Applied Surface Science 351 (2015) 410–415

Contents lists available at ScienceDirect

Applied Surface Science

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

Preparation of novel functional Mg/O/PCL/ZnO composite biomaterials and their corrosion resistance

Zhongxian Xi, Cui Tan, Lan Xu, Na Yang, Qing Li*

School of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China

ARTICLE INFO

Article history:
Received 18 March 2015
Received in revised form 26 May 2015
Accepted 26 May 2015
Available online 4 June 2015

Keywords:
Magnesium alloys
Composite biomaterials
Corrosion
Zinc ion

ABSTRACT

In this study, novel and functional Mg/O/PCL/ZnO (magnesium/anodic film/poly(ε-caprolactone)/zinc oxide) composite biomaterials for enhancing the bioactivity and biocompatibility of the implant was prepared by using anodization treatment and dip-coating technique. The surface morphology, microstructure, adhesion strength and corrosion resistance of the composite biomaterials were investigated using scanning electron microscopy (SEM), adhesion measurements, electrochemical tests and immersion tests respectively. In addition, the biocompatible properties of Mg (magnesium), Mg/PCL (magnesium/poly(ε-caprolactone)) and Mg/O/PCL (magnesium/anodic film/poly(ε-caprolactone)) samples were also investigated. The results show that the Mg/O/PCL/ZnO composite biomaterials were with low porosity and with the ZnO powders dispersed in PCL uniformly. The adhesion tests suggested that Mg/O/PCL/ZnO composite biomaterials had better adhesion strength than that of Mg/PCL composite biomaterials obviously. Besides, an in vitro test for corrosion demonstrated that the Mg/O/PCL/ZnO composite biomaterials had good corrosion resistance and zinc ion was released obviously in SBF.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

As lightest structural metals, magnesium and its alloys have been widely used in the fields of auto-motive industry, aerospace, electronics, telecommunication, computer manufacturing for their outstanding physical and mechanical properties, such as good vibration, shock adsorption and high damping capacity. Besides, the specific density (1.74–2 g/cm^3) and Young's modulus (41–45 GPa) of magnesium alloys is close to human body's bone (1.8–2.1 g/cm^3, 3–20 GPa) make them quite suitable for using as bone repairing materials [1–4]. Moreover, Mg^{2+} is an essential element to human metabolism and was reported to stimulate the growth of new bone tissue [3,5–8]. However, the applications of magnesium alloys are limited by their poor corrosion resistance, especially in the environment of body fluid and blood plasma [9,10]. Poly(ε-caprolactone) (PCL), as a typical aliphatic polyesters, is completely biocompatible, biodegradable, and nontoxic to living organisms [11–13]. ZnO powders are a newer type of promising candidate because of their high safety [14,15], low price, and lacking of polluting effects. In addition, the ZnO powders can release zinc ion in vivo and zinc ion could promote bone formation [16–21]. Here we have designed a novel functional Mg/O/PCL/ZnO composite material to solve the poor corrosion resistance of magnesium, lead to improvement of bioactivity and biocompatibility. As a popular and simple surface treatment, anodization can produce a relatively adherent, hard, thick and abrasion-resistance oxide/hydroxide films on magnesium [22–25]. We use anodization treatment to construct the rough structure, which can improve the adhesion strength between PCL and AZ91 magnesium alloy and protect the magnesium alloy better. Meanwhile, ZnO powders were doped in the PCL to improve the bioactivity and biocompatibility of the implant and decrease the degradation rate of magnesium alloys.

Finally, the Mg/O/PCL/ZnO composite biomaterials were fabricated by anodizing treatment and dip-coating method in this study. The synthesis method for Mg/O/PCL/ZnO is simple, environment-friendly and non-toxic, which might be applicable in other fields. The concrete preparation process of Mg/O/PCL/ZnO composite materials is shown in Fig. 1.

