Journal of Alloys and Compounds 658 (2016) 555–560

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Deposition behaviour of nickel phosphorus coating on magnesium alloy in a weak corrosive electroless nickel plating bath

Rong Hu*, Yongyao Su, Hongdong Liu**

Research Institute for New Materials Technology and Co-innovation Center for Micro/Nano Optoelectronic Materials and Devices, Chongqing University of Arts and Sciences, Chongqing 402160, PR China

A R T I C L E I N F O

Article history:
Received 14 July 2015
Received in revised form
18 October 2015
Accepted 31 October 2015
Available online 5 November 2015

Keywords:
Magnesium alloy
Electroless nickel plating bath
Ni–P coating
Deposition behaviour
Coating property

A B S T R A C T

To inhibit the corrosion of magnesium alloy in electroless nickel plating bath, nickelous hydroxide and phytic acid were used as main salt and corrosion inhibitor to inhibit the dissolution of substrate during the nickel deposition process. Effects of nickel ion and phytic acid concentration on plating rate and porosity were studied by single-factor experiment, and the optimum concentrations were obtained at 8.8 g/L and 4 ml/L, respectively. Deposition process of nickel phosphorus (Ni–P) coating was observed by using scanning electron microscope (SEM) and activation energy of Ni deposition process was estimated by Arrhenius equation. SEM observation showed that Ni deposition process could be divided into two stages, the first stage was Ni replacement reaction competition with corrosion inhibition reaction of substrate, the second stage was Ni autocatalysis reduction process. Potentiodynamic polarization curve revealed that Ni–P coating exhibited good corrosion resistance in protecting magnesium alloy. Scratch and thermal shock tests showed excellent adhesion between the Ni–P coating and magnesium alloy substrate.

1. Introduction

Magnesium alloys have outstanding advantages in low density, high specific strength, processability, electromagnetic shielding etc. [1–3], and they are widely used for many commercial applications, including aerospace, automobile components, electronic equipments, bioimplant and other industrial products [4–7]. However, poor corrosion resistance is an important challenge to the successful use of magnesium alloys [8,9]. Therefore, surface anti-corrosion technology such as micro-arc oxidation film, chemical conversion coating, physical vapor deposition, thermal spraying, electroplating and electroless plating are developed for magnesium alloys [10–16]. Among these technologies, electroless nickel-phosphorus (Ni–P) alloy coatings have good performance in anti-corrosion, anti-friction and electromagnetic characteristics. Hence, electroless deposition Ni–P coating on magnesium alloy attracts a great deal of attention and scientific research [17–19].

Generally, nickelous sulfate, nickelous chloride, nickelous acetate and basic nickelous carbonate are usually used as metal ion sources in the electroless plating bath [17,20–22]. Nevertheless, these anions of nickel salt can deteriorate the corrosion of magnesium substrate during the plating process, especially in an acidic bath. An approach to overcome this problem is use of high concentration fluoride salt as corrosion inhibitor in the plating bath to inhibit the corrosion of magnesium alloys [21,23]. However, the high concentration fluorinion is harmful to environment and human. Accordingly, it is necessary to develop an environmental, efficient and weak corrosive electroless nickel plating bath for magnesium alloys.

In the present work, we developed a novel electroless nickel plating process for AZ91D magnesium alloy and the characteristic of this process was as follows. Firstly, the pretreatment solutions of magnesium alloy were chromium-free and fluoride-free. Secondly, in order to weaken the corrosiveness of electroless nickel plating bath, nickelous hydroxide was used as main salt to provide metal ion, and phytic acid (RH_{12}, R = $C_6H_6O_6(PO_3)_6$) was added into electroless bath as corrosion inhibitor to decrease the working concentration of fluorinion. According to plating rate and porosity of the Ni–P coating, the optimum concentration parameters of nickel ion and phytic acid were studied. Based on this process, the deposition process of the Ni–P coating was observed by using

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* Corresponding author.
** Corresponding author.
E-mail addresses: hurong_82@163.com (R. Hu), yongyaosu@126.com (Y. Su), lhd0415@126.com (H. Liu).

http://dx.doi.org/10.1016/j.jallcom.2015.10.300

scanning electron microscope (SEM), and the reaction activation energy was estimated by Arrhenius equation. The properties of the Ni–P coating, i.e. corrosion resistance and adhesion were evaluated by potentiodynamic polarization test, scratch and thermal shock test, respectively.

2. Experimental

The substrate was AZ91D die cast magnesium alloy with a size of 2 cm × 1 cm × 0.5 cm. The chemical compositions (mass fraction) of the alloy were 91% of Mg, 8.5% of Al and 0.5% of others. The substrate was polished with no. 500 SiC paper before pretreatment processes, then rinsed with deionized water, immersed in degreasing solution for 5 min at 65 °C, followed by acid pickling in 2% nitric acid solution and 2% acetic acid solution for 20 s, respectively, a final treatment was carried out in 10 g/L NaOH for 60 s at 50 °C. The substrate was cleaned by deionized water between each step. The bath composition and operation parameters for electroless Ni–P deposition are listed in Table 1. The electroless Ni–P bath contains nickelous hydroxide as the nickel ion provider, sodium hypophosphite acts as a metal reducing agent, and lactic acid as complexing agent. Ammonium bifluoride acts as buffering agent and inorganic corrosion inhibitor. Phytic acid is used to inhibit the corrosion of magnesium in the bath. Thiourea also acts as a solution stabilizing agent and brightening agent.

