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The assembly of ZSM-5 layer on Mg–Li alloy by hot-pressing using silane coupling agent as bond and its corrosion resistance

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ABSTRACT

The synthesis of ZSM-5 (Zeolite Socony Mobile-Five) layer on Mg–Li alloy has so far proved difficult. Here we report an effective strategy to assemble ZSM-5 layer on Mg–Li alloy by hot-pressing, using silane coupling as a bonding agent. The high crystalline ZSM-5 showed that the hexagon crystals appeared to be attached firmly to the support. The corrosion behaviour, assessed by electrochemical measurements, showed that ZSM-5 layer reduced the corrosion activity of Mg–Li alloy. The hot-pressing served as an environmentally friendly, corrosion-resistant coating for Mg–Li alloy. The method can potentially provide a general route to synthesize various, uniform layers on other active metals.

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1. Introduction

Zeolites are a class of microporous crystalline aluminosilicates. Zeolites are nontoxic and have been actively investigated as carriers, controlled release agents, and adjuvants for certain drugs [1–3]. Thus a zeolite coating, if proved to be corrosion resistant, has the potential to become an environmentally coating for substrates. ZSM-5 zeolite is a kind of high-silica or pure silica zeolite, which is known for its thermal stability, chemical stability and solvent resistance with diverse fine-tunable zeolite characteristics. An increasing number of researchers are examining ZSM-5 zeolite with three-dimensional sinusoidal and straight channels of molecular dimension for its excellent characteristics [1,3]. ZSM-5 zeolite has been coated on different supports using several strategies including direct hydrothermal synthesis, a secondary growth method after seeding of the support, and a support self-transformation technique [4–7]. Most of these supports for growing ZSM-5 layer are stable at high temperature or in an acidic/alkaline environment. These studies were motivated by the potential application of these materials as separation membrane and membrane reactors. In recent years, people began to focus on the development of zeolite films as low dielectric constant (low-k) insulators for environmentally benign corrosion-resistant coatings for aerospace alloys [8]. So if ZSM-5 layer covers the Mg–Li alloys, the corrosion resistance of Mg–Li alloys will improve.

Mg–Li alloys are super-light alloys, which have been attracting much interest from researchers for their characteristics of low density, high stiffness-to-weight ratio, superior strength-to-weight ratio, good deformation ability and good damping ability [9–11]. Recently, more attention has been given to Mg–Li alloys, which have already been used in the fields of aerospace and military [12–14]. However, Mg–Li alloys have poor corrosion resistance, which has limited their practical application. Research to investigate the suitability of surface treatments is necessary to expand the application of Mg–Li alloys.

Research findings about surface treatments to protect Mg–Li alloys have been reported, including conversion coatings, anodizing, ion implantation, microarc oxidation and organic coatings, which have been widely used for magnesium alloys [15–19]. However, due to the high chemical activity of lithium, Mg–Li alloys differ from the traditional magnesium alloys. The drawbacks of surface treatments include, for example, the failure of organic coatings to protect Mg–Li alloy in water for a long time. Other films for Mg–Li alloy commonly show that the reaction time is short and the alloy has corroded prior to the forming of a coating. In order to reduce the corrosion and the loss of Mg–Li alloys, new methods and materials should be researched for application and protection of the surface of Mg–Li alloys.

ZSM-5 layer can protect Mg–Li alloy from corrosion effectively. However, Mg–Li alloy is very active and it will be destroyed easily

