Effect of melting method on the bio-corrosion resistance of Mg67Zn28Ca5 cast magnesium alloy in simulated body fluid

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Abstract
In recent years, biodegradable magnesium alloys have attracted considerable attention in medical devices, such as permanent implants and stents. However, poor corrosion resistance is a major problem limiting the practical application of magnesium alloys. In this study, Mg67Zn28Ca5 alloys were prepared via two different methods, namely, vacuum induction melting and sulphur hexafluoride shielded melting. The effect of melting method on the bio-corrosion resistance of MgZnCa cast magnesium alloy was also studied. The microstructure and phase composition of Mg67Zn28Ca5 alloys were investigated by optical microscopy and X-ray diffraction. The element distribution and surface morphology of Mg67Zn28Ca5 alloys were examined by scanning electron microscopy and energy-dispersive spectroscopy. The corrosion resistance of Mg67Zn28Ca5 alloys was measured via electrochemical and immersion tests. Results showed uniform composition of the Mg67Zn28Ca5 alloy melted by vacuum induction. Immersed in the simulated body fluid, the corrosion rate of Mg67Zn28Ca5 by vacuum induction melting (0.2618 mm/a) was lower than that by sulphur hexafluoride shielded melting (0.9686 mm/a); the corrosion potential of Mg67Zn28Ca5 melted by vacuum induction (−1313 mV) was nobler than that by sulphur hexafluoride shielded melting (−1483 mV); the corrosion current of Mg67Zn28Ca5 by vacuum induction melting (1.202 × 10−5 A) was lower than that by sulphur hexafluoride shielded melting (4.332 × 10−5 A). The Mg67Zn28Ca5 by vacuum induction melting showed uniform corrosion behavior.

1. Introduction
Traditional bone implant materials, such as stainless steel, cobalt-based alloys, and titanium-based alloys, produce stress shielding effects during bone healing due to the large difference in elastic modulus from bone [1]. This leads to slow healing and secondary fractures [2]. After the fracture has healed, the bone implant needs to be removed again, causing secondary damage to the patient. Magnesium alloys have many outstanding features, such as light weight, low density, high specific strength, easy processing, excellent biocompatibility, and degradability, showing great potential for applications in the biomedical field [3–8].

The elastic modulus of magnesium alloy is close to that of human bone (17–20 GPa) [9], so it can effectively reduce the stress shielding of materials. The density of Mg (1.74 g cm−3) is also very close to that of human bone (1.75 g cm−3). Compared with degradable iron-based and zinc-based alloys, the adult daily quota of Mg2+ is 240–420 mg, which is 52.5 times higher than that of Fe3+ (8–18 mg) and Zn2+ (8–11 mg) [10]. The release of Mg2+ in the human body can promote the growth and proliferation of osteoblasts and accelerate bone healing [9]. Unfortunately, the rapid degradation of magnesium alloys leads to a rapid increase in local pH and a large release of ions; consequently, the survival of cells on the surface of magnesium alloys is affected, resulting in decreased cell viability [11].
Mg-Zn-Ca alloy has great prospects in bone implant materials [12, 13]. Mg, Zn, and Ca are essential elements of the human body. Mg$^{2+}$ is involved in all metabolic processes and protein synthesis of the human body, maintaining bone growth and neuromuscular excitability [14]. Zn$^{2+}$ is a component of more than 200 enzymes in the human body and plays an important role in the metabolism of proteins, fats, sugars, and nucleic acids; Zn$^{2+}$ also exhibits antibacterial and anti-inflammatory functions [15, 16]. Ca$^{2+}$ maintains the normal muscle expansion and relaxation function of the human body and retains the integrity and permeability of the cell membrane [17]. Mg-Zn alloy has good biocompatibility and high plasticity [18], and the third element of Ca can refine the grain size. The properties of magnesium alloys are not only related to their composition [19] but also to their microstructure and melting process [20]. Traditional melting usually occurs in an atmosphere rich in argon and sulfur hexafluoride (SF$_6$) shielding gas [21]. Studies have shown a thin protective oxide film can be formed on the surface of the magnesium alloy melt. However, given the activity of magnesium, magnesium alloys are oxidized during traditional melting, resulting in their uneven composition. This phenomenon changes the alloy properties. This oxidation originates from the presence of 0.2–0.5 vol% oxygen in a space filled with protective gases [22–24]. By contrast, no reaction occurs between the magnesium alloy and gas, and no effect of adsorbed gas is observed during induction melting under vacuum. The effect of densification is good and can play an important role of purification and reduction [25]. During melting, given the characteristics of the induction melting technology, the metal liquefied inside the container is subjected to electromagnetic force interaction, thereby achieving automatic agitation and making the alloy composition uniform.

