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Effects of MgO modified β-TCP nanoparticles on the microstructure and properties of β-TCP/Mg-Zn-Zr composites

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ABSTRACT

The mechanical properties and corrosion resistance of magnesium alloy composites were improved by the addition of MgO surface modified tricalcium phosphate ceramic nanoparticles (m-β-TCP). Mg-3Zn-0.8Zr composites with unmodified (MZZT) and modified (MZZMT) nanoparticles were produced by high shear mixing technology. Effects of MgO m-β-TCP nanoparticles on the microstructure, mechanical properties, electrochemical corrosion properties and cytocompatibility of Mg-Zn-Zr/β-TCP composites were investigated. After hot extrusion deformation and dynamic recrystallization, the grain size of MZZMT was the half size of MZZT and the distribution of m-β-TCP particles in the matrix was more uniform than β-TCP particles. The yield tensile strength (YTS), ultimate tensile strength (UTS), and corrosion potential (Ecorr) of MZZMT were higher than MZZT; the corrosion current density (I_{corr}) of MZZMT was lower than MZZT. Cell proliferation of co-cultured MZZMT and MZZT composite samples were roughly the same and the cell number at each time point is higher for MZZMT than for MZZT samples.

1. Introduction

In order to meet clinical requirements, improvements in the mechanical properties and corrosion resistance of biodegradable magnesium (Mg) must be addressed. Alloys have been shown to raise the corrosion resistance and mechanical properties of the material [1], however few elements are biologically safe. There are many ways of preparing a surface coating of biomedical Mg alloy and these methods have been shown to effectively slow down the corrosion rate of the Mg alloy substrate at the early stages of implantation [2,3]. To prevent corrosion overtime, the bonding strength between the surface coating and Mg substrate must increase.

The addition of bioactive ceramic particles for reinforcement can improve the mechanical properties and corrosion resistance of biomedical Mg matrix composites, such as 20% n-ZnO/Mg [4], AZ91/FA [5] and β-TCP/Mg-Zn [6]. Sunil et al. [7] determined the strength, hardness, and corrosion resistance of Mg-HA composites prepared by spark plasma sintering (SPS) technology increased with the increase of ceramic particles, but particle agglomeration and the interface non-metallurgical state between the particles and the matrix led to poor plasticity, toughness, and comprehensive mechanical properties of the composites. Huan et al. [8] introduced bioactive glass (BG) into semi-solid ZK30 alloy under high pressure by a stir casting method to produce ZK30/BG composites with 0–20 wt% BG. Feng et al. [9] concluded the selection of ultrafine CPP particles (<750 nm) improved the mechanical properties of CPP/ZK60, demonstrating the yield tensile strength (YTS) and elongation of 5%CPP/ZK60 composites increased to 319.5 MPa and 30.5%, respectively.

Due to the poor wettability between biological active ceramic particles and the Mg alloy melt, ceramic particles are difficult to disperse evenly in a Mg composite matrix prepared by the stir casting method and the bonding interface may be affected by chemical reactions. Researchers have addressed this problem by forcing infiltration or surface modification of the ceramic particles. Ye et al. [10] modified HA with gelatin to prepare 1% HA/Mg-Zn-Zr composites by stir casting. Liu et al. [11] adopted a combination of high shear and adjustable, advanced melt shear technology to

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prepare β-TCP/Mg-3Zn-Ca composites. This method improved the dispersion of β-TCP particle and reduced particles agglomeration. Further studies showed that Mg alloy had no effect on osteoblast toxicity and cell differentiation, suggesting Mg alloy could promote osteoblast differentiation, proliferation, growth, and adhesion by promoting the expression of related genes [12].

Our previous work showed the addition of tricalcium phosphate (β-TCP) or hydroxyapatite (HA) ceramic nanoparticles refine grain size and improve the mechanical properties and corrosion resistance of Mg-Zn-Zr alloy [13,14]. However, due to the poor wettability between ceramic nanoparticles and the Mg-Zn-Zr matrix, ceramic particle agglomeration was observed in the composite materials. In this paper, a semi-coherent boundary is formed between the ceramic nanoparticles and a Mg alloy matrix by modifying β-TCP with MgO in order to disperse the β-TCP in the Mg crystal core effectively. Using this method the problem of agglomeration was solved, the grain size of materials was refined, and the comprehensive performance of composite materials was raised. Effects of m-β-TCP nanoparticles on the microstructure, mechanical properties, electrochemical corrosion properties, and cytocompatibility of Mg-Zn-Zr/β-TCP composites were investigated.

2. Material and methods

2.1. Preparation of ceramic nanoparticles

β-TCP nanoparticles were obtained by slowly adding 100 ml aqueous $(NH_4)_2HPO_4$ to 100 mL aqueous $Ca(NO_3)_2 \cdot 4H_2O$ (1.5 Ca/P molar ratio) with continuous stirring. NaOH was used to adjust the pH to 8 and the solution was stirred for 3—5 h at room temperature. The solution was allowed to rest for 24 h prior to centrifugation. The product was dried (120 °C, 10 h), calcined (800 °C, 3 h) and ground to a fine powder.