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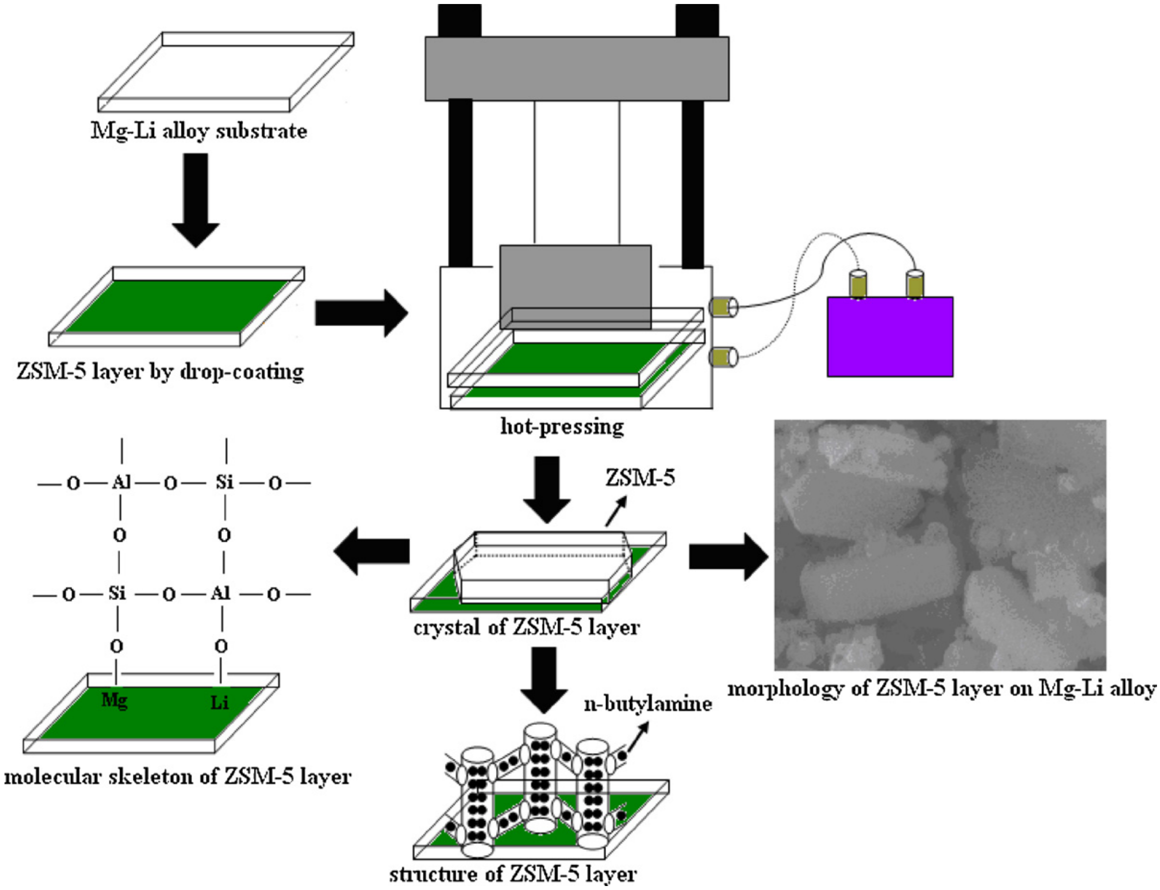

Fig. 1. The schematic diagram of ZSM-5 layer on Mg–Li alloy by hot-pressing method.

if in a high temperature solution for a long time. It is, therefore, difficult to assemble ZSM-5 layer onto Mg–Li alloy by direct hydrothermal synthesis or secondary growth method. In order to obtain a high quality surface ZSM-5 layer on Mg–Li alloy, we use a novel hot-pressing method. The method cannot destroy the structure of Mg–Li alloy and ZSM-5 zeolite easily adheres to the substrate. Although ZSM-5 zeolite has a uniform microporous character, n-butylamine (NBA) was used as a template agent in the process of synthesis to block ZSM-5 channels effectively, and so prevent the corrosive ions reaching the substrate from the zeolite pores. ZSM-5 layer with its pores blocked enhances the corrosion resistance of substrates.

In this paper, the method of hot-pressing was used to assemble ZSM-5 zeolite layer on Mg–Li alloy. In the present work, we report the preparation of ZSM-5 zeolite using n-butylamine as template and the assembly of ZSM-5 layer onto Mg–Li alloy by the method of hot-pressing using silane coupling as a bonding agent. An appropriate pretreatment was used for Mg–Li alloy support. ZSM-5 zeolite was dispersed in silane coupling agent solution forming a suspension. The suspension was dropped onto the surface of Mg–Li alloy. The layer was obtained by hot-pressing, as shown in Fig. 1. With the method of hot-pressing, the ZSM-5 layer of hexagonal structure was formed and covered the surface of Mg–Li alloy. ZSM-5 zeolite can be combined with magnesium and lithium using the function of Mg–O–Si and Li–O–Al. The channel of ZSM-5 zeolite was blocked by n-butylamine, which can improve the corrosion resistant of Mg–Li alloy.

