Materials Science and Engineering C 74 (2017) 582–596

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Improvement of the mechanical properties and corrosion resistance of biodegradable β-$Ca_3(PO_4)_2$/Mg-Zn composites prepared by powder metallurgy: the adding β-$Ca_3(PO_4)_2$, hot extrusion and aging treatment

Yang Yan [a,b,d], Yijun Kang [c,d], Ding Li [a,c,d], Kun Yu [a,b,d,*], Tao Xiao [c,d], Youwen Deng [c,d], Han Dai [b], Yilong Dai [a,b], Hanqing Xiong [a,b], Hongjie Fang [b]

[a] School of Materials Science and Engineering, Central South University, Changsha 410083, China
[b] Department of Materials Science and Engineering, Yantai Nanshan University, Yantai 265713, China
[c] The Second Xiangya Hospital, Central South University, 410011, China
[d] Orthopedic Biomedical Materials Engineering Laboratory of Hunan Province, Changsha 410011, China

ARTICLE INFO

Article history:
Received 23 August 2016
Received in revised form 7 December 2016
Accepted 16 December 2016
Available online 6 January 2017

Keywords:
β-$Ca_3(PO_4)_2$/Mg-Zn composite
Hot extrusion
Aging treatment
Mechanical properties
Corrosion behavior
Cytocompatibility

ABSTRACT

In this study, 10%β-$Ca_3(PO_4)_2$/Mg-6%Zn (wt.%) composites with Mg-6%Zn alloy as control were prepared by powder metallurgy. After hot extrusion, the as-extruded composites were aged for 72 h at 150 °C. The effects of the adding β-$Ca_3(PO_4)_2$, hot extrusion and aging treatment on their microstructure, mechanical properties and corrosion resistance were investigated. The XRD results identified α-Mg, MgZn phase and β-$Ca_3(PO_4)_2$ phase in these composites. After hot extrusion, grains were significantly refined, and the larger-sized β-$Ca_3(PO_4)_2$ particles and coarse MgZn phases were broken into linear-distributed β-$Ca_3(PO_4)_2$ and MgZn phases along the extrusion direction. After aging treatment, the elements of Zn, Ca, P and O presented a more homogeneous distribution. The compressive strengths of the β-$Ca_3(PO_4)_2$/Mg-Zn composites were approximately double those of natural bone, and their densities and elastic moduli matched those of natural bone. The immersion tests and electrochemical tests revealed that the adding β-$Ca_3(PO_4)_2$, hot extrusion and aging treatment could promote the formation of protective corrosion product layer on the sample surface in Ringer's solution, which improved corrosion resistance of the β-$Ca_3(PO_4)_2$/Mg-Zn composites. The XRD results indicated that the corrosion product layer contained $Mg(OH)_2$, β-$Ca_3(PO_4)_2$ and hydroxyapatite (HA). The cytotoxicity assessments showed the as-extruded β-$Ca_3(PO_4)_2$/Mg-Zn composite aged for 72 h was harmless to L-929 cells. These results suggested that the β-$Ca_3(PO_4)_2$/Mg-Zn composites prepared by powder metallurgy were promising to be used for bone tissue engineering.

1. Introduction

Recently, Mg-based alloys and composites for bone implant applications have attracted great attention due to their suitable mechanical properties and unique biodegradability [1,2]. Magnesium as the essential nutritional element has been reported to possess excellent biocompatibility in the human body, and its daily intake for adults is 240–420 mg day^{-1}, which is more than that of iron (8–18 mg day^{-1}) and zinc (8–11 mg day^{-1}) [3]. And magnesium is well known to involve in many metabolic reactions: magnesium can activate many enzymes and stabilize DNA and RNA, and it is the co-regulator of protein synthesis and muscle [4]. In addition, Magnesium shows no signs of local or systemic toxicity, though a magnesium level in serum exceeding 1.05 mmol l^{-1} can lead to muscular paralysis, hypotension and respiratory distress [5,6]. There are few reports on toxic reactions caused by Mg or Mg^{2+}, when Mg metal or composites are immersed in body fluids [7,8].

However, Mg-based implants are extremely susceptible to corrosion when they are contacted with abundant aggressive ions like chlorine in body fluids, which results in the loss of mechanical integrity before bone tissues have been healed completely [9,10]. The poor corrosion resistance of Mg-based implants leads to the hydrogen accumulation and the pH value increase, which are detrimental for the healing of local bone tissues [11]. Therefore, there is an urgent demand to improve the corrosion resistance of Mg-based implants for bone tissue engineering.

