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Electrodeposition of aluminum on magnesium from ionic liquid (EMIM)Br-$AlCl_3$

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Abstract: An ionic liquid was prepared by mixing $AlCl_3$ and 1-methyl-3-ethylimidazolum bromide (EMIM)Br under dry argon atmosphere. Electrodeposition of aluminum on magnesium was conducted at 298.15 K for 1 h by the ionic liquid and the electrochemical behavior was discussed. The results show that the aluminium deposition occurs at a potential about −0.1 V. Cathode surface was analyzed by SEM, XRD and EDS. Aluminum is successfully electrodeposited on magnesium from (EMIM)Br-$AlC1_3$ ionic liquid, and the crystal grain quality of the deposit at 15 mA/cm^2 is ideal with the perfect boundary of crystal grain.
Key words: aluminum; ionic liquid; (EMIM)Br-$AlC1_3$; electrodeposition

1 Introduction

Magnesium is a very important metal because of its excellent mechanical properties and lowest density among all of the metals. So far, the use of magnesium has been already extended into civil industry department. Although magnesium is very stable at room temperature under dry atmosphere, it gets eroded when exposed to wet environment. Furthermore, aluminum film shows advantageous anti-corrosion performance. Hence, the electrodeposition of aluminum on magnesium can protect this metal against corrosion.

Ionic liquid, also known as room temperature ionic liquid (RTIL), is an organic salt that consists entirely of anion and cation. Due to the large nonsymmetrical organic cations the melting point is less than 100 ℃[1−3]. The room temperature ionic liquids such as BPC/$AlCl_3$ and EMIC/$AlCl_3$ that are considered the most promising electrolytes are studied widely. They have many excellent properties: wide electrochemical window, good conductivity, negligible vapor pressure (at high temperature the vapor pressure is small), good solubility for inorganic and organic materials, high thermal stability and non-flammability, and adjustable acidity[4−9]. In recent years, there are many new reports[10−16] about electrodeposition of aluminum and its alloy from ionic liquids. The morphology, crystalline size and compactness of the aluminum coating are usually dependent on the electroplating parameters, such as current density. In this work, ionic liquid (EMIM)Br-$AlCl_3$ was prepared by $AlCl_3$ and 1-methyl-3-ethylimidazolum bromide (EMIM)Br, and the aluminum electrorefining with three-electrode system was studied. The effects of current density on morphology and crystalline size of aluminum coating were also investigated.

2 Experimental

The preparation of electrolyte and following electrodeposition experiments were conducted under inert gas condition. (EMIM)Br was synthesized by adding certain amount of bromoethane(＞99%) and N-methylimidazolum(>99%) into a conventional three-neck flask, and the mixture was continuously stirred by a slow magnetic bar for 4 h under dry purified argon atmosphere. To ensure complete reaction, it needs excessive amount of bromoethane. After drying in vacuum at 343 K for 12 h to remove residual moisture, the intermediate was moved into an indigenous glove box (Nanjing University Instrument Plant, Model

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NDZKX, China) under nitrogen atmosphere. An acidic ionic liquid of $AlCl_3$-EMIMBr with molar ratio of 2:1 was prepared by slow addition of $AlCl_3$.

All electrochemical measurements were conducted by IM6e electrochemical workstation. Constant current depositions were performed with a three-electrode electrolytic cell in a glove box filled with nitrogen. Magnesium was used as the cathode, aluminum was employed as the anode, and platinum was used as reference electrode. After electrodepositon the samples were washed with ethanol and dried in air, and then the surface appearance of sample was examined with a scanning electron microscope (SEM, Veeco Multimode NS3a) and the elements of the sample were analyzed by X-ray energy diffraction spectrometer (EDS, Oxford INCA Energy), and the crystal phase structures were examined with D8 advance type X-ray diffractometer (XRD, Brucker.axs Company, German).