Studies on the effect of melting methods on the bio-corrosion resistance of Mg-Zn-Ca casting alloys are limited. In this study, Mg-Zn-Ca alloys were prepared via vacuum induction melting (VIM) and traditional sulfur hexafluoride shielded melting (USM). The effect of melting on the bio-corrosion resistance of Mg-Zn-Ca alloys was studied and discussed to promote the application of magnesium alloys in the biomedical field.

2. Material and methods

2.1. Preparation of alloy

The raw materials used were as follows: industrial pure Mg (99.9 wt%), Zn (99.9 wt%), and Mg-4Ca master alloy (4 wt% Ca). These alloys with the Mg$_{67}$Zn$_{28}$Ca$_{5}$ composition were prepared by vacuum induction melting (LZG-25K) and sulfur hexafluoride shielded melting (BTZ-15KW). The melting furnace under the sulfur hexafluoride atmosphere was heated to 750 °C for 60 min to keep the metal completely dissolved and then cooled to 620 °C for 20 min. The carbon steel crucible was selected for the experiment. During the melting process, the output pressure of the three gases (air, CO$_2$ and sulfur hexafluoride) is about 0.07 MPa, and then the respective flowmeters were adjusted to make the gas mixing ratio of air : CO$_2$ = 3:1, and with 0.2% sulfur hexafluoride. Subsequently, the crucible was removed and poured into the metal mold (Material: 3Cr2W8V, Dimension: 60 × 300 mm) at room temperature to obtain a master alloy (ρ = 2.672 g·cm$^{-3}$). After the vacuum induction melting furnace was charged, the vacuum was evacuated to 0.67 Pa to start heating the charge. The magnesium oxide (MgO) crucible was selected for the experiment. The temperature was gradually increased to completely melt the metal and refined at 750 °C for 60 min. The degree of vacuum during refinement was 0.3 Pa, followed by casting cooling with an arc preheating mold device to obtain a master alloy (ρ = 2.743 g·cm$^{-3}$) with a preheating temperature of 350 °C. The weight of master alloy was 2 kg. The sample was cut into a size of 10 mm × 10 mm × 10 mm. The sample's surface was ground with the use of water-based abrasive papers of SiC paper of grit (800, 1000, 1500, and 2000) and mechanically polished with deionized water and ethanol to obtain a smooth surface. Acetone and ethanol were used for ultrasonic cleaning and drying.

2.2. Microstructure analysis

The specimens were etched using a solution (0.5 ml of nitric acid, 99.5 ml of ethanol) to observe the metallurgical microstructure by using a metallographic microscope (Axio Scope A1). The surface topography and elemental distribution of the specimens were studied using a scanning electron microscope (SEM, Quanta 250FEG) equipped with an energy-dispersive spectrometer (EDS, Oxford X-max20). The crystalline phase of the Mg$_{67}$Zn$_{28}$Ca$_{5}$ alloys were investigated using X-ray diffraction (XRD, D8 Discover) with Cu Kα source (λ = 0.154 056 nm) operated at 20 kV and 30 mA. The XRD patterns were collected using angular step sizes of 0.02° from 20° to 80° at the room temperature.