One of the possible methods to control the corrosion rate is to obtain Mg-based composites by adding calcium-based bioceramic [12,13]. And the corrosion behavior of magnesium-matrix composites prepared by powder metallurgy is related to not only the reinforcement but also

* Corresponding author at: School of Materials Science and Engineering, Central South University, Changsha 410083, China; Department of Materials Science and Engineering, Yantai Nanshan University, Yantai 265713, China.
E-mail address: yukun2010@csu.edu.cn (K. Yu).

http://dx.doi.org/10.1016/j.msec.2016.12.132
0928-4931/

the magnesium alloy matrix. Lately, the Zn-containing magnesium implants have been widely investigated as biodegradable materials [4]. Gu et al. [14] explored in vitro corrosion rates of several magnesium alloys and pointed out that Zn could be an appropriate candidate. Cai et al. [15] proposed that the Zn addition could obviously refine the grains of Mg-Zn alloys, which contributed to the improvement of strengths and corrosion resistance. Zhang et al. [16] mentioned that Mg-6%Zn (wt.%) alloy provided suitable tensile strength and elongation for bone implant applications and it showed excellent in vivo biocompatibility. Therefore, the Mg-based implants with 6 wt.% Zn added were designed in this study.

The microstructure of biodegradable Mg-based implants generally influences their mechanical properties and corrosion behavior, and hot extrusion and heat treatment are effective methods to modify their microstructure [17,18]. Gu et al. [19] reported that the ZK60 alloy (6 wt.% Zn) in the as-extruded state with finer grains exhibited a slower corrosion rate than the same alloy in the as-cast state. Neil et al. [20] reported that aging treatment could significantly alter the corrosion resistance of ZE41 alloy due to the microstructure changes in the Zr-rich regions and the grain boundaries T-phase. And Oh-Ishi et al. [21] found that the Mg-Zn precipitates of Mg-6%Zn-0.4%Ag-0.2%Ca alloy (wt.%) were eliminated by solution heat treatment and more fine MgZn particles were precipitated by aging treatment (160 °C for 72 h), resulting in an enhanced yield strength of the extruded alloy. Besides, our previous studies [22] found that the aging treatment (150 °C for 24 h) could effectively modify the Mg-Zn intermetallic phase morphology of the as-extruded Mg-6%Zn alloy (wt.%) prepared by powder metallurgy and improve its corrosion resistance. Thus, the aging treatment (150 °C for 72 h) was chosen to further study its influence on Mg-Zn intermetallic phases, and the effects of hot extrusion and aging treatment on the properties of experimental samples were also investigated in this study.

One major advantage of magnesium-matrix composites is that their mechanical properties and corrosion rates can be adjusted by changing the category and content of reinforcements. The β-tricalcium phosphate (β-$Ca_3(PO_4)_2$) and hydroxyapatite (HA) have been considered as ideal reinforcements for Mg-based composites, because their chemical composition and crystal structure are similar to those of natural human bone tissue and they exhibit good biocompatibility in body fluids [23,24]. Compared with HA, β-$Ca_3(PO_4)_2$ shows higher dissolution in human bio-environment and better wettability with magnesium alloys [25,26]. Therefore, β-$Ca_3(PO_4)_2$ can be a better reinforcement of degradable Mg-based implants. He et al. [27] found that the adding β-$Ca_3(PO_4)_2$ improved the mechanical properties and corrosion resistance of Mg-3Zn-0.8Zr alloy. Wang et al. [28] proposed that the corrosion resistance of the β-$Ca_3(PO_4)_2$/Mg-Zn-Mn composite was better than that of Mg-Zn-Mn bulky alloy, and the β-$Ca_3(PO_4)_2$ scaffold was left after immersion test due to its much slower degradation rate. In our previous studies [29,30], 5, 10, 15%β-$Ca_3(PO_4)_2$/Mg-6%Zn (wt.%) composites were prepared by powder metallurgy, and the 10%β-$Ca_3(PO_4)_2$/Mg-6%Zn composite showed the best corrosion resistance in these composites and exhibited good biocompatibility with the tissue of experimental rabbits. Therefore, 10% β-$Ca_3(PO_4)_2$ (wt.%) particles were chosen to add in the alloy matrix by powder metallurgy.