2. Materials and methods

2.1. Materials

The following chemicals were used without further purification or modification: aqueous ammonia solution, ethanol, dichloromethane (DCM) (Chuandong Chemical Reagent Factory,

* Corresponding author. Tel.: +86 23 68256320; fax: +86 02368367675.
E-mail address: liqingdswu@163.com (Q. Li).

http://dx.doi.org/10.1016/j.apsusc.2015.05.163
0169-4332/© 2015 Elsevier B.V. All rights reserved.

www.spm.com.cn

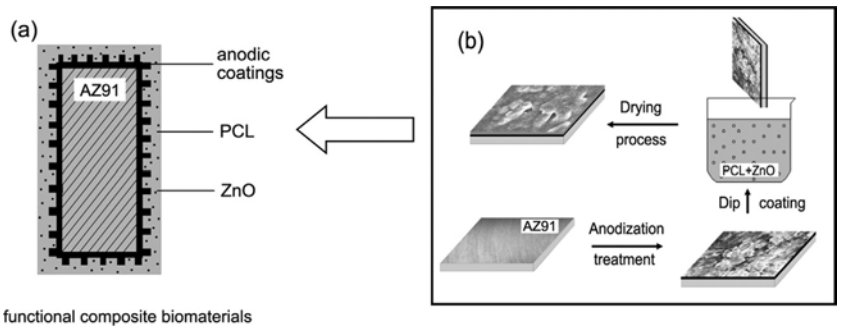

Fig. 1. The designed functional composite materials (a) and preparation process of Mg/O/PCL/ZnO composite materials (b).

China), and PCL (Mw: 80,000, Beijing Essen Technology, China), ZnO powders (80–100 nm, Chengdu Kelong Reagent Co., Ltd., China). Hank's balanced solution was utilized as a simulated body fluid (SBF) (8.0 g L^{-1} NaCl, 0.35 g L^{-1} $NaHCO_3$, 0.4 g L^{-1} KCl, 0.14 g L^{-1} $CaCl_2$, 1.0 g L^{-1} $C_6H_6O_6$ (glucose), 0.1 g L^{-1} $KH_2PO_4{\cdot}H_2O$, 0.2 g L^{-1} $MgSO_4{\cdot}7H_2O$, 0.06 g L^{-1} $Na_2HPO_4{\cdot}7H_2O$) [3]. Die-cast magnesium alloy AZ91 (Chongqing Boao Mg-Al Manufacturing Co., Ltd., China) was used as a substrate material.

2.2. Sample preparation

In this work, die-casted Mg alloy (AZ91) with a chemical composition (wt.) of 8.77% Al, 0.74% Zn, 0.18% Mn, 90.31% was used for investigation. The dimensions of all samples were 40 mm × 15 mm × 5 mm. Before used, the samples were polished by silicon carbide papers from 150 to 1500 mesh, then ultrasonically cleaned in acetone and rinsed with de-ionized water. Finally, the samples were dried at 60 °C and cooled to room temperature.

2.3. Preparation of Mg/O/PCL/ZnO composite materials

The AZ91 samples were anodized in 3 mol L^{-1} KOH solution at 60 °C for 10 min. Anodization treatment process was at a constant voltage of 10 V. After anodic oxidation, the samples were washed thoroughly with distilled water and followed by air dried. The washed samples were treated under 95 °C for 30 min, and then cooled to room temperature.

The Mg/O/PCL/ZnO composite materials were prepared by anodization and dip-coating method with suitable concentrations of PCL solutions. Two different concentrations of PCL solutions (2.5 wt.% and 10 wt.%) were prepared. PCL granules were dissolved in dichloromethane (DCM) solvent under magnetic stirring for 5 h. Then colloids were prepared by mixing the ZnO powders with PCL polymer solution (10 wt.%). The obtained colloidal solution was stirred continuously for 10 h. The prepared samples were immersed into the mixed solutions for 30 s and then pulled out of the solution at a speed of 2 mm/s for the first layer. After the films dried, the subsequent layers were prepared in the same way. Then the Mg/O/PCL/ZnO composite materials were prepared. Table 1 showed the layers of four groups of the samples (Mg, Mg/PCL, Mg/O/PCL and Mg/O/PCL/ZnO).

2.4. Microstructure characterization and property tests

The surface morphologies and cross-section examination were observed by digital camera and scanning electron microscopy (SEM, Hitachi S-4800). Roughness of composite samples was measured by atomic force microscope (AFM, CSPM5500). Electrochemical tests were performed using a CorrTest CS350 electrochemical workstation. The concentration of zinc ion in the immersed solution was determined by atomic absorption spectrophotometry (HITACHI 180-50).

