Applied Surface Science 258 (2012) 2648–2654

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

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

Molybdate and molybdate/permanganate conversion coatings on Mg–8.5Li alloy

Wang Guixiang*, Zhang Milin, Wu Ruizhi

Key Laboratory of Superlight Material and Surface Technology, College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, China

ARTICLE INFO

Article history:
Received 23 May 2011
Received in revised form 14 October 2011
Accepted 20 October 2011
Available online 31 October 2011

Keywords:
Mg–Li alloy
Molybdate
Permanganate
Conversion coating
Corrosion resistance

ABSTRACT

A novel environment-friendly conversion coating for Mg–8.5Li alloy was obtained by immersing in a solution of molybdate. The concentration of ammonium molybdate and the addition of potassium permanganate were discussed in this experiment. The surface morphology of the conversion coatings was observed by scanning electron microscopy (SEM), and the chemical composition was investigated by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). The corrosion resistance of Mg–8.5Li alloy and conversion coatings were investigated by means of potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and weight loss measurement. The results showed that the coatings with cracked morphology were homogeneous and uniform. The conversion coatings were mainly composed of metal-oxide as detected by XPS. The results of electrochemical measurement and weight loss measurement revealed that the molybdate conversion coating had better corrosion resistance than bare alloy and chromate conversion coating, and the molybdate/permanganate conversion coating had lower corrosion current density and higher coating resistance than the molybdate conversion coating.

1. Introduction

Magnesium–lithium alloys are the lightest metallic engineering materials with a density of 1.35–1.65 g/cm^3 [1]. Therefore, the alloys have received much attention in recent years for its wide application in the field of aerospace components, automobile and computer parts, mobile phones, lightweight weapon, etc. [2–4]. However, magnesium–lithium alloys have a number of undesirable properties including poor corrosion resistance and high chemical reactivity that have hindered its widespread use in many applications [5,6]. Thus, it is necessary to perform suitable surface treatments to improve the corrosion resistance of magnesium–lithium alloys.

There are a number of technologies available for coating magnesium–lithium alloys, such as electrochemical plating, electroless plating [7], chemical conversion coatings [8], anodizing, micro arc oxidation coatings [9], organic coatings, hybrid coatings and vapor-phase deposition [10]. Among these various surface treatment techniques, chemical conversion coatings has been attracting more and more concerns because the conversion coatings are easy to apply, low cost and good paint-base properties to the magnesium–lithium metal. Conversion coatings protect the substrate from corrosion by acting as an insulating barrier of low solubility between the metal surface and the environment. It is well known that the traditional chromate coatings can provide good protection for alloys, but hexavalent chromium has shown to be highly toxic carcinogens. The development of an environmentally friendly process is a necessity due to the more stringent environmental protection laws. There are a number of different types of conversion coatings including chromate [11], phosphate [12], rare earth [13], stannate [14], phytic acid [15] conversion coatings, and so on [16,17]. However, there has been little published paper on molybdate and molybdate/permanganate conversion coating treatments for Mg–Li alloys.

The aim of the present work is to develop molybdate and molybdate/permanganate conversion coatings on Mg–8.5Li alloy by the simple immersion method. The conversion solution used is environmentally friendly. The morphology, composition and corrosion resistance of the conversion coatings were investigated.

2. Experimental

2.1. Preparation of conversion coatings

Mg–8.5Li alloy is used for this study. Its chemical compositions are as follows (in wt.%): Al 3.2, Li 8.5, Y 1.2, Ce 1.2, Mg balance. All samples are from the same casting in order to minimize the difference resulted from the variation in compositions and microstructure among samples. The samples were cut into cylinder shaped of Φ17 mm × 5 mm exposed. Prior to formation of conversion coating, specimens were polished with 500#, 800#, 1000#, and 2000# grit SiC paper to obtain an even surface, and pretreated with alkaline degreasing and acid pickle, then were treated in molybdate solution, respectively rinsed twice in flow distilled water as

* Corresponding author. Tel.: +86 13804586152; fax: +86 451 82533026.
E-mail address: wgx0357@126.com (G. Wang).