2.3. Electrochemical and immersion tests

The electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization tests were performed using CH1660D electrochemical workstation in simulated body fluid (SBF). The SBF solution [26] was synthesized in laboratory, consisting of 8 g·l$^{-1}$ NaCl, 0.35 g·l$^{-1}$ NaHCO$_3$, 0.224 g·l$^{-1}$ KCl, 0.228 g·l$^{-1}$
K$_2$HPO$_4$·3H$_2$O, 0.278 g·l$^{-1}$ CaCl$_2$, 0.305 g·l$^{-1}$ MgCl$_2$·6H$_2$O, and 0.071 g·l$^{-1}$ Na$_2$SO$_4$. The electrochemical corrosion cell consists of three electrodes, in which the sample was the working electrode, the platinum electrode was the auxiliary electrode, and the Ag/AgCl electrode was the reference electrode. The specimens were sealed with epoxy resin before testing. The exposed area of each sample (10 mm × 10 mm × 10 mm) was 1 cm$^2$. Potentiodynamic polarization was conducted from −2.0 V to −0.9 V at a scanning rate of 1 mV·s$^{-1}$. EIS tests were operated over the frequency from 30 000 Hz to 0.01 Hz with the signal amplitude of 10 mV. To ensure repeatability, three parallel specimens were prepared for each test.

For immersion test, the specimens were sealed with ethylene oxide, and only the working surface was exposed and immersed in SBF solution at 37 °C. Weight loss and pH of solution were recorded at 1, 3, 7, 12, 24, 48, 72, 96, 120, 144, and 168 h. After soaking, the specimens were cleaned with deionized water to remove the sediments on the surface and then dried immediately. The microstructure of the sample was observed under the optical microscope, the corrosion morphology was observed by SEM, and the composition of corrosion products was analyzed by EDS.

3. Experimental results

3.1. Immersion tests

Figure 1 shows the relationship between the weight loss ratio and immersion time of Mg$_{67}$Zn$_{28}$Ca$_5$ alloy by vacuum induction melting and sulfur hexafluoride shielded melting. The weight loss rate of Mg$_{67}$Zn$_{28}$Ca$_5$ alloy during the immersion time was lower than that of the specimen via sulfur hexafluoride shielded melting. The weight loss of Mg$_{67}$Zn$_{28}$Ca$_5$ alloy melted by sulfur hexafluoride shielded slightly changed before 7 h of immersion. The weight loss of Mg$_{67}$Zn$_{28}$Ca$_5$ alloy prepared by vacuum induction melting remained almost unchanged before soaking for 24 h. Subsequently, the weight loss rate increased significantly. The protection layer (CaCO$_3$, Mg(OH)$_2$) [27] formed on the surface of magnesium alloy could prevent the contact between the corrosion medium and matrix. With the increase in time, obvious pitting corrosion occurs by appearing pits on the alloy’s surface; the appearance of these pits could increase the surface activity of the sample, thereby accelerating the corrosion rate and causing serious local corrosion [28]. The corrosion of magnesium alloys was due to the fact that Mg is a highly active metal in the couple sequence, which can easily form Mg$^{2+}$. In a material, galvanic corrosion can occur between the α-Mg matrix and the Ca$_2$Mg$_5$Zn$_{13}$ phase. In Mg$_{67}$Zn$_{28}$Ca$_5$ alloy, galvanic corrosion occurs between the high potential second phase and low potential α-Mg matrix, accelerating the corrosion rate of the α-Mg matrix [29]. The corrosion rate curve shows that the time of pitting corrosion in Mg$_{67}$Zn$_{28}$Ca$_5$ alloy by vacuum induction melting was later than that of Mg$_{67}$Zn$_{28}$Ca$_5$ alloy melted by sulfur hexafluoride shielded. Notably, Mg$_{67}$Zn$_{28}$Ca$_5$ produced by vacuum induction melting exhibited good corrosion resistance.