3. Results and discussion

3.1. Characteristics of the surface

The surface morphology of anodized magnesium sample, composite materials and their cross-section examination were shown in Fig. 2. The anodized magnesium exhibits a heterogeneous surface with micro-scaled roughness (Fig. 2a). The SEM images show that the surface morphologies of Mg/PCL materials produced fairly interconnected pore networks and the thickness of PCL coating was about 5–7 μm (Fig. 2b). The PCL coating of the Mg/O/PCL composite materials is not thick enough to cover the anodic magnesium completely and the cross-section examination showed that the thickness of O/PCL part (anodic and PCL coating) on magnesium was about 10 μm (Fig. 2c). In Fig. 2d, the Mg/O/PCL/ZnO materials were prepared with low porosity and the ZnO particles were dispersed in the PCL films uniformly and the thickness of the O/PCL/ZnO part (anodic and PCL/ZnO coating) was about 20 μm (Fig. 2d). From their cross-section examination, the thickness of the coating became thicker after doping the ZnO powders into PCL solutions and the Mg/O/PCL/ZnO sample was with the thickest coating which could provide enough corrosion protection to magnesium.

The roughness of samples was investigated with atomic force microscopy. Images were obtained at 8 × 8 μm with a cut-off of 2 μm. The roughness of the Mg/PCL and Mg/O/PCL samples were 111.97 nm and 335.93 nm, respectively. And the roughness of Mg/O/PCL/ZnO sample was >2 μm. It also demonstrated that the Mg/O/PCL/ZnO sample was with rougher surface which could provide enough space for bone tissue growth.

3.2. Adhesion measurements

The adhesion strength between films and AZ91 magnesium alloy was evaluated according to American Society for Testing and Materials (ASTM) D3359-09 method [26,27]. The results of adhesion measurement tests are shown in Fig. 3. It can be seen that the rough anodic film could improve the adhesion strength between PCL and AZ91 magnesium. The PCL of Mg/PCL was detached off the magnesium completely. However, there is no obvious delamination or detachment of the Mg/O/PCL and Mg/O/PCL/ZnO samples was observed, which indicate that the addition of intermediate anodic film indeed improves the bonding strength between PCL (or PCL/ZnO) and AZ91 samples.

3.3. Electrochemical corrosion behavior

Electrochemical impedance spectra (EIS) were carried out in SBF. In a water bath the electrochemical tests were conducted with

www.sjm.com.cn

Table 1
The coating of the samples.

Layer	Mg	Mg/PCL	Mg/O/PCL	Mg/O/PCL/ZnO
First layer	None	2.5 wt.%. PCL	2.5 wt.%. PCL	2.5 wt.%. PCL
Second layer	None	10 wt.%. PCL	10 wt.%. PCL	10 wt.%. PCL 5 wt.%. ZnO

