Electrodeposition of aluminum and aluminum-magnesium alloys from organic solvent system

H.M. Kan, X.D. Wei, X.J. Feng, N. Zhang, X.Y. Wang & H.B. Long

Key Laboratory of Advanced Materials Technology of Liaoning Province, Shenyang University, Shenyang, China

Abstract: Aluminum and aluminum-magnesium alloys were prepared by direct current electrodeposition and pulse electro-deposition in AlCl3-LiAlH4-benzene-tetrahydrofuran (THF) system. Electrochemistry experiment was conducted by three electrode system and analyzed by Chronoamperometric plots. The surface morphology, composition and content of aluminum and aluminum magnesium alloys were studied by scanning electron microscope (SEM) and energy spectrum (EDS). The results show that the coatings of aluminum and aluminum magnesium are superior when the pulse duration ratio (ton:toff) is 0.08s:0.02s. The coatings are best when DC deposition current density in 14.89mA/cm2. SEM shows that by DC deposition the grain sizes are thick and the surface is rough. But the coatings obtained by pulse electro-deposition are more uniform, thinner and the surface is flatter than obtained by DC deposition.

1 Introduction

Aluminum-magnesium alloys are one of the lightest alloys in practical alloys. It is widely used in aviation and transport fields, etc. because of it has lots of advantages, such as good electrical and thermal conductors, low density, high strength, anti-oxidation, better corrosion resistance, recycling and so on [1, 2]. The major preparation method of aluminum-magnesium alloys is that pure aluminum and pure magnesium are mixed according to certain ratio in molten condition [3-5]. It is not only waste of resources, but also high of cost by this method. So many experts use electro-deposition method to prepare aluminum-magnesium alloys. The electro-deposition method is divided into direct current (DC) deposition and pulse electro-deposition. Pulse electro-deposition has comparatively greater advantage than DC electro-deposition. Pulse is a relatively new deposition technology. Activation polarization is increased and concentration polarization of cathode is decreased by the relaxation of pulse of current or voltage. The purity, density and uniformity of coating are improved, and its porosity is decreased [6, 7]. Not only the operation is simple, but also the surface of coating is uniform and compact, the aesthetic perception is also greatly improved. In this paper, aluminum and aluminum-magnesium alloys were prepared by direct current deposition and pulse electro-deposition in AlCl3-LiAlH4-benzene-THF system. The best duration ratio is studied, the technological conditions of improving magnesium content in aluminum-magnesium coating is explored in pulse electro-deposition.
2 Experimental

2.1 Experimental principles

In this paper, anhydrous AlCl₃ and LiAlH₄ are used for organic solutes. And benzene and THF is used for organic solvent in this system. The principle of electro-deposition is as followed:

\[ \text{LiAlH}_4 + 4\text{AlCl}_3 \rightarrow 4\text{AlHCl}_2 + \text{LiAlCl}_4 \quad (1) \]

The reaction in cathode is that H⁺, Cl⁻ ion and Al are produced after AlHCl₂ gains three mole electrons, the reaction equation is as followed:

\[ \text{AlHCl}_2 + 3\text{e}^- \rightarrow \text{H}^+ + 2\text{Cl}^- + \text{Al} \quad (2) \]

H⁺ ion and the redundant AlCl₃ reacts from cathode, and then AlHCl₂ are acquired again, as follows:

\[ \text{AlHCl}_2 + 3\text{e}^- \rightarrow \text{H}^+ + 2\text{Cl}^- + \text{AlCl}_3 \quad (3) \]

\[ \text{AlHCl}_2 + \text{AlCl}_3 \leftarrow \text{H}^+ + 2\text{Cl}^- + \text{AlCl}_3 \quad (4) \]

This system is a circulatary system. Aluminum-magnesium alloys are prepared at room temperature [8-10]. Its not produced other redundant substances and its current efficiency is high.

2.2 Experimental process

16.02g anhydrous AlCl₃ and 1.14g LiAlH₄ were handled in a glove box under argon atmosphere. And then they were sealed in a beaker. The electrolyte was prepared in ventilated kitchen. 80ml benzene and 20ml THF was putted into sealed beaker in ice-bath condition and then they were stirred for three hours in magnetic stirring apparatus.

The electrochemical experiments were conducted by using three electrode systems. The platinum sheet was used as working electrode. The spiral aluminum wire was used as counter electrode. The high-purity aluminum wire was used as reference electrode. And the Chronoamperometric plots were recorded and analyzed. After electrochemical experiments, pulse and direct current electro-deposition were conducted. The pulse experimental was conducted by changing duration ratio.

During DC deposition experiments, the current density was changed. Deposit morphology of aluminum and aluminum-magnesium alloys were tested by scanning electron microscope(S4800), and the chemical compositions were monitored using energy dispersive spectroscopy (EDS).