3 Results and discussion

3.1 Cyclic voltammetry behavior during electrodeposition process

The electrodeposition process of aluminium on magnesium substrate from (EMIM)Br-$AlCl_3$ ionic liquid with molar ratio of 2:1 was investigated. Fig.1 shows a typical cyclic voltammogram recorded on magnesium electrode at a scan rate of 50 mV/s. It is apparent that the cathodic process in curve a corresponds to the deposition of aluminium, and aluminium deposition occurs at the potential about −0.1 V, whereas the anodic peak in curve b is ascribed to the subsequent stripping of the deposited aluminium. The anodic oxidation current decreases to almost zero at 0.5 V due to passivation of the aluminium. The passivation behaviour of aluminium was previously found to occur in $AlCl_3$-based molten salts containing KCl-NaCl, LiCl, or TMPAC ionic liquids[17]. Although the anodic passivation behaviour of aluminium in chloroaluminate electrolytes has not been satisfactorily elucidated, it could be attributed to $AlCl_3$ precipitation on the electrode surface, or to the adsorbed monovalent to trivalent aluminium intermediates[17].

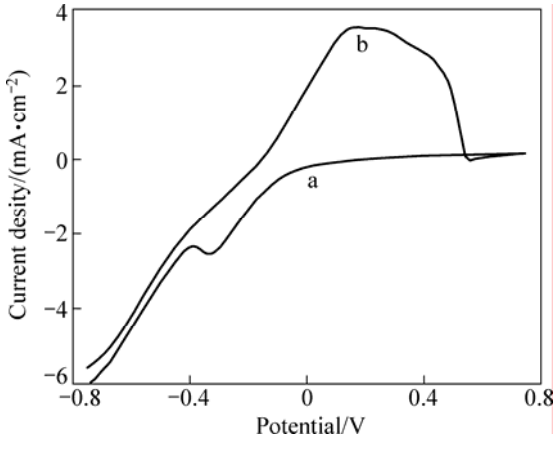

Fig.1 Typical voltammogram recorded at scan rate of 50 mV/s

3.2 Analysis of electrode after electrodeposition

After electrodeposition, electrodes were removed and cleaned carefully. SEM was used to observe the surface appearance of anode, and the new cathode aluminum was analyzed by EDS and XRD.

After electrodeposition, it can be seen that aluminum can be electrodeposited by using ionic liquids at room temperature, and the cathode becomes silver-gray. The morphologies and crystalline sizes of aluminum electrodeposit coating microstructures are different at different current densities. The surface morphologies of the deposits obtained at current densities of 5, 10 and 15 mA/cm^2 were further inspected by SEM, as shown in Fig.2. The deposits at a current density of 5 mA/cm^2 are not continuous, consisting of

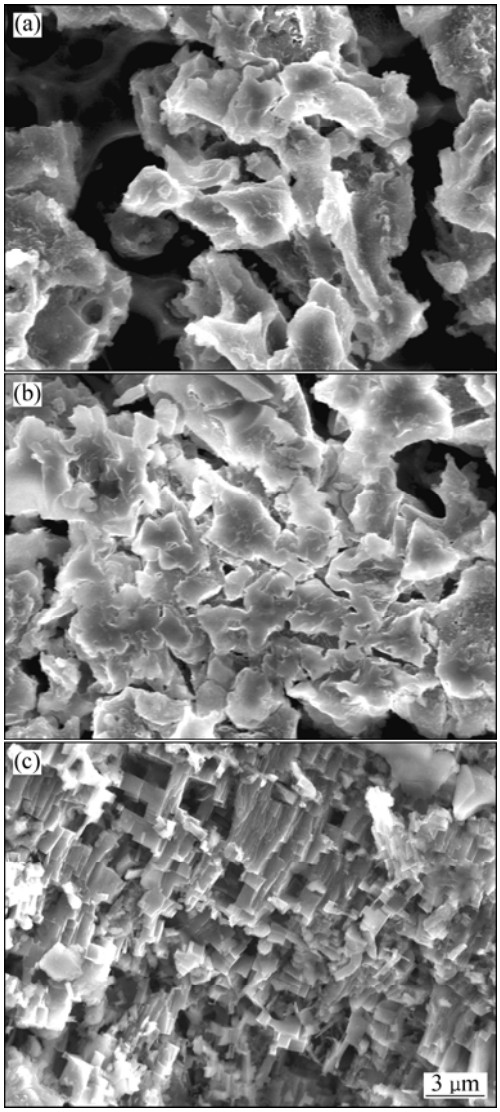

Fig.2 SEM images of cathode surface at different current densities: (a) 5 mA/cm^2; (b) 10 mA/cm^2; (c) 15 mA/cm^2