The key question we attempt to answer in this study is whether we can use the simple treatment method and the ZSM-5 formulation coating we have developed for Mg–Li alloy and other active alloys. The ability to use one common method means tremendous cost savings. Another goal of this study is to apply a commonly used adhesion test method to demonstrate that the coatings not only have corrosion resistance but also remarkable adhesion.

2. Experimental

2.1. Coating solution formulation

ZSM-5 powder was prepared by in situ hydrothermal crystallization method. First, a clear solution with molar composition Al_2O_3:80SiO_2:9.6NBA:7Na_2O:2480H_2O was prepared by dissolving sodium aluminate aqueous solution in silica sol followed by drop-wise addition of sodium hydroxide aqueous solution and n-butylamine under stirring. Prior to being transferred to a Teflon-lined stainless steel autoclave, the above synthesis solution was aged for 12 h at room temperature. Crystallization was carried out in a convection oven at 180 °C for 24 h. The autoclave was then removed and cooled down. After hydrothermal treatment, a solid cake was obtained from the slurry by filtration. Then it was washed using distilled water with intense stirring and repeated the process for five times. The ZSM-5 zeolite was obtained by drying the solid cake at 60 °C in vacuum oven for 12 h.

2.2. Substrate pretreatment

The substrate material used for this study was Mg–9.95Li–1.62Al–0.66RE alloy synthesized by melting method. The alloy was sized to 15 mm × 15 mm × 5 mm. The samples were abraded with SiC paper to obtain an even surface, ultrasonically cleaned using acetone and washed with an alkaline detergent. The samples were then rinsed with distilled water and wiped clean with filter paper. Substrates were dried with hot air and stored at ambient conditions before use in ZSM-5 layer synthesis.

2.3. Preparation of ZSM-5 layer

The ZSM-5 zeolite powder was dispersed in bis-[triethoxysilylpropyl] tetrasulfide silane coupling agent. The mixture was then ultrasonically dispersed and formed a suspension. The suspension was dropped onto the pretreated Mg–Li alloy uniformly. The samples were dried for 12 h at room temperature and

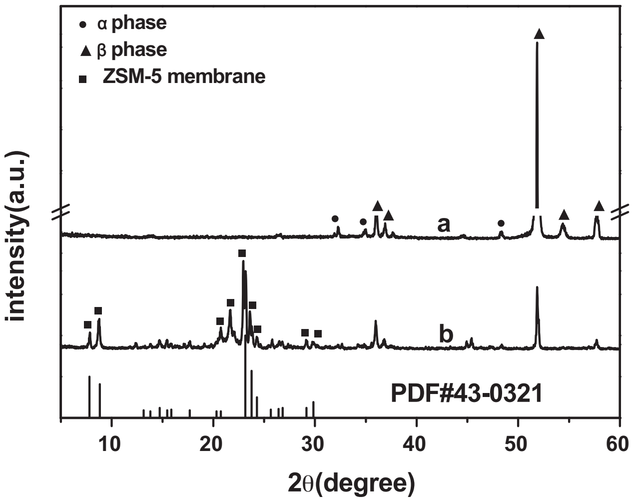

Fig. 2. XRD patterns of ZSM-5 layer on Mg–Li alloy and the standard card of ZSM-5 zeolite (PDF#43-0321): (a) Mg–Li substrate and (b) ZSM-5 layer.

subsequently pressed onto the surface of Mg–Li alloy by hydraulic machine to enhance the adhesion and to form the layer. The process of assembling ZSM-5 layer onto Mg–Li alloy is shown in Fig. 1.