3 Results and Discussion

3.1 Results of Timing current curve

The nucleation process of Al(III) in AlCl₃-LiAlH₄-benzene-THF system was investigated by means of Chronoamperometric plot. The current-time transients of aluminum and aluminum-magnesium alloys are shown in Figure 1. The shape of the curve is apparently dependent on the overvoltage. The curve is divided into three stages. The first stage is that current also follows an abrupt change, due to the charge of the double layer. With the decrease of the charge current, the current begins to decrease at about 0.1s. The second stage is that current increase reaches the maximum value(Im) due to increase in effective electrode area, either because each independent nucleus forms and grows in size, or because the number of nuclei increases. The third stage is that current decreases with the increase of applied potential and gradually flatten. Because the diffusion zones of the growing nuclei begin to overlap. When the voltage is -3.5V, these transients show relatively intact. Electro-deposition current is different in different voltage, when voltage is greater. the current is greater in the figure. Meanwhile, peak current time continues to reduce when the one-step potential increases. It proves that the electrical crystallization nucleation is faster in the condition of high negative potential.
Figure 1. Chronoamperometric plot of aluminum and aluminum-magnesium alloys: (a) aluminum, (b) aluminum-magnesium alloys.

3.2 Electro-deposition of Al and Al-Mg alloys

In this paper, the coatings of Aluminum and aluminum-magnesium alloys are prepared by pulse electro-deposition or DC deposition. SEM pictures of aluminum coatings by two deposition technologies are shown in Figure 2. SEM showed that the grains of the coatings obtained by pulse electro-deposition are smaller and more uniform. However the obtained coatings of DC deposition have obvious uneven. The amount of deposition metal is relatively lower. It can be obviously seen by copper matrix. So pulse electro-deposition is conducive to produce fine and uniform coating. The metal ions near cathode can be sufficiently reduced when the current is turned on during pulse electro-deposition. Electrochemical polarity is increased. The coating is meticulous and light. When current is shut down, discharge ions near cathode again recover initial concentration, the concentration polarization is eliminated. Based on the analysis, the aluminum coating obtained by pulse electro-deposition is better than obtained by DC deposition in this experimental system.

Figure 2. SEM picture of aluminum by pulse electro-deposition or DC deposition; (a) pulse electro-deposition, (b) DC deposition.

Mg$^{2+}$ ions are introduced into the electrolyte by a preliminary electrolyzing process of using a pure Mg anode. The SEM and EDS pictures of aluminum-magnesium alloys by pulse electro-deposition are shown in Figure 3. When duration ratio is 0.04s:0.06s, the magnesium content in the coating is 0.39wt%.

When the duration ratio is 0.05s:0.05s, the magnesium content is 0.48wt%. When the duration ratio is 0.08s:0.02s, the magnesium content is 0.52wt%. The magnesium content in aluminum-magnesium alloys coating are the highest and the coating are compact when the duration ratio of 0.08s:0.02s. The reason of this phenomenon is that deposited grains would coalesce during the power-off period to form irregular and larger grains. So smaller denser and grains are obtained when $t_{on}$:$t_{off}$ is long.
Figure 3. The SEM and EDS picture of aluminum-magnesium alloys by pulse electro-deposition at different pulse duration ratio: (a) $t_{on}$:$t_{off}$=0.04s:0.06s, (b) $t_{on}$:$t_{off}$=0.05s:0.05s, (c) $t_{on}$:$t_{off}$=0.08s:0.02s

The SEM and EDS pictures of aluminum-magnesium alloys by DC deposition at different current density are shown in Figure 4. When current density is 0.127A/cm$^2$, the magnesium content in coating is 0.46wt%. When the current density is 0.254A/cm$^2$, the magnesium content is 2.23wt%. When the current density is 0.382A/cm$^2$, the magnesium content is 7.56wt%. So the higher the current density, the greater the magnesium content in aluminum-magnesium alloys coating.

Comparing magnesium content of the coatings by different deposition technology, the conclusion are drawn that magnesium content by DC deposition is more than that by pulse electro-deposition in the same experimental conditions. And magnesium content of coatings is greater when high pulse duration ratio is used. This is due to conduction time is longer when high pulse duration ratio, approaching direct current. So magnesium content of coatings is higher.

Figure 4. The SEM and EDS picture of aluminum-magnesium alloys by DC deposition at different current density: (a) $i$=0.127A/cm$^2$, (b) $i$=0.254A/cm$^2$, (c) $i$=0.382A/cm$^2$
4 Conclusion
(1) The coatings of aluminum and aluminum-magnesium alloys are prepared in AlCl₃-LiAlH₄-benzene-tetrahydrofuran (THF) system. Chronoamperometric plot of aluminum and aluminum-magnesium alloys at different voltages are analyzed. It is proved crystallization nucleation is faster at high negative potential condition.
(2) The magnesium content is the best when the current density of DC deposition is 0.382 A/cm². The greater the current density, the higher the magnesium content of aluminum-magnesium alloys coating within limits. The magnesium content of the coating obtained by DC deposition is more than that of the coating obtained by pulse electro-deposition under same experimental conditions. When pulse duration ratio is 0.08s:0.02s, the coating of pulse electro-deposition is the best, the magnesium content in coating is the highest. The reason is that in the high pulse duration ratio, the conduction time is longer, close to direct current, the magnesium content of coatings increases.

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