0169-4332/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2011.10.112

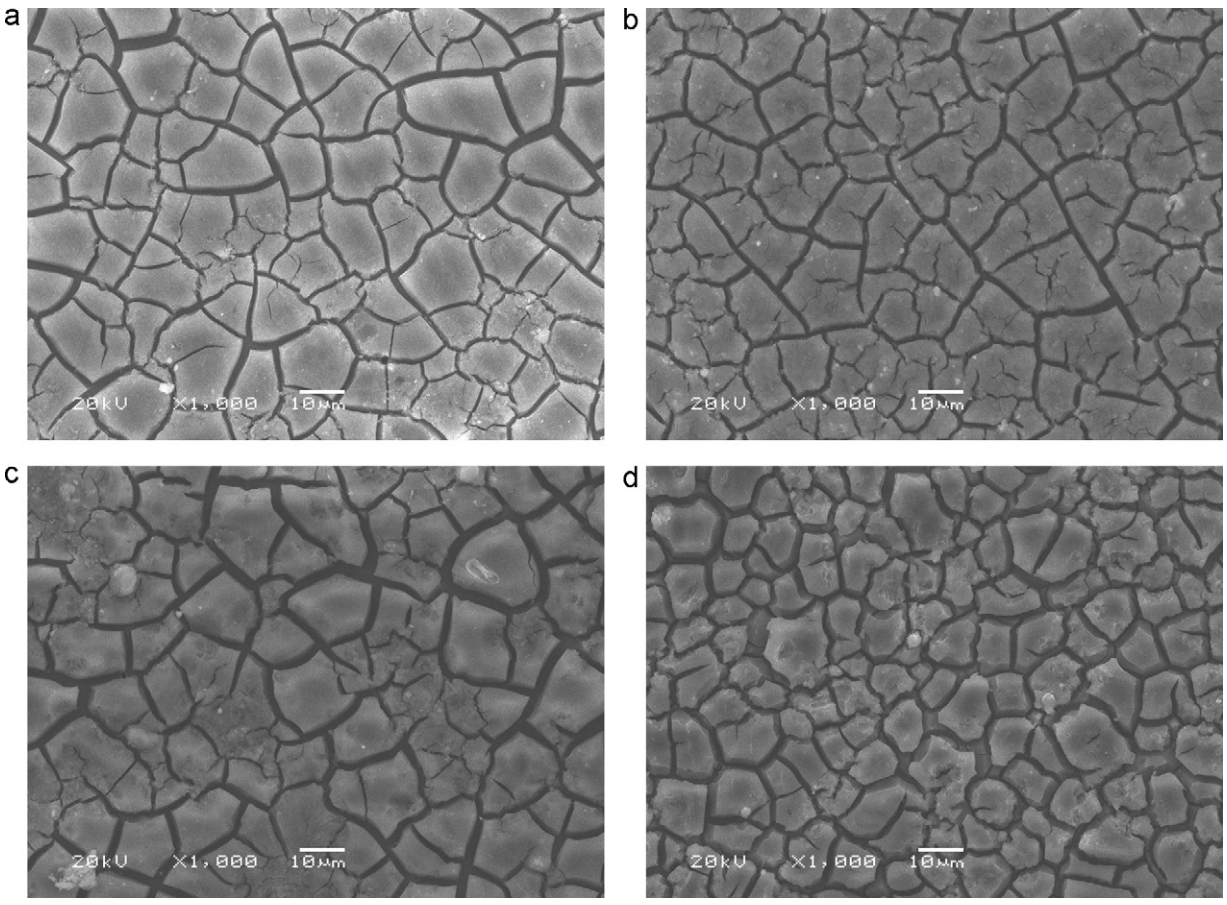

Fig. 1. Surface morphology of molybdate (a, 10 g/L; b, 14 g/L; c, 16 g/L) and molybdate/permanganate (d, 14 g/L molybdate + 3.5 g/L permanganate) conversion coating.

quickly as possible between each step to remove all the contaminations. Alkaline cleaning was conducted in the following solution which composed of 50 g/L sodium carbonate, 25 g/L sodium silicate and 50 g/L trisodium phosphate ($Na_3PO_4{\cdot}12H_2O$) at $45 \pm 5\,^{\circ}C$ for 5 min. Acid pickling was conducted in the following solution which composed of 195 mL/L CH_3COOH and 40 g/L $NaNO_3$ at room temperature for 30–45 s. The molybdate bath for deposition of conversion coating contained $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ 10–20 g/L, and pH value was adjusted to 3.0 by H_3PO_4. The bath for deposition of molybdate/permanganate conversion coating was prepared by adding 0–4.5 g/L $KMnO_4$ to molybdate solution which contained 14 g/L $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, and pH value was adjusted by H_3PO_4 to 3.0. The temperature was 50 °C and deposition time was 10 min, and then dried in hot air.

2.2. Evaluation of the coating

The morphologies of the conversion coating were observed using scanning electron microscope (JSM-6480). The chemical composition of the coating was investigated using Physical Electronics, PHI 5700 EICA XPS with Al Ka (1486.6 eV) monochromatic source. Data were taken after 120 s of ion etching. All energy values were corrected according to the adventitious C 1s signal, which was set at 284.62 eV. The data were analyzed with XPSPEAK 4.1 software. The corrosion resistance of the coating was measured by electrochemical tests and weight loss measurement. Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization were conducted using a commercial Model CHI760B electrochemical workstation in a three-electrode system [18] with sample (1 cm × 1 cm surface area) as working electrode, saturated calomel electrode as reference electrode and platinum sheet with 1 cm × 1 cm surface area as counter electrode. The corrosive medium was 3.5 wt.% NaCl solution. The potentiodynamic polarization curves were tested with a scan rate of 0.01 V/s. The corrosion potential and corrosion current density were calculated by Tafel extrapolation method using the CHI version 6.28 software (by CH Instruments). The EIS measurements were carried out at open circuit potential, and the frequency range was between 0.01 and 100,000 Hz. The measurements were performed after the samples were immersed in 3.5 wt.% NaCl solution for 1 h. The spectroscopy was analyzed with ZSimpWin software. All of the measurements were carried out at room temperature.

The weight loss experiments were carried out using Mg–8.5Li alloy with molybdate and molybdate/permanganate conversion coatings. The samples were firstly dried and weighted (m_1), and suspended in 100 mL solution of 3.5 wt.% NaCl for 4 h at 25 °C. Secondly, each sample was washed with distilled water, acetone in an ultrasonic bath, then dried and weighted again (m_2). Weight loss measurements were made in triplicate and the loss of weight was calculated by taking an average of these values.

The crystal structure of the alloy and conversion coatings were determined by X-ray diffraction (XRD) with a glancing incident angle of 2°, the detected angle was from 10° to 80° at a speed of

Table 1
The XPS results of surface element compositions of molybdate and molybdate/permanganate conversion coating.

Atomic %	Mg	O	Mo	P	Mn
Molybdate	8.61	79.31	3.67	8.41	–
Molybdate/permanganate	5.74	70.96	8.68	5.99	8.63