2.4. Evaluation of the layer

The surface observation and qualitative elemental chemical analysis of the layers were characterized by SEM (JSM-6480A, Japan Electronics) and the attached energy dispersive X-ray spectroscopy EDS (INC250, Japan Electronic), respectively. The structures of the samples were analyzed using X-ray diffraction (XRD, Japan Rigaku, D/max-TTR-III) with a Cu target and a monochromator at 40 kV and 150 mA. Three-dimensional surface morphology of the ZSM-5 layer was probed using confocal laser scanning microscopy (VK-9700, Japan Keyence). The corrosion resistance of the layer was measured by electrochemical tests and immersion tests. EIS and potentiodynamic polarization curves were conducted using a commercial Model EC-lab electrochemical analyzer in a three-electrode system with the sample as working electrode, saturated calomel electrode as reference electrode and platinum sheet as counter electrode. The corrosive medium of 3.5 wt% NaCl solution was used. The EIS measurements were carried out at open circuit potential, and the frequency range was between 0.01 and 100,000 Hz. The spectroscopy was analyzed with Zsimpwin software. The potentiodynamic polarization curves were tested with a scan rate of 0.01 V/s and the potential ranged from −1.8 V to −1.0 V. The corrosion condition of bare alloy and ZSM-5 layer on Mg–Li alloy after immersion in corrosive solution was used to evaluate the corrosion resistance.

3. Results and discussion

3.1. Crystal structure of Mg–Li alloy and ZSM-5 layer

The XRD patterns of Mg–Li alloy and ZSM-5 layer are displayed in Fig. 2. Mg–Li alloy has a mixed α phase and β phase (Fig. 2a). It is well known that Mg–Li alloy is a typical eutectic alloy and there is a mixture of α phase and β phase when Li content is within 5–11 wt% [20]. In addition, for the sample treated with ZSM-5 layer, MFI structure (Fig. 2b) can be easily observed besides α and β phases of Mg–Li alloy. With the coating of layer, the peak intensity of Mg–Li alloy phase decreases. The XRD pattern (Fig. 2b) for ZSM-5 is in agreement with the pattern of standard card PDF# 43-0321 and confirmed the presence of ZSM-5 on Mg–Li alloy. No additional diffraction lines were seen, and the baseline of the XRD patterns was flat, indicating that the ZSM-5 layer was essentially free of amorphous materials.

3.2. Surface morphology of ZSM-5 layer

The morphology of ZSM-5 layer coated on Mg–Li alloy was examined by scanning electron microscopy (SEM), and the obtained images were shown in Fig. 3. The SEM images indicate that ZSM-5 layer has a complete and even coverage over the entire substrate surface. The polycrystalline and compact zeolite layer showing a structure of regular hexagon is fully intergrown on the surface of Mg–Li alloy. The zeolite micropores are plugged by the n-butylamine molecules, so pinholes become the most crucial parameter in determining corrosion resistance of a polycrystalline zeolite barrier coating. It is expected that higher intergrowth would lead to higher corrosion resistance [21].

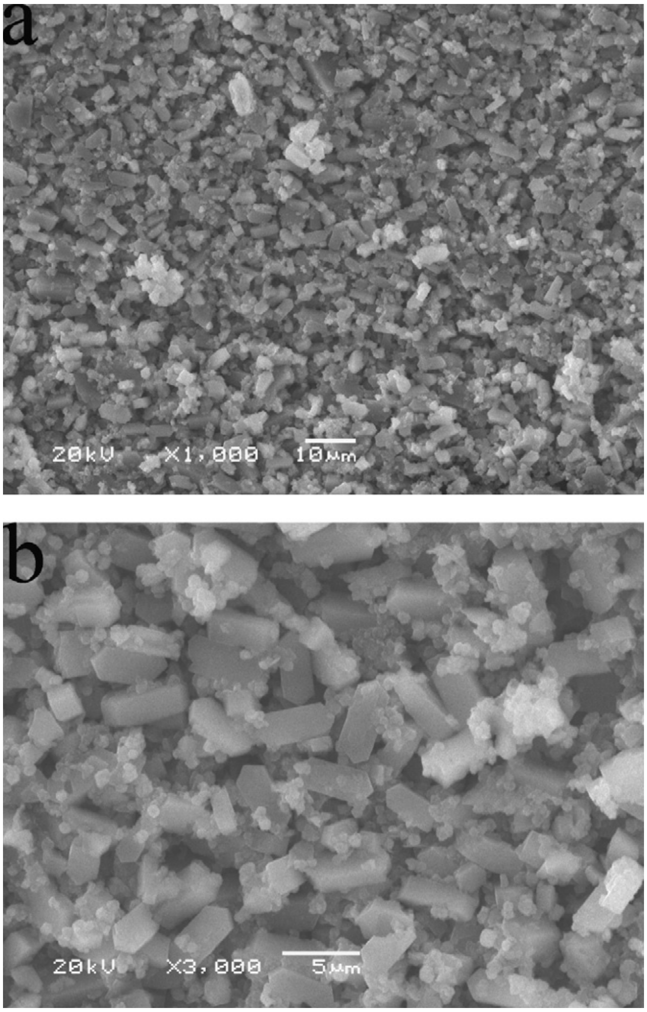

Fig. 3. SEM micrographs of the ZSM-5 layer on Mg–Li alloy.

