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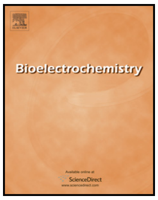

Effects of solidification cooling rate on the corrosion resistance of a biodegradable β-TCP/Mg-Zn-Ca composite

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ABSTRACT

Biodegradable beta-tricalcium phosphate (β-TCP) particle reinforced magnesium metal matrix composites (Mg-MMC) have attracted increasing interest for application as implant materials. This investigation was conducted to study the effect of cooling rate on the microstructure and corrosion behavior of a biodegradable β-TCP/Mg-Zn-Ca composite. The composite was fabricated under a series of cooling rates using a wedge-shaped casting mold. The microstructure of the composite was examined by optical and scanning electron microscopy, and the corrosion behavior was investigated using an electrochemical workstation and immersion tests in a simulated body fluid (SBF). Faster cooling rates were shown to refine the secondary phase and grain size, and produce a more homogenous microstructure. The refined microstructure resulted in a more uniform distribution of β-TCP particles, which is believed to be beneficial in the formation of a stable and compact corrosion product layer, leading to improved corrosion resistance for the composite.

1. Introduction

Magnesium and magnesium alloys have received increasing attention as metallic implant materials due to their biocompatibility, biodegradability, and mechanical properties [1–4]. Although extensive effort has been made to improve the performance of magnesium for biomedical applications, including the exploitation of alloy composition, surface modification and fabrication technologies [5–7], there are still persistent problems that need to be solved before magnesium alloys can be utilized as clinical implant material. A major challenge is the poor corrosion resistance of the material in physiological environments, which leads to the loss of mechanical strength before biological tissues have sufficiently healed [8–9]. The mechanical strength of magnesium alloys also needs to be improved. Adding suitable alloying elements and forming magnesium-matrix composites (MMCs) are two major approaches for improving both corrosion resistance and mechanical properties. Among many magnesium alloys developed as biodegradable orthopedic implant materials, Mg-Zn-Ca series alloys have attracted extensive attention in recent years. This is because both Zn and Ca are essential elements in the human body and are biocompatible within certain limits [10]. Both are effective grain refiners in magnesium and therefore are expected to improve the microstructure [11]. Zn is particularly important in strengthening through precipitation. Additionally, a surface film containing zinc is observed to form on Mg-Zn alloy surface upon corrosion, which protects the material, to certain extent, from further corrosion [12]. Ca is a major component of human bone and has a function of promoting osseointegration and bone growth. A special reason for using Ca is that it forms a high density CaO atmosphere on top of the Mg melt, effectively protecting the Mg melt from being severely oxidized. Furthermore, a suitable amount of Zn and Ca can improve both the mechanical properties and corrosion resistance of magnesium alloys [13–15]. Generally, however, alloying elements and Mg complexing compounds are cathodic to the matrix and prone to galvanic corrosion, therefore it is difficult to improve the corrosion resistance through alloy composition modifications [16]. Surface coating has been shown to offer good protection against corrosion but merely delays the onset of corrosion and accelerated corrosion typically occurs once the coating breaks down [17]. Recently, magnesium metal matrix composites (Mg-MMC) reinforced by ceramic particles of natural human bone constituents such as hydroxylapatite (HA), were found to be effective in increasing mechanical strength and improving corrosion resistance simultaneously [18,19]. One of the advantages of Mg-MMC as a biomaterial is that both mechanical and corrosion properties can be adjusted by changing the reinforcing particle characteristics such as their size, morphology and volume fraction. β-TCP has a higher dissolution rate than HA and therefore is useful for achieving complete degradation of the implant materials

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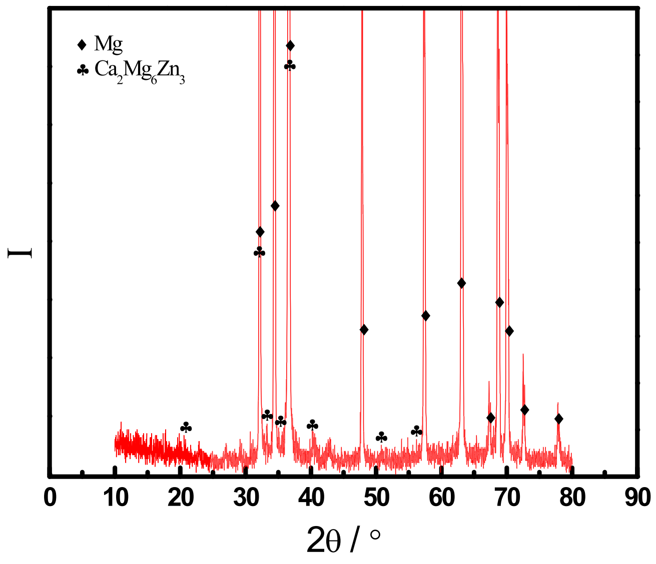


Fig. 1. XRD patterns for the 1β-TCP/Mg-2Zn-0.5Ca composite.

[20]. β-TCP has also been shown to exhibit desirable wettability with Mg-Zn-Ca alloy [21]. β-TCP reinforced magnesium alloy composites have been considered as bone graft substitutes due to their excellent biocompatibility, bioactivity, and osteoconductive properties.

