Journal of Materials Science & Technology xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Journal of Materials Science & Technology

journal homepage: www.jmst.org

Effect of applied potential on the microstructure, composition and corrosion resistance evolution of fluoride conversion film on AZ31 magnesium alloy

Liping Wu, Changgang Wang, Durga Bhakta Pokharel, Ini-Ibehe Nabuk Etim, Lin Zhao, Junhua Dong*, Wei Ke, Nan Chen

Environmental Corrosion Center, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, 110016, China

ARTICLE INFO

Article history:
Received 2 November 2017
Received in revised form 30 January 2018
Accepted 30 March 2018
Available online xxx

Keywords:
Potentiostatic
Fluoride conversion film
AZ31 magnesium alloy
KF solution
Corrosion

ABSTRACT

AZ31 magnesium (Mg) alloy was potentiostatic polarized in 0.1 M deaerated KF solution with pH 7.5 from −0.4 V to −1.4 V with an interval of −0.2 V. The polarization process was described by the potentiostatic current decay. The resultant film was analyzed by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and electrochemical impedance spectroscopy (EIS). The results demonstrated that the deposited film included a $Mg(OH)_2/MgF_2$ containing inner layer and a $Mg(OH)_2/MgF_2/KMgF_3$ comprising outer layer. The high polarized potential produced high content of MgF_2 but low content of $KMgF_3$ and thin film. Conversely, the low polarized potential produced small content of MgF_2 but high content of $KMgF_3$ and thick film. The optimal corrosion resistance of the deposited film was obtained at −1.4 V, which was closely related with the content of MgF_2 and $KMgF_3$ and the film thickness.

1. Introduction

Since the 21 st century, magnesium (Mg) alloys have been attracting great attention as a new orthopedic material because they possess many intriguing characteristics including similar elastic modulus to that of the natural bone, excellent bio-compatibility, high bio-security, unique ability to stimulate growth of new bone tissue, complete bio-degradation of Mg element and thus the elimination of the need of a secondary surgery [1–6]. However, Mg based alloys normally degrade very fast in vivo and fail before the damaged bone heal [5,6], and the spontaneously generated hydrogen (H_2) likely causes separation of tissue and tissue layers [3–6]. Currently, the chemical conversion film such as fluoride conversion film (FCF) [7–13], hydroxyapatite coating [14–18] and Mg-Al hydrotalcite conversion film [19] are proved to be the most promising ways to solve the corrosion problems. Amongst the chemical conversion film enlisted, FCF shows great potential in enhancing cell adhesion and proliferation, damaged bone healing and osseointegration [7,12,20–34] and in preventing biofilm formation [25–27]. However, the traditional method to form FCF on Mg alloy is through immersing Mg alloy in 40% or 48% hydrofluoric acid, which has brought many challenges like high toxicity, corrosivity of the solution and many pinholes throughout FCF caused by the quickly released H_2. However, when applying potentiostatic anodic polarization on Mg alloy, Mg substrate can be uniformly dissolved. The coating film can be evenly and compactly formed on Mg substrate, which decreases the micro-holes and thus improves the corrosion resistance of the resultant film. Obviously, potentiostatic polarization method may be used for depositing FCF on Mg alloy in neutral KF solution without the above mentioned troubles [28,29]. Researchers [28–32] found that KF concentration had an effect on the film composition, and $KMgF_3$ was rich in 0.1 M KF solution while MgF_2 in 1 M KF solution. To the best of our knowledge, the effect of the applied potential on FCF has not been studied yet. It is known that the applied anodic potential can accelerate the anodic dissolution of Mg alloy and influence the FCF formation process and its corrosion resistance, and the present study will focus on discussing the effect of applied potential on the composition, microstructure and corrosion resistance evolution of FCF.

