanced Mg. Bulk CPP was prepared according to Ref. [29], and then mounted in a high energy ball mill (pulverisette 4 Vario-Plantary Mill, Fritsch) to produce fine CPP powder under the condition of ball-to-powder weight ratio of 10 at 400 rpm for 16 h. Four kinds of mixed powders with CPP contents of 2.5, 5, 7.5 and 10 wt.% were obtained by addition of CPP into ZK60A and mixing them using a three-dimension blending machine in argon atmosphere at a rotation speed of 50 rpm for 8 h. The mixed ZK60A and CPP powders were then dried at 120 °C in a vacuum oven for 2 h. Each kind of the mixed powder was cold-pressed into cylindrical compact with diameter 40 mm at pressure of 400 MPa. The cylindrical compact was then hot-pressed at temperature of 380 °C and pressure of 150 MPa for 20 min, followed by hot extrusion at 380 °C to a rod of 10 mm in diameter. For comparison purpose, monolithic ZK60A rod was prepared using similar processing steps.

The sizes of the fine CPP particles were measured with laser particle size analyzer (Mastersizer 2000, Malvern Instruments) and observed by transmission electron microscopy (TEM; JEM-2100F, JEOL). The samples cut from the composites rods were ground with SiC papers, polished with diamond paste, and then etched in an acetic picric solution for 10 s at room temperature. Their microstructures were conducted using scanning electron microscopy (SEM; JSM-7000F, JEOL) coupled with energy dispersive spectroscopy. X-ray diffraction (XRD) analysis was carried out using a RIGAKU D/MAX-2400 diffractometer with Cu K_α ray (λ = 1.5406 Å) at a scan step of 0.02°.

The tensile tests of the composites were performed using an Instron 1195 universal testing machine. For tensile tests, specimens with 5 mm in diameter and 25 mm in gauge length were machined from the extruded rods with tensile axes parallel to the extrusion direction.

In vitro degradation investigations were performed by immersing the composites samples in 50 ml physiological saline opened to air at 37 °C for 1 to 12 days, without refreshing the solutions during the experiments. The tested specimens were 9.5 mm in diam-

eter and 3 mm in height. Once the tests were finished for each immersion time, the samples were extracted from the solutions, rinsed with distilled water, dried in hot air, and their surface morphologies were observed using SEM without removing corrosion product. The weight loss percentage of each composite sample subjected to physiological saline immersion was calculated from the expression $(M_0 - M_1)/M_0$, where 'M_0' is the initial weight and 'M_1' is the final weight which was obtained by weighting the sample after removing the corrosion product with chromic acid. The pH values, Mg and Ca concentrations of the samples-immersed solutions were measured with pH meter (PHSJ-4A, Leici) and inductively coupled plasma atomic emission spectrometry (ICP-AES; IRIS-Advantage, Thermo Fisher Scientific Incorporation), respectively.

3. Results and discussion

3.1. Microstructure characterization of the ball-milled CPP powder and composites

In Fig. 1 shows the XRD profiles of the starting ceramic powder before and after high energy ball milling which is identified as the β-CPP particles. After high energy ball milling, it had been observed that the tendency of grain refinement or amorphous nature was obvious due to the broad diffraction bands. The typical SEM graph of the ball-milled CPP particles is presented in Fig. 2, in which the upper inset shows their TEM image and the lower inset shows the curve of their size distribution. It indicates that the particles appear sphere or sphere-like, having the highest probability of size at 750 nm. In comparison with triangular or multiangular particles, the sphere or sphere-like particles may avoid stress concentration and subsequently the initiation and propagation of crack upon loading of particle-reinforced composite [30].

In Fig. 3 shows the microstructures of the CPP_p/ZK60A composites with different CPP contents. It is indicated that the ultrafine CPP particles uniformly distribute in the ZK60A matrices without voids for the composites containing 2.5 and 5 wt.% CPP. For the
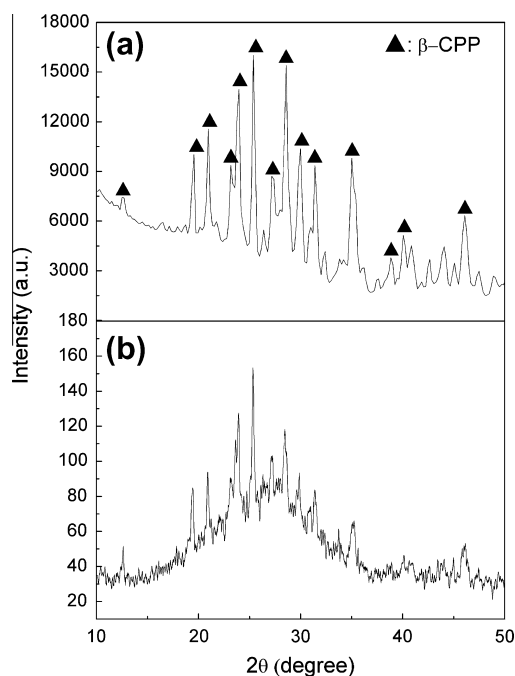

Fig. 1. XRD patterns of the β-CPP ceramic powders: (a) before and (b) after high energy ball milling.