In order to analyze the three-dimensional morphology of the ZSM-5 layer, confocal laser scanning microscopy image was obtained of the sample. Fig. 4 corresponds to the topography and three-dimensional image of the sample using VK-9700. The surface morphology and roughness of the layer can be observed in this figure. The image shows that the surface of the layer is composed of regular balls distributed with homogeneous grain size and the surface of the sample is flat and smooth.

3.3. The composition and adhesion analysis of ZSM-5 layer on Mg–Li alloy

The EDS microprobe analysis (Fig. 5) shows that the ZSM-5 layer is mainly composed of silicon and oxygen. The mean amount of silicon and oxygen on the surface of Mg–Li alloy is also more than magnesium (Fig. 5), which indicated that the surface of substrate was covered by ZSM-5 zeolite completely. Moreover, carbon and nitrogen were detected on the surface of Mg–Li alloy from the EDS investigation, which confirmed the presence of n-butylamine in

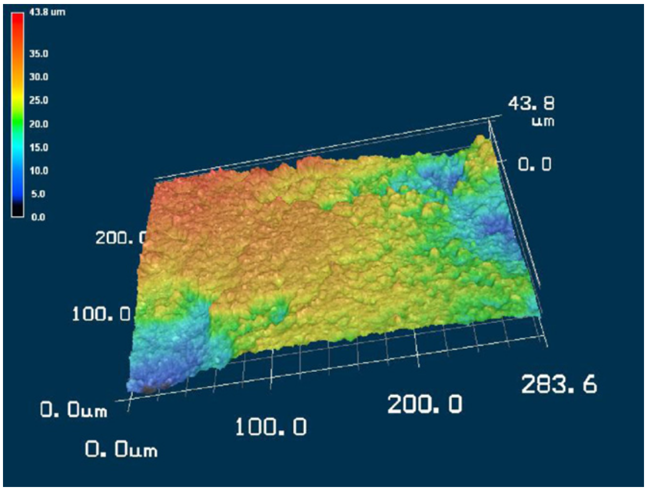

Fig. 4. Three-dimensional morphology of Mg–Li alloy after assembly of ZSM-5 layer.

the framework of ZSM-5 zeolite. From the EDS analysis, it can be concluded that the synthesized coating on the surface of Mg–Li alloy was ZSM-5 layer with n-butylamine as template.

To quantify the adhesion of the ZSM-5 layer to Mg–Li alloy, cross cut tape test [22] was used. The cross cut tape test is applied to characterize the adhesion of coatings. Herein, the surface of a sample is cut cross-wise after coating. Afterwards, an adhesive tape is stuck onto the cut surface and then peeled off. If parts of the coating remain on the tape, the coating's adhesion is insufficient. ZSM-5 layer on Mg–Li alloy gave a satisfactory result for strength of adhesion. The tested samples were analyzed with SEM to provide a more critical look at the adhesion of ZSM-5 layer on Mg–Li alloy (Fig. 6). Note that the gap between the blades was very small, and there was no significant peeling off of layer after the cross cutting through the ZSM-5 layer for Mg–Li alloy.

ZSM-5 is composed of oxygen–silicon tetrahedron and oxygen–aluminum tetrahedron. There is also a Si–O–Si functional group in bis-[triethoxysilylpropyl]tetrasulfide silane coupling agent which was used as solvent to form the ZSM-5 suspension covering Mg–Li alloy. The alkoxy groups of the silane molecules could convert to SiOH [23]. These SiOH groups can be absorbed onto metal surface via formation of hydrogen bonds between SiOH groups and surface metal hydroxyls (MeOH). Such bonds further convert to metallo-siloxane bonds (MeOSi) at the interface by releasing water. The coupling agents can connect the ZSM-5 zeolite and Mg–Li alloy by the chemical bond of Mg–O–Si and Li–O–Si (Fig. 1). So the force between ZSM-5 zeolite and substrate was enhanced. The hot-pressing improved the force further. In this manuscript, the channel of ZSM-5 zeolite was blocked by the template agent that was not removed. The ZSM-5 zeolite having the thermal stability and chemical stability gradually formed the hexagonal shape, which improved the corrosion resistance of Mg–Li alloy to some extent.