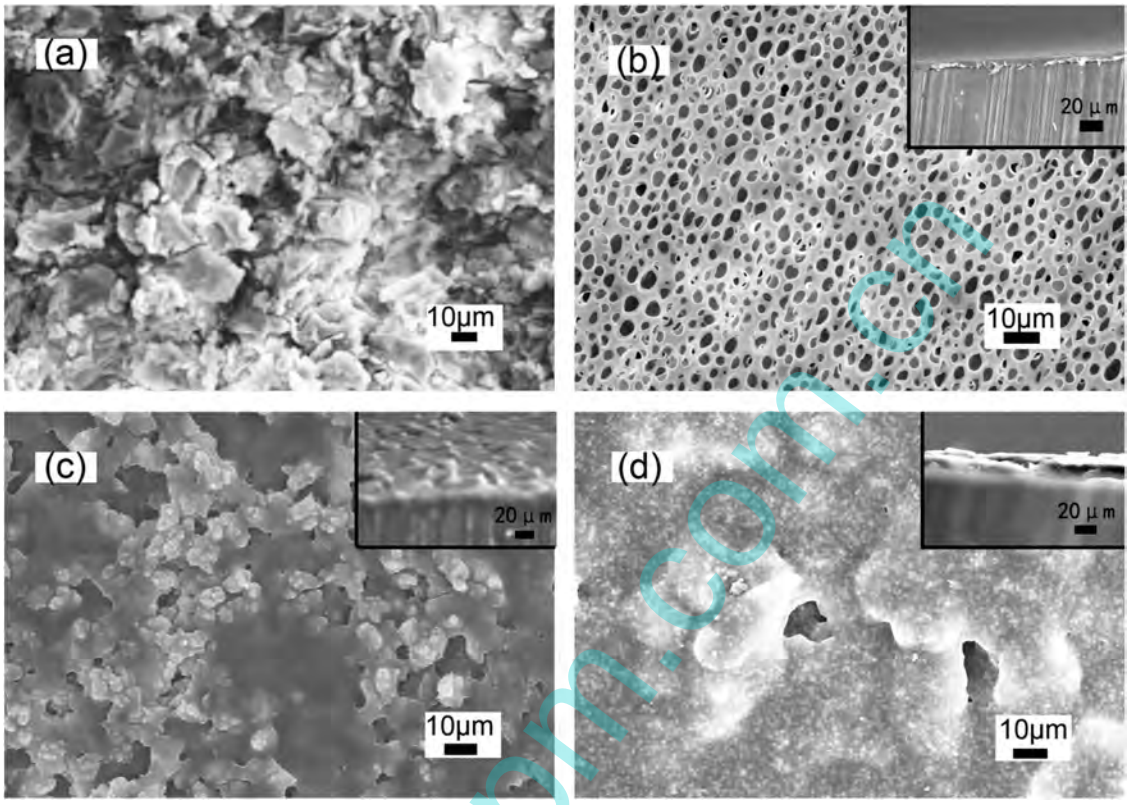

Fig. 2. SEM micrographs of surface morphologies of anodized magnesium and composite materials: (a) anodized magnesium; (b) Mg/PCL; (c) Mg/O/PCL and (d) Mg/O/PCL/ZnO.

a three-electrode system in 200 mL SBF. Samples were embedded in epoxy resin and exposed with a surface area of 1 cm^2. A platinum mesh and a saturated calomel electrode were used as the counter and the reference electrode, respectively.

The EIS plots of the four groups (Mg, Mg/PCL, Mg/O/PCL, Mg/O/PCL/ZnO) in SBF are represented in Fig. 4. It is known that in the Nyquist plane the diameter of the capacitive loop represents the impedance value of the working electrode [28]. As shown in Fig. 4, Mg/O/PCL/ZnO samples showed the best anticorrosion performance compared with Mg, Mg/PCL and Mg/O/PCL samples. The value of R_{ct} for the Mg/O/PCL/ZnO samples (>700 kΩ) is about 46 times larger than that of the Mg samples (15 kΩ). EIS results indicated that Mg/O/PCL/ZnO samples could have desirable anticorrosion performance as the effective blocking barrier. That is because the anodic film provides protection to the magnesium and the doped ZnO fills PCL film's pore to produce smooth surface with low porosity. From the results, Mg/O/PCL/ZnO shows the best anticorrosion performance among four groups.

The result is consistent with that derived from the potentiodynamic polarization curves of four groups shown in Fig. 5. It is obvious that the Mg/O/PCL/ZnO exhibits the best corrosion resistance compared with that of Mg/PCL and Mg/O/PCL. The anodic

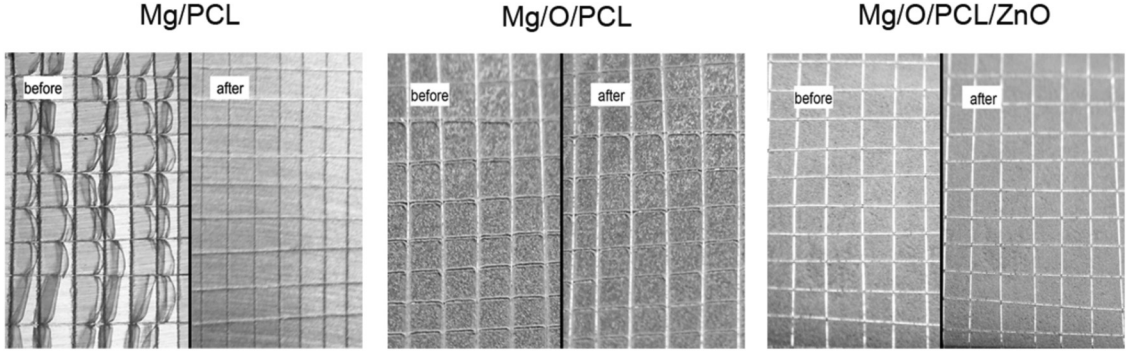

Fig. 3. Optical images of Mg/PCL, Mg/O/PCL and Mg/O/PCL/ZnO samples before and after adhesion tests by ASTM D3359-09.

