Materials Letters 148 (2015) 134–137

Contents lists available at ScienceDirect

Materials Letters

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

A novel functional HPPS/PCL/ZnO composite layer on AZ91 for anticorrosion

Zhongxian Xi, Cui Tan, Lan Xu, Yuzhu Meng, Chongyang Zhang, Na Yang, Qing Li*

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

ARTICLE INFO

Article history:
Received 1 February 2015
Accepted 11 February 2015
Available online 20 February 2015

Keywords:
Magnesium alloy
Adhesion
Surfaces
Layer
Corrosion resistance

ABSTRACT

AZ91 magnesium alloy was coated with a novel and functional hyperbranched polyphenylene sulfide/poly(ε-caprolactone)/ZnO composite (HPPS/PCL/ZnO) using dip-coating method in methenyl trichloride containing solution for improved corrosion resistance of the alloy in simulated body fluid (SBF). The surface of the coated sample is with lower porosity and high uniformity. The electrochemical and immersion tests suggested that the corrosion resistance of the sample coated HPPS/PCL/ZnO composite layer coated alloy was higher than that of the PCL coated one. After 20 days' immersion in SBF, the HPPS/PCL/ZnO coated composite was still smooth and hardly changed. Therefore, the HPPS/PCL/ZnO composite layer can protect the AZ91 magnesium more efficiently.

1. Introduction

Magnesium and its alloys have been widely used in the industry, electronics, bone repair materials and other fields because of their low density, inherent biocompatibility and high mechanical properties [1,2]. However, the poor corrosion resistance of magnesium alloys limits their applications, especially in body fluid or blood plasma [3,4]. Hyperbranched polyphenylene sulfide (HPPS), the most popular thermoplastics for aerospace applications, has the properties of processing temperature, high stiffness and hardness [5,6]. Poly(ε-caprolactone) (PCL), one of the most popular FDA approved ones, is fully biocompatible, biodegradable and nontoxic [7,8]. ZnO powder is a promising candidate biological material with high safety, low price and good stability. The ZnO powder can release Zinc ion in vivo and the Zinc ion has the ability to promote bone formation [9,10].

The current magnesium alloy scaffolds have a high corrosion rate, resulting in losing the mechanical strength. Surface modification is not only an effective method to enhance the properties of these magnesium alloys in physiological conditions but also stimulate bone formation. To the best of our knowledge, there is no study on employing HPPS, PCL and ZnO to coat magnesium scaffolds. In this article, the HPPS/PCL/ZnO composite layer can raise the resistance and the corrosion potential of the magnesium alloy in SBF. Furthermore, the PCL and ZnO powders with good biocompatibility make the HPPS/PCL/ZnO layer promising in bone engineering applications.

In this article, we have studied three kinds of coated samples as shown in Fig. 1. We also prepared PCL, PCL/ZnO and HPPS/PCL/ZnO layers on pre-corrosion treated magnesium samples.

2. Materials and methods

The following chemicals were used: HPPS (Mn = 10 000 g/mol), methenyl trichloride ($CHCl_3$), ZnO powder (−20 + 100 nm), PCL (Mn = 80 000 g/mol), ethanol and Hank's balanced solution were utilized as simulated body fluid (SBF) [1]. AZ91 magnesium alloy (wt. fraction: Al 8.8%, Zn 0.74%, Mn 0.18%, balance Mg) was used in current experiments. The samples with the dimensions of 45 mm × 17 mm × 5 mm were ground and treated by the following processes. Then it was polished by silicon carbide papers from 150 to 1500 mesh, then ultrasonically cleaned in acetone and rinsed with de-ionized water. After that the samples were dried at 60 °C. The prepared AZ91 samples were immersed in pre-corrosion solution (0.618 M NaCl, 0.027 M $NaHCO_3$) for 6 h at 37 °C. After pre-corrosion treatment, the samples were washed with distilled water followed by air drying [11]. The HPPS/PCL/ZnO composite layer was prepared by a dip-coating method with suitable solutions with HPPS (3 wt%), PCL (10 wt%.) and ZnO (5 wt%). The HPPS, PCL and ZnO were dissolved in $CHCl_3$ in order and the mixed solutions were stirred for 24 h. The pre-corrosion treated samples were immersed into the mixed solutions for 45 s and then pulled out of the mixed solution with a speed of 2 mm/s. The fabrication process of multi-functional composite (PCL, PCL/ZnO and HPPS/PCL/ZnO) coated alloy by dip-coating is shown in Fig. 1.

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

http://dx.doi.org/10.1016/j.matlet.2015.02.056
0167-577X/

The surface morphologies were observed by digital camera and scanning electron microscopy (SEM, Hitachi S-4800). The adhesion strength between layer and AZ91 magnesium alloy was evaluated according to ASTM D3359-09 method [12]. Electrochemical tests were performed using a CorrTest CS350 electrochemical workstation in SBF. Samples were embedded in epoxy resin and exposed with a surface area of 1 cm^2. Electrochemical impedance spectra (EIS) test was carried out with AC amplitude of 10 mV from 10^{-5} to 10^{-2} Hz in SBF at 25 °C. Potentiodynamic polarization tests of samples were performed at a scan rate of 0.5 mV/s. The electrochemical tests were conducted with a three-electrode system and incubated in 200 ml SBF. Immersion tests were performed in SBF for 20 days at 37 °C, with 3 samples for each group being immersed in 150 ml SBF. The exposed sample area is 1 cm^2. The SBF was updated every 5 days during immersion and the pH value of SBF solution was monitored with a pH meter.