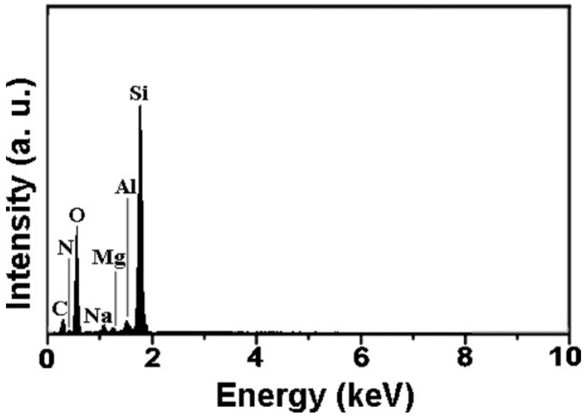

Fig. 5. EDS spectrum of the ZSM-5 layer on Mg–Li alloy.

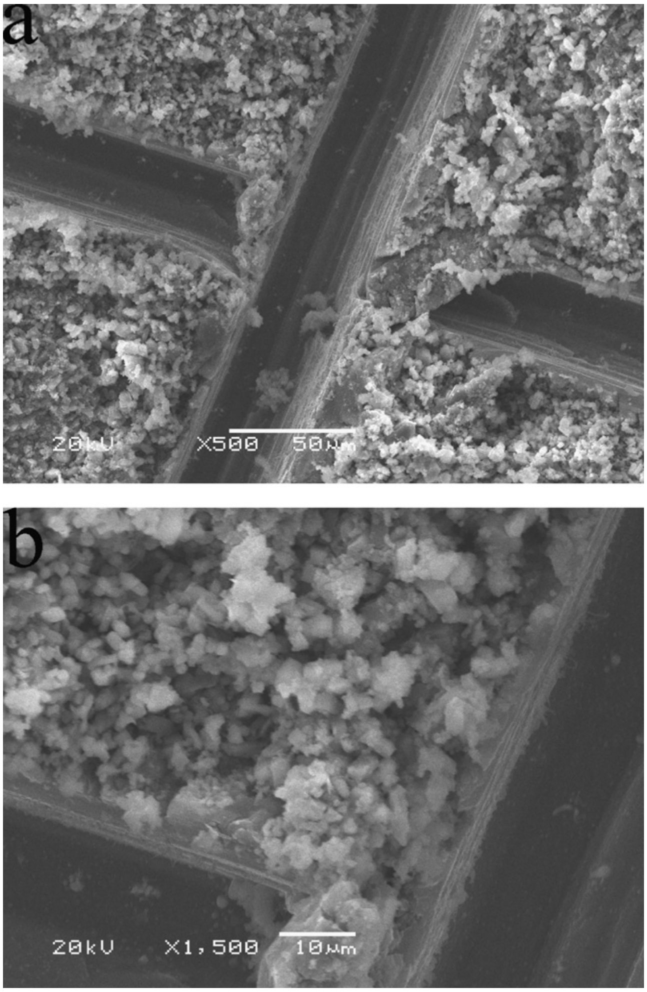

Fig. 6. SEM micrographs of the ZSM-5 layer on Mg–Li alloy tested for adhesion.

3.4. Corrosion resistance

Fig. 7 shows dc polarization results of ZSM-5 layer in corrosive media of neutral 3.5 wt% NaCl aqueous solution. From these curves, it can be obviously seen, the corrosion potential E_{corr} of the Mg–Li alloy substrate and ZSM-5 layer are −1.614 V and −1.490 V, respectively. The corrosion potential E_{corr} of the sample with ZSM-5 layer shifts positively about 124 mV compared with that of the substrate. ZSM-5 layer (Fig. 7b) shows much lower polarization current than bare alloy (Fig. 7a), suggesting its superior corrosion protection. As it was appropriate to evaluate the corrosion rate by corrosion current density [24], it can be seen that ZSM-5 layer presented an obvious reduction in I_{corr} relative to the bare alloy.