www.spm.com.cn

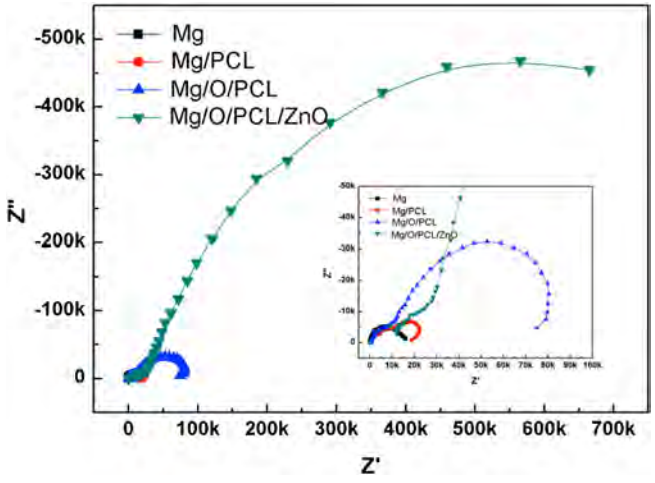

Fig. 4. Electrochemical impedance spectroscopy (EIS) of samples in SBF.

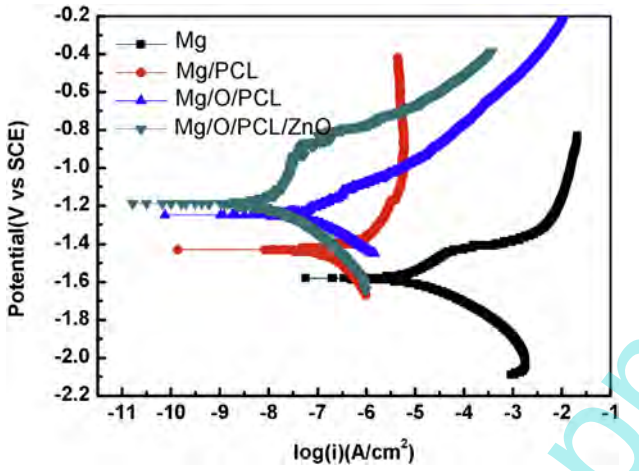

Fig. 5. Potentiodynamic polarization curves of samples in SBF.

polarization of the Mg/O/PCL/ZnO surface brought about a stable and long passivation region. Besides, corrosion potential (E_{corr}), corrosion current density (i_{corr}) and corrosion rate (CR) were calculated from the polarization curves by using Tafel extrapolation methods (Table 2). This could be a good indication of the materials' stability: (i) all types of the composite materials decreased the substrate corrosion current density, significantly; (ii) anodic film and doped ZnO can improved the corrosion resistance in some extent and enhance the surface bioactivity. The results showed that the Mg/O/PCL/ZnO materials had the best corrosion resistance among the four groups.

3.4. Immersion test

An immersion test was performed for 35 days at 37 °C, with 3 substrates for each group being immersed in 150 mL SBF. The SBF was updated every 5 days during immersion. The pH value of SBF solution was monitored with a pH meter. In Fig. 6, the pH change of composite materials in the SBF was minor than that of the Mg

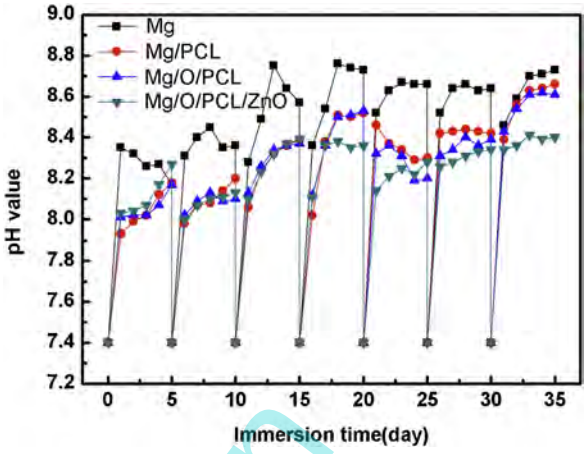

Fig. 6. Change of pH values of samples with immersion time at 37 °C for 35 days in SBF.

during immersion process, and the Mg/O/PCL/ZnO group had the slightest pH value change between 7.4 and 8.4 in 35 days' immersion of SBF. The pH change of Mg samples was the highest among four group samples and that's because the magnesium alloys could easily occur corrosion in SBF without protection. And the corrosion products of magnesium alloys contains $Mg(OH)_2$, $Ca(OH)_2$ and phosphate salts which can rapidly dissolved into SBF to improve the pH of SBF. However, the composite materials have the functional protection part which can prevent corrosion in SBF. The pH change result also suggests the Mg/O/PCL/ZnO biomaterials had the good protection to magnesium samples.