To study the effects of nickelous hydroxide and phytic acid on Ni–P coating, plating rate and porosity were introduced to evaluate the property of coating. The expression of plating rate was $v = (\Delta m/s\rho t) \times 10^4$, v, Δm, s, ρ and t represented plating rate, mass change, superficial area of magnesium alloy, density of the Ni–P coating (~7.9 g/cm^3) and deposition time, respectively. The method of porosity test was descripted in Ref. [20]. That is, a white filter paper (area: 2 cm^2) was soaked in a reagent solution of 10 g/L NaCl, 106 g/L ethanol and 0.1 g/L phenolphthalein. Then, the filter paper with the reagent solution was pasted onto the surface of Ni–P coating for 10 min. After removing the filter paper away, some red spots or areas were noted on the surface of the coating. The porosity of the Ni–P coating was estimated relatively by the ratio of red spot area to the zone area previously pasted by the filter paper.

The mass of magnesium alloy was weighed by electronic balance (AR2140, Ohaus). A scanning electron microscope (SEM, Hitachi S-4800) was employed to observe the surface and cross-section morphologies of the Ni–P coating. The adhesion between the coating and the substrate was tested by scratch and thermal shock experiments. The immersion test in the 10% HCl solution at 25 °C was carried out to evaluate the corrosion resistance of the Ni–P coating on AZ91D magnesium alloy. The time interval between the start of the acid immersion test and the first hydrogen bubble arising from the coating surface was recorded to evaluate the corrosion resistance of the coating [20,24]. To further evaluate the corrosion resistance and possible passive behavior of the Ni–P coating, potentiodynamic polarization test was performed on an electrochemical analyzer (CHI760C, Chenhua, China). Electrochemical experiment was carried out in a 3.5 wt.% NaCl aqueous solution using a classic tri-electrode configuration consisting of a working electrode (sample, 1 cm^2), a counter electrode (platinum) and a reference one (saturated calomel electrode). During the potentiodynamic sweep experiment, the sample was first immersed into electrolyte for 30 min to stabilize the open-circuit potential (E_0). Tafel plot was transformed from the recorded data and the corrosion current density (i_{corr}) was determined by extrapolating the straight-line section of the anodic and cathodic Tafel lines. The experiment sweeping rate was 5 mV/s and done at 25 °C.

Table 1
The composition and conditions of electroless nickel plating bath for magnesium alloy.

Composition and conditions	Concentration
Ni^{2+}	4.8–12.8 g/L
$C_3H_6O_3$	30 g/L
$Na_2H_2PO_2 \cdot H_2O$	30 g/L
NH_4HF_2	8 g/L
Phytic acid	1–6 ml/L
Thiourea	2 mg/L
pH	6.0
Temperature (°C)	90

3. Results and discussion

3.1. Pickling processes of magnesium alloy

Chromic acid and hydrofluoric acid (or fluoride salt) are usually used as pickling and activation solutions before electroless Ni–P plating on magnesium alloys [21,22]. According to Ref. [25], porous fluoride and magnesium oxide form on magnesium alloy substrate after activation treatment. Fluoride film is stable and insoluble in electroless plating bath, but magnesium oxide is unstable and soluble. Therefore, fluoride film protects the substrate efficiently, on the other hand, because of the dissolution of magnesium oxide, magnesium substrate is exposed to electroless plating bath, thus the replacement reaction between magnesium and nickel is possible. Nevertheless, two unfavorable factors should be mentioned, that is, chromic acid and hydrofluoric acid are harmful to environment, and fluoride film may influence the adhesion of the Ni–P coating. Hence, in this study, we used dilute nitric acid and acetic acid as pickling solutions to replace chromic acid and hydrofluoric acid. Fig. 1a shows the morphology image of magnesium alloy after pickling treatment in nitric acid solution, some micropores and microcracks can be observed, and the surface of substrate is uniform. Fig. 1b shows the SEM morphology of magnesium alloy after pickling treatment in acetic acid solution, the surface morphology of substrate is rougher than that of substrate in Fig.1a, this may be a advantage to enhance the adhesion of the Ni–P coating.

3.2. Effects of Ni^{2+} and phytic acid concentrations on plating rate and porosity

Plating rate and porosity are important parameters for Ni–P coating, thus it is necessary to study the effects of Ni^{2+} and phytic acid concentrations on plating rate and porosity. In Fig. 2a, the plating rate accelerates with the increase of Ni^{2+} concentration, in other words, the higher Ni^{2+} concentration, the faster reaction. When Ni^{2+} concentration is higher than 8.8 g/L, the plating rate decelerates instead, this may be caused by imbalance of concentration ratio between Ni^{2+} and reducing agent. In addition, at the concentration of 8.8 g/L, the porosity of the Ni–P coating is minimum. Therefore, this Ni^{2+} concentration is chosen for deposition Ni–P coating on magnesium alloy. Phytic acid conversion coating is an important corrosion protection method for magnesium alloys [26,27]. Thus, we tried to use phytic acid as corrosion inhibitor for magnesium alloy in electroless plating bath, and the effect of phytic acid concentration on plating rate and porosity is showed in Fig. 2b. When the concentration of phytic acid is lower than 1 ml/L, magnesium alloy substrate is corroded in electroless plating bath and no Ni–P coating deposits on its surface. Fortunately, when the concentration is higher than 1 ml/L, the corrosion of magnesium alloy is inhibited obviously and the plating rate of the Ni–P coating