In additional to composition, the fabrication process of magnesium alloys and matrix composites has an important impact on mechanical properties and corrosion resistance. Previous studies investigated the effect of cooling rate during the composite solidification process and found that a rapid cooling rate improved mechanical properties and corrosion resistance. Increasing cooling rates resulted in a reduction of intermetallic particle size [22]. Further, a fine distribution of intermetallic particles was shown to suppress internal galvanic corrosion and enhance corrosion resistance [23]. Liu et al. [24] reported refined grain size improved corrosion resistance of pure Mg during a rate-controlled solidification process. Izumi et al. [25] reported the relationship between corrosion and microstructure of Mg-Zn-Y alloys prepared by rapid solidification at various cooling rates (>10^3 K/s). They found that an increased cooling rate resulted in grain refinement and the formation of a supersaturated single α-Mg phase solid solution, which delayed the occurrence of filiform corrosion. However, the effects of cooling rate on the microstructure and physical properties of Mg-MMC are not well characterized.

Table 1
The values of cooling rate correspond to the specimens.

Label	C1	C2	C3	C4	C5	C6
T (K/s)	849.06	874.91	898.85	921.17	942.11	961.86

In this paper, 1β-TCP/Mg-2Zn-0.5Ca specimens were fabricated under a series of cooling rates using a wedge-shaped casting ingot, to investigate the microstructure and corrosion behavior in simulated body fluid (SBF). Prior to casting, the molten composite was stirred using a rotor-stator device, as shown in Fig. 1(a), which produced a shearing force to break up particle agglomerations and disperse the reinforcing particles [26, 27]. The high shear technique has been shown to engender a macro flow in the melt along the stirring direction with minimum turbulence at the surface, providing greater potential to reduce the embroiled gas content [28].

2. Materials and experimental method

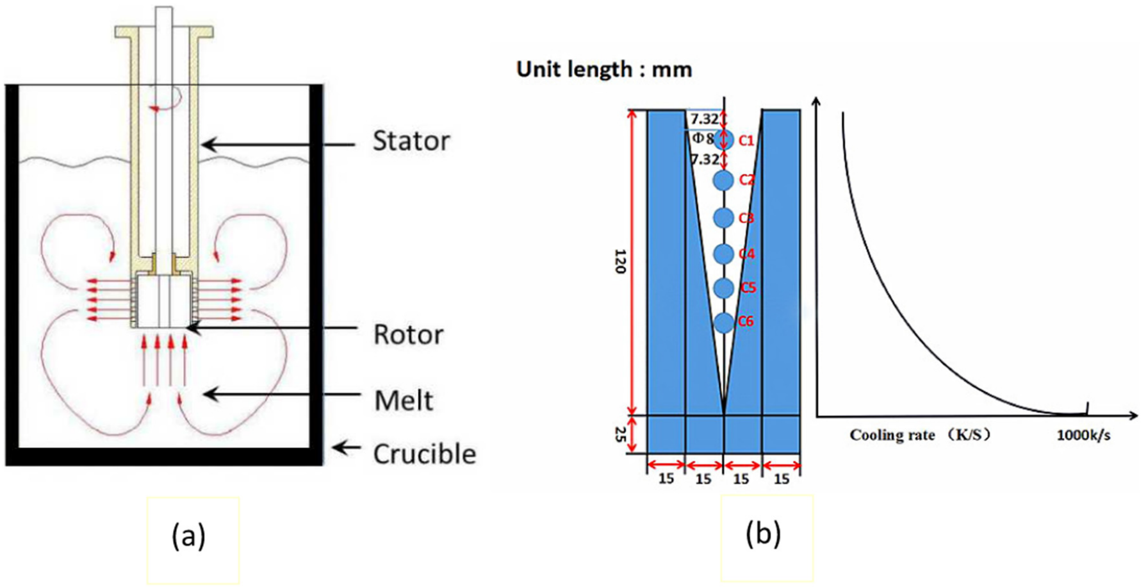
2.1. Material preparation

Pure Mg (99.95%) ingot and calculated amounts Mg–45%Ca master alloy were melted at 720 °C under a mixed gas atmosphere of SF_6 and N_2. Calculated amounts of pure Zn was added to the Mg-Ca alloy and stirred for 5 min to ensure homogeneity, the nominal composition of the alloy being Mg ~96.5, Zn ~2 and Ca ~0.5 wt% in weight percentage. Preheated β-TCP (C139913, Aladdin, biomedical grade, ≥98%, β-TCP basis, particle size ˂0.1 μm) was introduced, with 1 wt%, along the edge of the melt vortex and mixed with the alloy melt with the help of the high shear device as shown in Scheme 1(a). After stirring for 5 min, the 1β-TCP/Mg-2Zn-0.5Ca composite slurry was cast into a wedge-shaped copper ingot.

Following [29], the empirical relationship between cooling rate (C in K/s) and half the wedge thickness (z in mm) is given by

$$C = kz^n \tag{1}$$

where k is the thermal conductivity of the mold material and n is a constant relating to solidification time and power. For Cu, k is estimated as



(a)

(b)

Scheme 1. Illustrations of (a) the high shear mixing device and (b) the wedge-shaped copper casting ingot, showing the dimensions and typical cooling rate as a function of mold height.