In Fig. 7, the Mg/O/PCL/ZnO group had the best protective among four groups after 35 days' immersion in 150 mL SBF at 37 °C. After immersion, the Mg group was serious rotted (Fig. 7a), the films of Mg/PCL (Fig. 7b) and Mg/O/PCL (Fig. 7c) groups were also destroyed partly. However, the films of Mg/O/PCL/ZnO group still had the strong protection to magnesium alloy (Fig. 7d).

For zinc releasing test, we used the PCL films (20 mm × 30 mm) and PCL/ZnO films (20 mm × 30 mm) in 150 mL SBF at 37 °C for 35 days. Then the concentrations of zinc of the immersed solution were determined by atomic absorption spectrophotometry (HITACHI 180-50). The result is that the zinc ion release of PCL/ZnO films is about 90 μg and the PCL films do not release zinc ion. In SBF, ZnO powders could demonstrate slight dissolution generally as the following reactions [29]:

$$ZnO(s) + 2H^+ \leftrightarrow Zn^{2+} + H_2O(l) \quad (1)$$

$$ZnO(s) + H^+ \leftrightarrow Zn(OH)^+ \quad (2)$$

$$ZnO(s) + OH^- + H_2O(l) \leftrightarrow Zn(OH)^{3-} \quad (3)$$

$$ZnO(s) + 2OH^- + H_2O(l) \leftrightarrow Zn(OH)_4{}^{2-} \quad (4)$$

That means that the Zn ion is released from Mg/O/PCL/ZnO composite materials in body, which could act as the role of promoting bone formation. At the same time, the composite materials have good corrosion resistance. It is suggested that Mg/O/PCL/ZnO composite materials may have great potential in bone tissue engineering applications.

Table 2
Electrochemical parameters of samples.

Substrates	I_{corr} (A/cm^2)	E_{corr} (V)	Corrosion rate (mm/a)
Mg	9.55×10^{-6}	−1.58	2.06×10^{-1}
Mg/PCL	5.04×10^{-7}	−1.43	1.09×10^{-2}
Mg/O/PCL	5.77×10^{-8}	−1.25	1.25×10^{-3}
Mg/O/PCL/ZnO	4.33×10^{-9}	−1.19	9.36×10^{-5}