The corrosion performance of ZSM-5 layer was also examined by ac impedance method. EIS provided useful information on the corrosion processes in the coated samples when exposed to an aggressive environment. Fig. 8 demonstrates the Nyquist plot of bare Mg–Li alloy and ZSM-5 layer. The Mg–Li substrate exhibited one high frequency capacitance loop and one low frequency capacitance loop. The high frequency capacitance loop described the

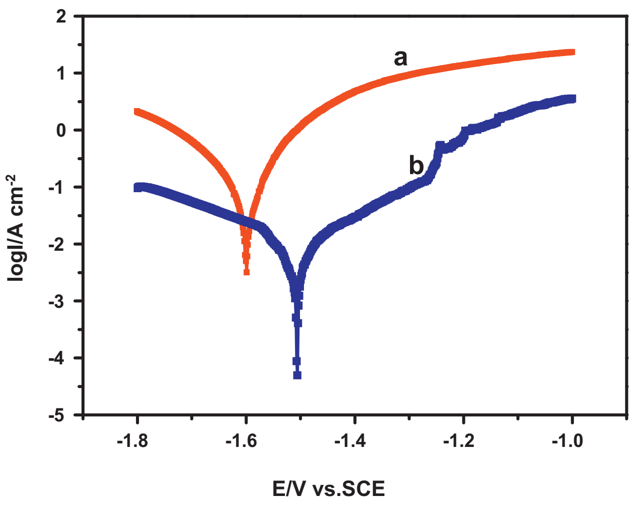

Fig. 7. The potentiodynamic polarization curves of bare alloy (a) and ZSM-5 layer (b).

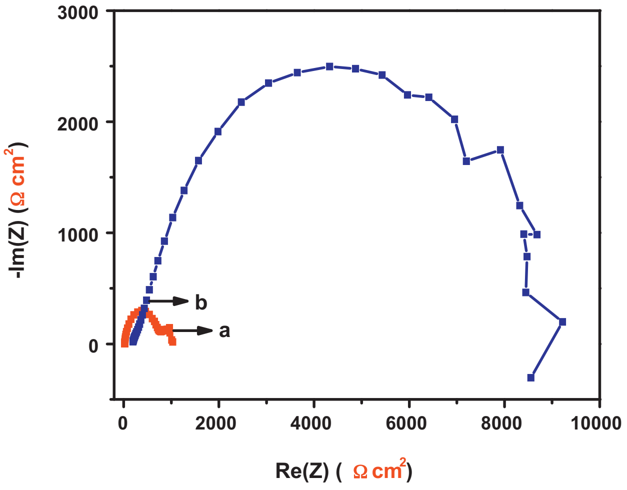

Fig. 8. Nyquist plots for bare alloy (a) and ZSM-5 layer (b).

characteristics of the electrical double-layer. The low frequency capacitance loop was related to the loose oxide film on Mg–Li alloy. The result indicated that the substrate had poor corrosion resistance in NaCl solution. The Nyquist plot of ZSM-5 layer only contained one capacitance loop, which described the characteristics of the layer. The result showed that the ZSM-5 layer could improve the corrosion resistance of Mg–Li alloy. In addition, some discrete test points were detected in the low frequency region of the ZSM-5 layer plot, which was due to a small quantity of lithium existing in the skeleton of ZSM-5 in the testing process of impedance. Lithium was oxidized and released leading to the open circuit potential vibration, thus affecting the stability of the system. The electrochemical results indicated that the ZSM-5 layer exhibited good corrosion resistance.

4. Conclusions

In summary, we have shown a novel method to assembled ZSM-5 layer onto Mg–Li alloy. The process of hot-pressing is intrinsically simple, clean, environmentally friendly and effective to assemble the layer. ZSM-5 zeolite successfully coated to date on Mg–Li alloy and the ZSM-5 layer showed good corrosion resistance. We believe that the layer strategy demonstrated here is simple and could be directly extended to other active metals and other nanocomposite layers.

Acknowledgments

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