3. Results and discussion

The surface morphologies of pre-corrosion AZ91 sample, PCL, PCL/ZnO, and HPPS/PCL/ZnO are shown in Fig. 2. It could be seen that the pre-corrosion AZ91 sample exhibited a surface with microscale roughness totally in Fig. 2(a), which would greatly increase the adhesion between the magnesium substrate and layer. The SEM images showed that the surface morphologies of PCL samples produced fairly interconnected pore networks in Fig. 2(a). After being doped with ZnO, the surface became smooth

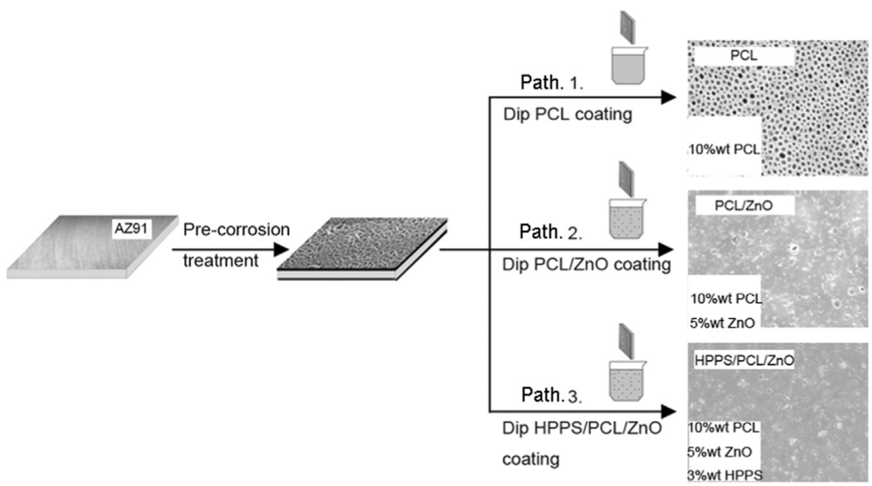

Fig. 1. The fabrication process of multi-functional composite layer.

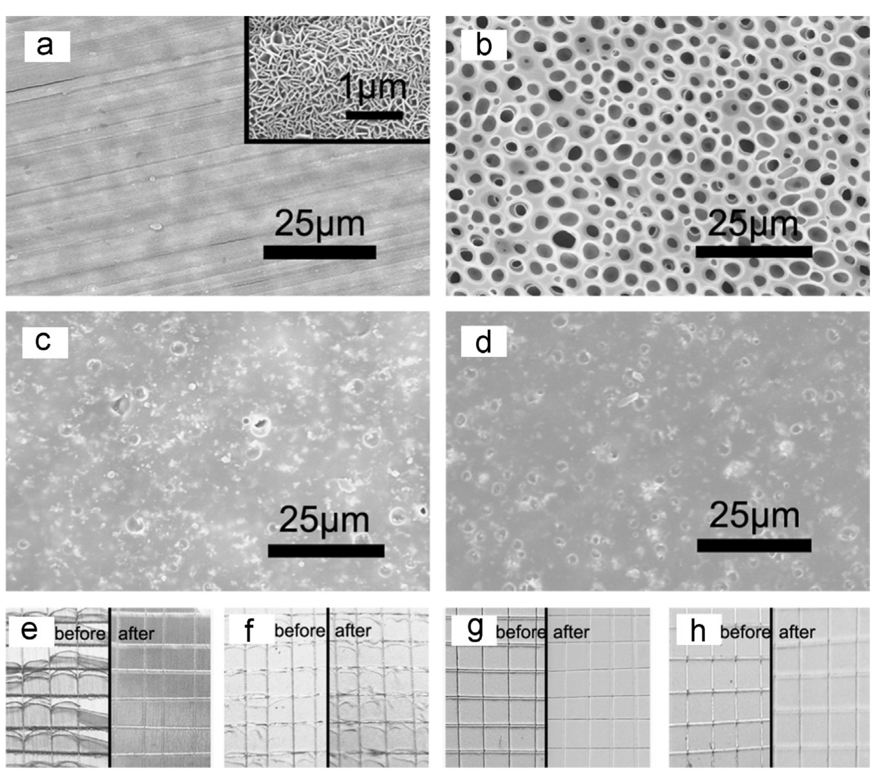

Fig. 2. SEM micrographs of samples (a–d) (pre-corrosion AZ91 sample (a); PCL (b); PCL/ZnO (c); HPPS/PCL/ZnO (d)) and optical images of samples before and after adhesion tests (e–g) (PCL on bare magnesium (e); PCL (f); PCL/ZnO (g); HPPS/PCL/ZnO (h)).