www.spm.com.cn

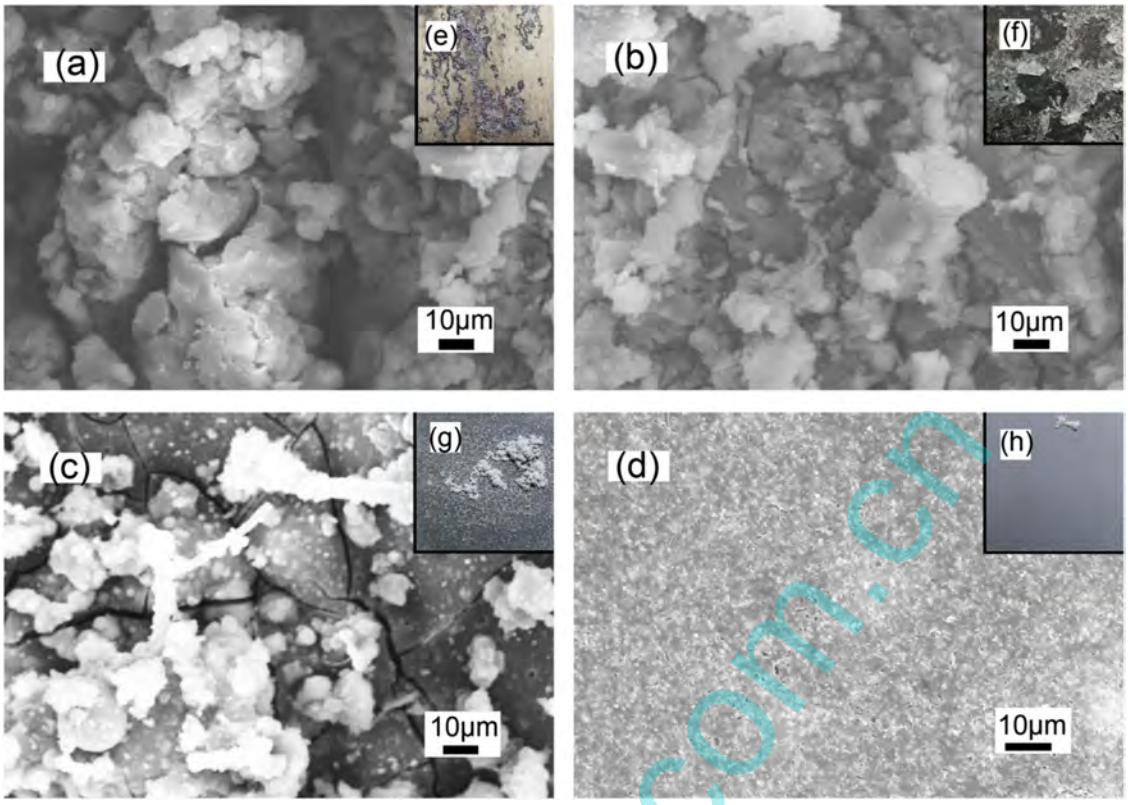

Fig. 7. SEM images (a, b, c, d) and digital pictures (e, f, g, h) of four groups (Mg (a and e), Mg/PCL (b and f), Mg/O/PCL (c and g), Mg/O/PCL/ZnO (d and h)) after 35 days' immersion in SBF at 37 °C.

4. Conclusion

In this article, novel adhesive Mg/O/PCL/ZnO composite materials were successfully prepared. The SBF electrochemical studies and 35 days' immersion test manifested that the Mg/O/PCL/ZnO had the outstanding corrosion resistance in SBF. Zinc ion releasing test showed that the Mg/O/PCL/ZnO biomaterials can release zinc ion to promote bone formation, which indicate that this materials may have great potential in tissue engineering applications. What'smore, the Mg/O/PCL/ZnO biomaterials can provide a feasible scheme in clinical bone repairing application.

Acknowledgement

The authors specially thank for the financial support of this work from the National Natural Science Foundation of China (51103120).