2. Experimental procedures

AZ31 magnesium alloy with chemical compositions (wt.%) of Al 2.98, Zn 0.88, Mn 0.38, Si 0.0135, Cu 0.001 and Mg balance and

---

* Corresponding author.
E-mail address: jhdong@imr.ac.cn (J. Dong).

https://doi.org/10.1016/j.jmst.2018.04.009
1005-0302/© 2018 Published by Elsevier Ltd on behalf of The editorial office of Journal of Materials Science & Technology.

dimensions of 20 mm × 15 mm × 4 mm was used as substrate. It was mechanically grinded with silicon carbide paper to 5000 grit, ultrasonically cleaned in ethanol, dried in cold air stream, welded to an electrical wire, and encapsulated into 704 RTV silicone with an exposed surface area of 10 × 10 mm. 5 min Later, the encapsulated sample was suspended in a three-electrode cell filled with 0.1 M KF solution which was prepared by dissolving analytical grade KF salts in deionized water. After the solution was deaerated with high purity of nitrogen (N_2) for 1 h, the encapsulated sample was immersed into the solution followed by the potentiostatic polarization with a M273A Potentiostat/Galvanosta in the range from −0.4 V to −1.4 V with an interval of −0.2 V at room temperature. The encapsulated sample was used as the working electrode, a platinum foil as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All potential values were with respect to SCE. The potentiostatic polarized samples were characterized by a Phillips FEI INSPECTF scanning electron microscopy (SEM) coupled with Energy Disperse Spectroscopy (EDS) for the surface morphology examination and elemental identification, a Phillips XL30 environmental scanning electron microscopy (ESEM) for the cross section observation, a Thermo VG ESCALAB X-ray photoelectron spectroscopy (XPS) for the surface chemical composition and elemental/compositional depth profiles analysis and a Philips PW1700 X'Pert X-ray diffraction (XRD, Cu $K\alpha$ radiation) for the crystallographic structure characterization. The working parameters of SEM, EDS, XRD and XPS were mentioned in Ref. [31]. Electrochemical impedance spectroscopy (EIS) was measured using a Potentiostat/Galvanostat 273A and a Signal Recovery Model 5210 lock in amplifier in a frequency range from 10^5 to 0.01 Hz with an applied 5 mV sinusoidal perturbation at open circuit potential, and the measurement began immediately after immersion of the polarized samples in 0.1 M NaCl solution. When preparing the samples for cross-section examination, the coated area of the polarized sample was cut off and vertically put in a plastic tube one end of which was taped onto adhesive tape. Afterwards, epoxy resin was poured into the plastic tube. Several days later, the tube can be used for polishing. Firstly, it was grinded using silicon carbide paper with 600 and 2000 grit, and then polished in an abrasive finishing machine using 3.5 μm polishing paste to the mirror face.

3. Results and discussion

3.1. Potentiostatic deposition process of FCF on AZ31 Mg alloy

Fig. 1 shows the potentiostatic current decay curves of AZ31 Mg alloy polarized in a potential range from −0.4 V to −1.4 V with an interval of −0.2 V for 16 ks in deaerated 0.1 M KF solution with pH 7.5. According to Ref. [31], all of the initial current decease from the beginning of the polarization to 56 s at −0.4 V, 16 s at −0.6 V, 96 s at −0.8 V, 16 s at −1.0 V, 56 s at −1.2 V and 250 s at −1.4 V is ascribed to the combined effect of the decrease in the charging current density of the electric double layer capacitor and the increase in the faraday current density of the electrode reactions occurring on the AZ31 Mg alloy. When the former is larger than the latter, the net current density drops with time. In contrast, the net current density increases with time as the former is smaller than the latter. As the potential shifts to more noble values, the time of the turning point becomes shorter. With time extending, the faraday current density increases to a maximum at 96 s at −0.4 V, 80 s at −0.6 V, 300 s at −0.8 V, 368 s at −1.0 V, 496 s at −1.2 V and 1200 s at −1.4 V, and the time at the maximum prolongs with nobly shifting the applied potential. Furthermore, the applied potential also has an effect on the maximum, which first decreases with a decrease in the potential from −0.4 V to −0.8 V, followed by an increase with a decrease in the potential from −0.8 V to −1.0 V and finally another decrease with decreasing the potential from −1.0 V to −1.4 V. It is noted that the maximum at −1.0 V is bigger than that at −0.4 V. A further time extension induces the current density to decay to a new minimum at 660 s at −0.4 V, 840 s at −0.6 V, 1230 s at −0.8 V, 1080 s at −1.0 V, 1688 s at −1.2 V and 1800s at −1.4 V, and the time at the new minimum also extends with decreasing the applied potential. After the first maximum, the AZ31 Mg alloy suffers a faraday current density increase and then a faraday current density decrease at the second maximum at 1800s at −0.4 V, 2180s at −0.6 V, 2848s at −0.8 V, 2272s at −1.0 V, 3328s at −1.2 V and 2700s at −1.4 V. The effect of the applied potential on the second maximum is similar to that on the first maximum. Finally, the faraday current density decays to a negative value, which means that the applied potential is smaller than open circuit potential of the polarized AZ31 Mg alloy. As reported in Ref. [31], the first peak corresponded to the formation of $Mg(OH)_2$ and the transformation of $Mg(OH)_2$ to MgF_2. However, the second peak was caused by the transformation process among $Mg(OH)_2$, MgF_2 and $KMgF_3$.