There are few reports of the influences of hot extrusion and aging treatment on properties of biodegradable magnesium-matrix composites. In this study, 10%β-$Ca_3(PO_4)_2$/Mg-6%Zn (wt.%) composites were prepared by powder metallurgy in order to design a new biomedical implant for meeting the strength, biocompatibility and biodegradability requirements of bone tissue engineering. The in vitro corrosion behavior of the β-$Ca_3(PO_4)_2$/Mg-Zn composites in Ringer's solution was studied at the physiological ambient temperature of 37 °C and then the cytocompatibility was evaluated. Finally, the effects of the adding β-$Ca_3(PO_4)_2$, hot extrusion and aging treatment on their mechanical properties and corrosion behavior were discussed.

2. Materials and methods

2.1. Materials preparation

The β-tricalcium phosphate (β-$Ca_3(PO_4)_2$) powders were prepared by the liquid-phase precipitation. According to Ca/P ratio of 1:1.5, 0.3 mol/L $Ca(NO_3)_2$ solution was slowly dropped into 0.2 mol/L $(NH_4)_2HPO_4$ solution in a water path at 37 °C. During stirring, ammonia was added to the resulting opaque solution to stabilize the pH at a value of 10.8 and the chemical reaction proceeded as follows [31]:

$$3Ca(NO_3)_{2+}2(NH_4)_2HPO_4 \rightarrow Ca_3(PO_4)_2\downarrow + 4NH_4NO_3 + 2HNO_3 \quad (1)$$

Subsequently, the solution was cooled to room temperature during stirring. The resulting suspension was allowed to be settled for 24 h, filtered and washed with absolute ethanol. And the resulting white precipitates were placed in drying oven 80 °C for 12 h to obtain β-$Ca_3(PO_4)_2$ powder front. The β-$Ca_3(PO_4)_2$ powder front was put into the muffle furnace and calcined 2 h at 800 °C. With the furnace cooling, the β-$Ca_3(PO_4)_2$ powders were obtained from the furnace.

The composition of the experimental composite was Mg-6%Zn with 10%β-$Ca_3(PO_4)_2$ (wt.%) particles added. The average particle diameter of the Mg and Zn powders used in the experiment was about 32.0 μm, and the purity was >99.95%. These powders were mixed together in a vacuum tank for 8 h. And the mixed powders were cold pressed with 100 MPa to billets and sintered at 550–600 °C for 2 h in a vacuum sinter furnace under argon gas. Then, the billets were preheated at 350 °C for 2 h and extruded at that temperature with an extrusion ratio of 15:1 into bars. Finally, the extruded bars were aged at 150 °C for 72 h. In addition, the sintered Mg-6%Zn (wt.%) was used as the control group. The abbreviation of alloy and composites under different state is showed in Table 1. Three samples were tested for each state of alloy and composites in each experiment and the average values were presented as the results.

2.2. Microstructure characterization

The samples were all ground with 1000 grit paper and polished by absolute ethanol. The metallographs were observed by Polyvar-MET. The surface morphology of Mg-Zn alloys before and after immersion was observed using a Quanta-200 scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectrometer (EDS). Phase identification of the corrosion products were performed by DMAX-2500x X-ray diffraction (XRD) using CuKa radiation with a wavelength of 1.5406 Å.

2.3. Porosity measurement and mechanical testing

The samples for porosity measurement and mechanical testing were a diameter of 10 mm and thickness of 20 mm. The porosities of samples were measured using Archimedes Principle. The dimensions of the samples were measured using the Vernier calliper to produce a total volume (V). The dry weight (m_{dry}) was measured with an analytical balance. And then the sample was dipped into in deionized water and suspended from an analytical balance to obtain wet weight (m_{wet}). All weights were in grams and ρ was the density of deionized water (1 g/cm^3).

Table 1
The abbreviation of different state β-$Ca_3(PO_4)_2$/Mg-Zn composites and Mg-Zn alloy.

Abbreviation	Design component (mass fraction)	State
PM-0	Mg-6%Zn	As-sintered
PM	Mg-6%Zn/10%β-$Ca_3(PO_4)_2$	As-sintered
E	Mg-6%Zn/10%β-$Ca_3(PO_4)_2$	As-extruded
A	Mg-6%Zn/10%β-$Ca_3(PO_4)_2$	As-extruded + aging treatment