References

[1] B.L. Mordike, T. Ebert, Magnesium properties-applications-potential, Mater. Sci. Eng. A 302 (2001) 37–45.
[2] M.K. Kulekci, Magnesium and its alloys applications in automotive industry, Int. J. Adv. Manuf. Technol. 39 (2008) 851–865.
[3] G.L. Song, Control of biodegradation of biocompatible magnesium alloys, Corros. Sci. 49 (2007) 1696–1701.
[4] M.P. Staiger, A.M. Pietak, J. Huadmai, G. Dias, Magnesium and its alloys as orthopedic biomaterials: a review, Biomaterials 27 (2006) 1728–1734.
[5] A.S.M.F. Chowdhury, D. Mari, R. Schaller, Thermal stress relaxation in magnesium matrix composites controlled by dislocation breakaway, Compos. Sci. Technol. 70 (2010) 136–142.
[6] H. Fukuda, K. Kondoh, J. Umeda, B. Fugetsu, Interfacial analysis between Mg matrix and carbon nanotubes in Mg-6 wt.% Al alloy matrix composites reinforced with carbon nanotubes, Compos. Sci. Technol. 71 (2011) 705–709.
[7] T. Okuma, Magnesium and bone strength, Nutrition 17 (2001) 679–680.
[8] F.I. Wolf, A. Cittadini, Chemistry and biochemistry of magnesium, Mol. Aspects Med. 24 (2003) 3–9.
[9] G.L. Song, Recent progress in corrosion and protection of magnesium alloys, Adv. Eng. Mater. 7 (2005) 563–566.
[10] V. Kaesel, P.T. Tai, F.W. Bach, et al., Approach to control the corrosion of magnesium by alloying, in: Proceedings of the Sixth International Conference Magnesium Alloys and Their Application, Wiley-VCH, New York, 2004, pp. 534–539.
[11] J. Pena, T. Corrales, I. Izquierdo-Barba, A.L. Doadrio, M. Vallet-Regi, Long term degradation of poly(ε-caprolactone) films in biologically related fluids, Polym. Degrad. Stab. 91 (2006) 1424–1432.
[12] F. Wu, C.S. Liu, B. O'Neill, J. Wei, Y. Ngothai, Fabrication and properties of porous scaffold of magnesium phosphate/polycaprolactone biocomposite for bone tissue engineering, Appl. Surf. Sci. 258 (2012) 7589–7595.
[13] H. Kweon, M.K. Yoo, I.K. Park, T.H. Kim, H.C. Lee, H.S. Lee, J.S. Oh, T. Akaike, C.S. Cho, A novel degradable polycaprolactone networks for tissue engineering, Biomaterials 24 (2003) 801–808.
[14] M. Yazdimamaghani, M. Razavi, D. Vashaee, L. Tayebi, Development and degradation behavior of magnesium scaffolds coated with polycaprolactone for bone tissue engineering, Mater. Lett. 132 (2014) 106–110.
[15] J.L. Liu, J.Z. Ma, Y. Bao, J. Wang, Z.F. Zhu, H.R. Tang, L.M. Zhang, Nanoparticle morphology and film-forming behavior of polyacrylate/ZnO nanocomposite, Compos. Sci. Technol. 98 (2014) 64–71.
[16] B.S. Moonga, D.W. Dempster, Zinc is a potent inhibitor of osteclastic bone resorption in vitro, J. Bone Miner. Res. 10 (1995) 453–457.
[17] H.M. Xiong, ZnO nanoparticles applied to bioimaging and drug delivery, Adv. Mater. 25 (2013) 5329–5335.
[18] A. Yamamoto, R. Honma, M. Sumita, Cytotoxicity evaluation of 43 metal salts using murine fibroblasts and osteoblastic cells, J. Biomed. Mater. Res. 39 (1998) 331–340.
[19] C.L. Yan, D.F. Xue, Conversion of ZnO nanorod arrays into ZnO/ZnS nanocable and ZnS nanotube arrays via an in situ chemistry strategy, J. Phys. Chem. B 110 (2006) 25850–25855.
[20] H. Fukui, M. Horie, S. Endoh, H. Kato, et al., Association of zinc ion release and oxidative stress induced by intratracheal instillation of ZnO nanoparticles to rat lung, Chem. Biol. Interact. 198 (2012) 29–37.
[21] N. Tripathy, T.K. Hong, K.T. Ha, H.S. Jeong, Y.B. Hahn, Effect of ZnO nanoparticles aggregation on the toxicity in RAW 264.7 murine macrophage, J. Hazard. Mater. 270 (2014) 110–117.
[22] H.Y. Hsiao, H.C. Tsung, W.T. Tsai, Anodization of AZ91D magnesium alloy in silicate-containing electrolytes, Surf. Coat. Technol. 199 (2005) 127–134.
[23] D.P. Barbosa, G. Knörnschild, Anodization of Mg-alloy AZ91 in NaOH solutions, Surf. Coat. Technol. 203 (2009) 1629–1636.
[24] R. Hahn, J.G. Brunner, J. Kunze, P. Schmuki, S. Virtanen, A novel approach for the formation of $Mg(OH)_2$/MgO nanowhiskers on magnesium: rapid

www.cpm.com.cn

anodization in chloride containing solutions, Electrochem. Commun. 10 (2008) 288–292.
[25] H. Fukuda, Y. Matsumoto, Effects of Na_2SiO_3 on anodization of Mg–Al–Zn alloy in 3 M KOH solution, Corros. Sci. 46 (2004) 2135–2142.
[26] ASTM D3359-09, Standard Test Methods for Measuring Adhesion By Tape Test, ASTM, Philadelphia, PA, 2009.
[27] M.J. Wang, C.F. Li, S.K. Yen, Electrolytic MgO/ZrO_2 duplex-layer coating on AZ91D magnesium alloy for corrosion resistance, Corros. Sci. 76 (2013) 142–153.
[28] M. Zidoune, M.H. Grosjean, L. Roué, J. Huot, R. Schulz, Comparative study on the corrosion behavior of milled and unmilled magnesium by electrochemical impedance spectroscopy, Corros. Sci. 46 (2004) 3041–3055.
[29] S.W. Bian, I.A. Mudunkotuwa, T. Rupasinghe, V.H. Grassian, Aggregation and dissolution of 4 nm ZnO nanoparticles in aqueous environments: influence of pH, ionic strength, size, and adsorption of humic acid, Langmuir 27 (2011) 6059–6068.

www.spm.com.cn