Figure 2 shows the pH changes of the solutions measured during the immersion periods. Rapid initial increases in pH may be attributed to the release of hydrogen in the solution caused by the degradation of the samples. In other words, Mg + 2H$_2$O → Mg(OH)$_2$ + H$_2$. As shown in the figure, the pH of the solution around the sample melted by sulfur hexafluoride shielded increased rapidly from 7 h to 24 h. This result indicated
the corrosion rate of the sample during this period. The pH of the solution increased slowly and became stable. By contrast, the pH of the solution around the Mg₆₇Zn₂₈Ca₅ alloy by vacuum induction melting increased slowly before 24 h and then increased rapidly within 24–48 h. Moreover, the pH of the solution around the sample by vacuum induction melting was significantly lower than that of the sample melted by sulfur hexafluoride shielded at corresponding time. This result corresponded well with the weight loss curve in figure 1.

3.2. Corrosion morphology
Figure 3 demonstrates the surface corrosion of the different Mg₆₇Zn₂₈Ca₅ specimens after immersion in SBF solution for different times. As shown in figure 3(b), for Mg₆₇Zn₂₈Ca₅ alloy melted by sulfur hexafluoride shielded, obvious corrosion areas appeared on the surface after 7 h of immersion. After 48 h of immersion, serious local corrosion occurred on the alloy’s surface (figure 3(d)). By contrast, the Mg₆₇Zn₂₈Ca₅ alloy prepared by vacuum induction melting presented only slight corrosion characteristics after 7 h of immersion (figure 3(f)), and a uniform distribution of small corrosion pits formed on the surface after 48 h of immersion (figure 3(h)). These results showed that Mg₆₇Zn₂₈Ca₅ produced by vacuum induction melting possessed good corrosion resistance.

Figures 4 and 5 show the surface morphology and element distribution of Mg₆₇Zn₂₈Ca₅ alloy by different melting processes after immersion in SBF solution for 48 h. Figure 4 showed that the surface of the sample melted by vacuum induction was almost completely covered by a layer of fine particles. There is no serious corrosion area and corrosion crack on the surface. As noted in figure 5, the sample by sulfur hexafluoride shielded
melting exists pitting corrosion on the surface. In addition, slightly wider cracks were found in some places. The presence of Ca, P and O in the corrosion products indicates that apatite may be formed on the surface of the substrate after immersed in SBF solution.

### 3.3. Electrochemical results

Figure 6 shows the time-dependence of the OCP curves of the different Mg67Zn28Ca5 specimens in SBF solution. During immersion, the samples exhibited a similar trend in the evolution of the OCP: at the beginning, the potentials of the samples rose rapidly, and then slightly increased (USM) or maintained constant (VIM). The rapid increase of OCP at the beginning of immersion indicated that a certain kind passivation layer was formed on the surface of the sample. The Mg67Zn28Ca5 by sulfur hexafluoride shielded melting required more time to reach a stable potential, which shows that the speed of establishing a balance between corrosion and protection was relative slower. The Mg67Zn28Ca5 by vacuum induction melting exhibited higher OCP values than that by...
Figure 6. Time-dependence of the OCP curve of different Mg67Zn28Ca5 specimens in SBF solution.

Figure 7. Potentiodynamic polarization curves of different Mg67Zn28Ca5 specimens in SBF solution.

Table 1. Results of potentiodynamic corrosion tests and corrosion rate in SBF solution.

| Specimen | $E_{\text{corr}}$ (mV versus Ag/AgCl) | $i_{\text{corr}}$ (A cm$^{-2}$) | CR (mm/a) |
|----------|--------------------------------------|---------------------------------|-----------|
| USM      | $-1483$                              | $4.332 \times 10^{-5}$         | 0.9686    |
| VIM      | $-1313$                              | $1.202 \times 10^{-5}$         | 0.2618    |

Sulfur hexafluoride shielded melting in SBF solution, which demonstrates the Mg67Zn28Ca5 by vacuum induction melting has better chemical stability.