MgO was coated on the surface of the β-TCP nanoparticles to prepare the modified β-TCP nanoparticles (m-β-TCP). β-TCP nanoparticles (2 g) were slowly added into a $Mg(NO_3)_2 \cdot 6H_2O$ aqueous solution (1.0 mol/L, 100 ml) with ultrasonic dispersion. An aqueous Na_2CO_3 solution (1.0 mol/L, 100 ml) was slowly added into the solution with continuous stirring at 40 °C. The solution was then allowed to sit (3 h), filtered, centrifuged, dried (80 °C) and calcined (600 °C, 3 h) to produce m-β-TCP.

2.2. Preparation of MZZMT and MZZT composites

Pure Mg (99.99%) ingot, Zn (99.99%) particles, Mg-Zr master alloy (with 30.89 wt% Zr), β-TCP and m-β-TCP nanoparticles were used as raw materials to prepare the Mg-3Zn-0.8Zr/1β-TCP (MZZT) and Mg-3Zn-0.8Zr/1m-β-TCP (MZZMT) composites. The raw materials were melted in an electric furnace equipped with a high shear, agitation device (Fig. 1, developed by BCAST, Brunel University London) under a complex protection atmosphere of 99.6% N_2 and 0.4% SF_6 for 10 min at 720 °C, and then the melt was molded in a metal pattern. This stirring method under high shear force reduces impurities and gases in the materials, allowing for even mixing. After a homogenizing annealing at 420 °C for 13 h, the cast ingots were skinned, warmed (350 °C, 2 h) and extruded by a YQ 32-315 extruder (Shangdong DaYin Industry Machine Co., Ltd) into Ø8mm bars with an extrusion ratio of 56.

2.3. Microstructure and phase analysis of composites

Nanoparticle morphology and size, and composite microstructure and grain size were observed by optical microscopy (OM, UTV0.5XC-3 OLYMPUS) and scanning electron microscopy (SEM, JOEL, JSM-6700F, Japan). Transmission electron microscopy (TEM, H-7000) was used to observe the second phase of the samples. Energy dispersive spectroscopy (EDS) was used to analyze composition. X-ray diffraction (XRD, D/max-2500, Japan) was used to examine phases with a diffraction angle range from 10° to 80° with 8°/min velocity.

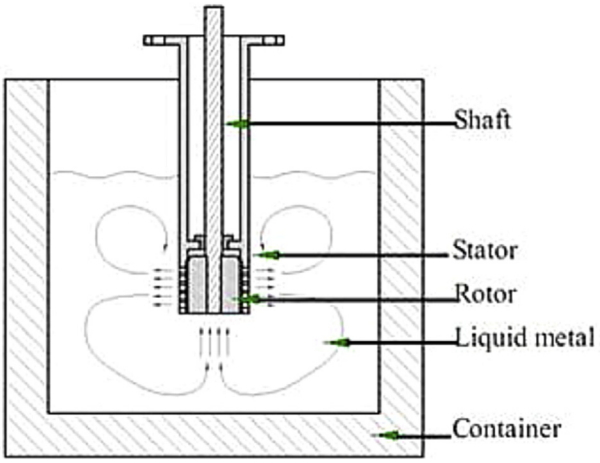

Fig. 1. Schematic diagram of the high shear, agitation device.

2.4. Mechanical properties of composites

A sclerometer (Japan HMV-2T) was used to determine the Vickers hardness of MZZT and MZZMT composites with a 9.8 N maximum load and 20 s loading time. At least 5 samples of each time point were tested to confirm reproducibility. Standard tensile samples of both composites were processed according to standard GB/T16865-1997. Tension tests were carried out on a WDW-100 electron universal testing machine with a strain rate of 0.5 mm/min. At each time point three samples were tested and the results were averaged.

2.5. Electrochemical testing

MZZT and MZZMT composites were processed into Ø8mm × 3 mm sample sizes and mechanically ground with SiC grit paper up to 3000. The electrochemical corrosion behavior of both composites were experimented in simulated body fluid (SBF) using an electrochemical workstation (Zennium, ZAHNER, Germany). SBF is composed of 3.273 g/L NaCl, 1.134 g/L $NaHCO_3$, 0.186 g/L KCl, 0.134 g/L $Na_2HPO_4 \cdot 7H_2O$, 0.152 g/L $MgCl_2 \cdot 6H_2O$, 0.184 g/L $CaCl_2 \cdot 2H_2O$, 0.036 g/L Na_2SO_4 and 3.029 g/L $(CH_2OH)_5CNH_2$ at pH 7.4 and 37 °C. A three-electrode system was set up for the electrochemical test. The counter electrode was made of graphite and the reference electrode was a saturated calomel electrode (SCE). 0.503 cm^2 of the working electrode (MZZT and MZZMT) was exposed to the SBF solution. Before each electrochemical test, the working electrode was immersed in SBF for 30 min to obtain a stable open circuit potential (OCP). The polarization scan was carried out at a scan rate of 1 mV/s. Three samples of each time point were tested to confirm reproducibility.

2.6. Cell culture experiments

For comparison, MZZT and MZZMT composites were used as a control and experimental group, respectively. Φ8 × 3 mm disks of the two composites were ground with increasing grades of SiC grit