polygon crystals with many porosities on the surface. The deposits at a current density of 10 mA/cm^2 are relatively dense and glossy, and have polygon crystals with some porosities on the surface. The deposits at a current density of 15 mA/cm^2 are denser and have metallic luster, composing of 1−2 μm cuboidal crystals, but the deposits have less porosities on the surface. The aluminum crystal grain size is uniform, crystal grain growth integrates, and the crystals grain boundary is clear and perfect.

In order to further analyze the new aluminum in the experiment, the cathode surface of fresh aluminium was analyzed by X-ray emission spectrum analysis. The spectrum of the new aluminium on the cathode by X-ray energy dispersive spectrum (EDS) is shown in Fig.3. It can be seen that there are no impurities on the cathode surface. Strong peaks indicate aluminum elements, and weak peaks denote oxygen elements with a low content. Because after electrodeposition the new aluminum is passivated during cleaning electrode, oxide films form on the surface of the grain aluminium, and as a result the weak peaks of oxygen elements occur on the spectrum.

Cyrstal structure for the above deposits at 15 mA/cm^2 was analyzed by XRD. Fig.4 shows the acquired diffraction pattern. As seen from Fig.4, the diffraction

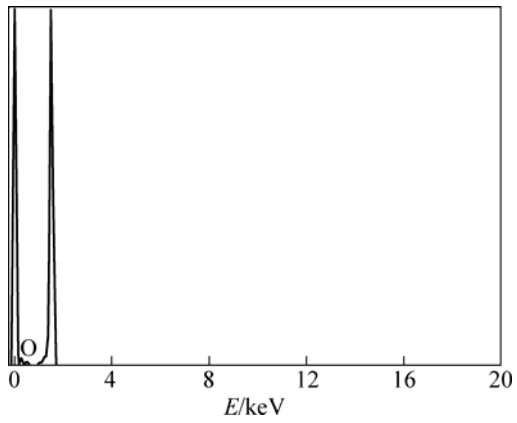

Fig.3 Energy spectrum of cathode surface

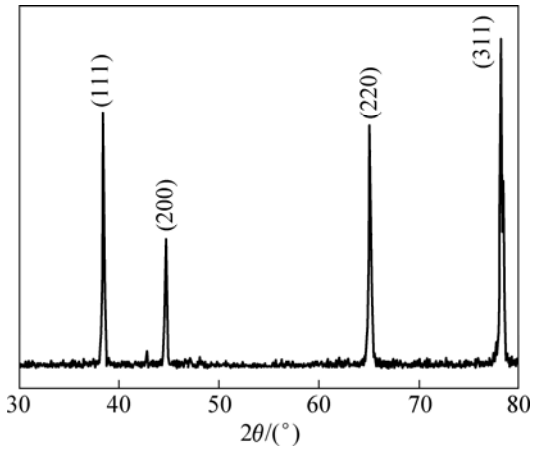

Fig.4 XRD pattern of cathode surface

peaks attributed to pure aluminum with face-centred cubic structure (FCC) are clearly detected from the sample. The diffraction patterns for deposits are composed of (111), (200), (220) and (311) faces. Peaks of (111) and (311) faces have high intensity, revealing the preferred stacking orientation of the electrodeposit.

4 Conclusions

1) Aluminum is successfully electrodeposited on magnesium from (EMIM)Br-AlC1$_3$ ionic liquid.

2) The deposits at 15 mA/cm^2 are denser and have metallic luster, composing of 1−2 μm cuboidal crystals, but the deposits have few porosities on the surface.

3) Aluminum crystal grain size is uniform, crystal grain growth is integrated, and the crystals grain boundary is clear and perfect.

4) The deposits at 15 mA/cm^2 are composed of (111), (200), (220), and (311) faces, presenting preferred stacking orientation of the electrodeposit.

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