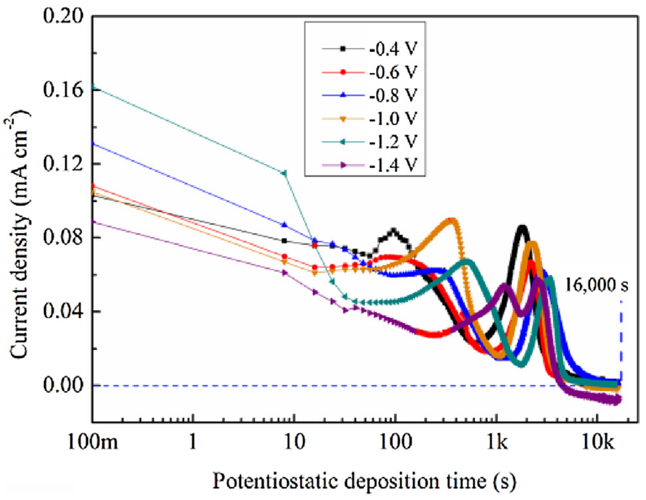

Fig 1. Potentiostatic current decay curves of AZ31 Mg alloy polarized at different potentials in deaerated 0.1 M KF solution of pH 7.5 for 16 ks.

3.2. Analysis of the FCF

3.2.1. Surface morphology and composition of FCF

Fig. 2(a–e) demonstrates the surface morphologies micrographs of AZ31 Mg alloy polarized at −0.4 V, −0.6 V, −0.8 V, −1.0 V and −1.2 V in deaerated 0.1 M KF solution with pH 7.5 for different time, respectively. Table 1 shows the chemical compositions derived from the EDS plots of corresponding surfaces polarized at different potentials for different time. Note that the surface morphologies micrographs and EDS plots of AZ31 Mg alloy polarized at −1.4 V in the same solution for different time were mentioned in Ref. [31]. In the initial stage of potentiostatic polarization, after 56 s at −0.4 V, 16 s at −0.6 V, 96 s at −0.8 V, 16 s at −1.0 V, 56 s at −1.2 V and 250 s at −1.4 V, scratches can be seen on all of the polarized surfaces, and O and Mg are detected on each surface, which means that O^{2-} and (or) OH^- first participate in the formation of the conversion film. With prolonging the polarization time to 96 s at −0.4 V, 80 s at −0.6 V, 300 s at −0.8 V, 368 s at −1.0 V, 496 s at −1.2 V and 1200s at −1.4 V, scratches on the polarized surface become shallow, and the surface composition varies with applied potentials. At −0.4 V and −0.6 V, F, O and Mg are detected, whereas O and Mg are detected in the other polarized surfaces. The detection of F indicates that it takes part in the formation of the conversion film. Meanwhile, it also illustrates that increasing anodic potential enhances the formation of fluoride conversion film. As the polarization time

Please cite this article in press as: L. Wu, et al., J. Mater. Sci. Technol. (2018), https://doi.org/10.1016/j.jmst.2018.04.009