Figure 7 exhibits the potentiodynamic polarization curves of the different Mg67Zn28Ca5 specimens in SBF solution. The corrosion potential ($E_{\text{corr}}$) and corrosion current density ($i_{\text{corr}}$) derived from the polarization curves were shown in Table 1. The Mg67Zn28Ca5 alloy ($-1313$ mV) melted by vacuum induction corrosion potential was more noble than that of sulfur hexafluoride shielding gas ($-1483$ mV). The corrosion voltage of the heat-treated Mg67Zn28Ca5 alloy ($-1.347$ mV) studied by Wang et al.[30] was equivalent to this value. The corrosion current density of magnesium alloys by vacuum induction melting was $1/3$ of that of magnesium alloys by sulfur hexafluoride shielded melting. The $i_{\text{corr}}$ (A cm$^{-2}$) was converted in corrosion rate CR (mm/a) with the Faraday’s law:
where \( n \) is the number of electrons transferred, \( F \) is the Faraday’s constant (96485 C·mol\(^{-1}\)), \( M \) is the molar mass of magnesium (g·mol\(^{-1}\)), \( \rho \) is the density of the Mg\(_{67}\)Zn\(_{28}\)Ca\(_{5}\) alloy (g·cm\(^{-3}\)) and \( S = 1 \text{ cm}^2 \). The corrosion rate was also listed in Table 1. The corrosion rate of Mg\(_{67}\)Zn\(_{28}\)Ca\(_{5}\) by vacuum induction melting (0.2618 mm/a) was lower than that by sulfur hexafluoride shielded melting (0.9686 mm/a). Thus, Mg\(_{67}\)Zn\(_{28}\)Ca\(_{5}\) alloy by vacuum induction melting exhibited good corrosion resistance. The cooling rate of vacuum induction melting was relatively slow, and the alloy composition was uniform. This condition was conducive to obtaining a near-equilibrium structure, thereby improving the alloy’s corrosion resistance.

As shown in Figure 8, EIS measurements were employed to further investigate the corrosion resistance of the different Mg\(_{67}\)Zn\(_{28}\)Ca\(_{5}\) specimens. Normally, in the Nyquist plane, the size of the capacitor ring represents the impedance value of the working electrode [31]. Compared with magnesium alloys melted by sulfur hexafluoride shielded, magnesium alloys melted by vacuum induction melting exhibited higher impedance values. In other words, Mg\(_{67}\)Zn\(_{28}\)Ca\(_{5}\) alloy melted by vacuum induction melting showed good corrosion resistance. These results were consistent with those of potentiodynamic polarization curves.

4. Discussion

Figure 9 shows the metallographic structure of Mg\(_{67}\)Zn\(_{28}\)Ca\(_{5}\) alloy by different melting processes. The composition of Mg\(_{67}\)Zn\(_{28}\)Ca\(_{5}\) alloy was a eutectic composition, which should be a eutectic structure after equilibrium solidification. Figure 9(B) shows the uniformly distributed eutectic structure of Mg\(_{67}\)Zn\(_{28}\)Ca\(_{5}\) alloy melted by vacuum induction melting. Vacuum induction melting facilitated arc preheating die device and self-stirring, which allowed the melt to cool in a near-equilibrium way and made the melt composition uniform. By
contrast, the Mg67Zn28Ca5 alloy melted by sulfur hexafluoride shielded in figure 9(A) demonstrated partial pre-eutectic precipitation with a shape similar to that of a circular one. The low melting point of Zn element (419.53 °C) and volatilization occurred during sulfur hexafluoride shielded melting, resulting in the deviation of the magnesium alloy composition and eutectic composition. Possibly, pouring the melt into the mold at room temperature causes the alloy to not melt. The cooling speed was fast, which resulting in the non-equilibrium solidification of the melt and the precipitation of the matrix; thus, an uneven alloy structure was obtained.

Figure 10 presents the XRD patterns of Mg67Zn28Ca5 alloy via two melting processes. The normal eutectic structure of Mg67Zn28Ca5 alloy should be hexagonal α-Mg, hexagonal MgZn2, and tetragonal Ca2Mg5Zn13 [32, 33]. Figure 10 shows the similar phases of Mg67Zn28Ca5 alloy via two melting processes. However, the phase content differed. The content of Ca2Mg5Zn13 phase in Mg67Zn28Ca5 alloy by vacuum induction melting was lower than that of magnesium alloy via SF6 shielded melting, and the content of α-Mg phase was higher than that of magnesium alloy by sulfur hexafluoride shielded melting. The diffraction peaks of the α-Mg phase in the XRD pattern shifted to a high angle (approximately 0.1°) compared with the standard diffraction peaks. This result may be due to the decrease in lattice parameters of magnesium due to the solid solution of zinc in magnesium during melting, causing the crystal phase of magnesium to shift to the right [34].

Figures 11 and 12 show the surface morphology and element distribution of Mg67Zn28Ca5 alloy melted by sulfur hexafluoride shielded. The coarse pre-eutectic phase as marked in figure 9(a) was mainly composed of element Zn, a small amount of element Mg and element Ca. Combined with the XRD spectra, the pre-eutectic phase in the alloy was Ca2Mg5Zn13. In figure 11(a), the black particles were MgZn2 phase and the white fine acicular was α-Mg phase. The existence of the second phase in the alloy accelerated the corrosion of magnesium alloy [35] due to the very low electrode potential of the α-Mg matrix and the cathodic behavior of Ca2Mg5Zn13 relative to the matrix. Microgalvanic corrosion formed between the second phase Ca2Mg5Zn13 and the matrix [36]. Moreover, the α-Mg phase around the Ca2Mg5Zn13 phase was preferentially corroded. In figure 3, the Mg67Zn28Ca5 alloy melted by sulfur hexafluoride shielded was affected pitting or local corrosion due to galvanic corrosion between the Ca2Mg5Zn13 phase and matrix. The eutectic structure of Mg67Zn28Ca5 alloy melted by vacuum induction melting was uniform in composition and in corrosion as a whole. These experimental results showed that the bio-corrosion resistance of Mg67Zn28Ca5 alloy improved by vacuum induction melting.

5. Conclusions

(1) The corrosion potential of Mg67Zn28Ca5 by vacuum induction melting (−1313 mV) was nobler than that by sulfur hexafluoride shielded melting (−1483 mV). The corrosion current of Mg67Zn28Ca5 by vacuum induction melting (1.202 × 10−5 A) was lower than that by sulfur hexafluoride shielded melting (4.332 × 10−5 A).

(2) The Mg67Zn28Ca5 alloy melted by sulfur hexafluoride shielded was non-equilibrium solidification, resulting in non-uniform alloy composition and more precipitated phases. Galvanic corrosion occurred between the
second phase (Ca$_2$Mg$_5$Zn$_{13}$ phase) and the $\alpha$-Mg phase. This phenomenon accelerated the corrosion rate of the matrix and made the Mg$_{67}$Zn$_{28}$Ca$_5$ alloy exhibit pitting corrosion in SBF solution.

(3) The Mg$_{67}$Zn$_{28}$Ca$_5$ alloy by vacuum induction melting presented uniform composition, less precipitated phase. The immersion test showed that the Mg$_{67}$Zn$_{28}$Ca$_5$ alloy by vacuum induction melting presents general corrosion behavior, which has good corrosion resistance.
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Author contributions

Guanghong Zhou and Hongyan Ding conceived and designed the experiments; Guoqing Wang, Hao Ding and Hong Li performed Mg67Zn28Ca5 alloys melting and bio-corrosion experiments and analyzed the data. Guoqing Wang and Guanghong Zhou wrote the paper.

Conflicts of interest

The authors declare no conflict of interest.

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