ELECTRODEPOSITION OF ALUMINUM–CHROMIUM ALLOY FROM AMBIENT TEMPERATURE MELT

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ABSTRACT

The electrodeposition of aluminum–chromium alloy has been studied in the \( \text{AlCl}_3-\text{EMICl} \) (1-ethyl-3-methylimidazolium chloride) melt containing \( \text{CrCl}_2 \). No clear wave for the deposition of pure chromium is observed by voltammetric methods. The deposits always contain both aluminum and chromium, while the chromium deposition is preferred at low overpotential. The chromium content in the deposit increases by the use of the rotating disk electrode.

INTRODUCTION

The mixtures of aluminum chloride (\( \text{AlCl}_3 \)) and 1-ethyl-3-methylimidazolium chloride (EMICl) are promising ambient temperature molten salts, since their wide electrochemical window suggests high potential for several applications such as electroplating, high energy density batteries and the medium for chemical reactions. Among them the ambient temperature melts are good solvents for the electroplating of aluminum (1,2) and its alloy such as Al–Ti (3).

Since aluminum and chromium have corrosion resistance, there is a possibility that the alloy of these metals will possess the high resistance to corrosion. It is, however, quite difficult to electroplate this alloy at room temperature. In the present study we discuss the electroplating of aluminum–chromium alloys to develop the new corrosion–resisting coating on the steel surface.
The AICI$_3$ was sublimed through a glass frit after melted with 1 wt% sodium chloride with 5N pure aluminum metal for one day at 478 K. The EMICl was recrystallized three times from a mixture of acetonitrile and ethylacetate, and washed with anhydrous ethylacetate. The purified EMICl was dried under vacuum for one day at 343 K before the mixing with AlCl$_3$. The mixture of purified AlCl$_3$ and EMICl was digested for a few days with the aluminum metal. The 3N pure CrCl$_2$ was used as received.

Vitreous carbon rod was used as working electrodes for the voltammetric studies. Nickel flag and steel flag electrodes were used to determine the composition of deposits. A nickel rotating disk electrode was also used to study the influence of the melt flow. The counter electrode was 5N pure aluminum foil. The reference electrode was a 5N pure aluminum wire which was separated from the main compartment by a fine glass frit.

The Al–Cr alloy was deposited by galvanostatic and potentiostatic methods with commercially available electrochemical instrumentation (Hokuto Denko Models HA–501 and HB–105). The films of deposited alloys were dissolved in hydrochloric acid to determine the composition by the inductively coupled plasma and atomic absorption spectroscopies. The current efficiency was determined by comparing the amount of each component in the deposits with the charge passed during the deposition. The deposits were also analyzed by X–ray photoelectron spectroscopy (XPS) with JEOL JPX–90SX. All measurements were done in a glove box filled with nitrogen of high purity.

RESULTS AND DISCUSSION

Figure 1 shows the differential pulse polarography measured in a 2/1 AlCl$_3$–EMICl melt with 8.1 mmol/kg CrCl$_2$. No clear cathodic wave for the deposition of pure chromium is observed in the potential range nobler than the aluminum deposition. The addition of CrCl$_2$ causes only the cathodic shift of the deposition potential of aluminum. The shift of deposition potential is also observed by other voltammetric methods.

Figure 2 depicts the composition of the alloy film obtained by potentiostatic method. The deposits always contain both aluminum and chromium. At the potentials more positive than –50 mV, the chromium content in deposits is higher than that of aluminum, which indicates the deposition of chromium is preferred. the coulombic efficiency for the alloy deposition is quite low at this potential region, which is caused
by the poor adherence of deposits or the reduction of impurities. The question then arises about the deposition potential of aluminum and chromium. Although no clear current of the chromium deposition is observed in voltammetric curves as shown in Fig. 1, chromium can mainly deposit at low overpotential. What has to be noticed is the shift of the deposition potential of aluminum by the addition of CrCl$_2$ into the melt, even if its concentration is quite low. This potential shift may be important to demonstrate the mechanism on the Al–Cr alloy deposition, while we have little clear information by now.

The coulombic efficiency for the deposition of the alloy approaches 100% with cathodic overpotential, where the chromium content in the deposits becomes quite low. As shown in Fig. 3, the partial current density for the chromium deposition becomes the diffusion limited values with current density. Because of the low concentration of CrCl$_2$ in the melt, the diffusion limited current density is low, which results in low chromium content in the deposits. Therefore, the rotating disk electrode was used to increase the content of chromium in deposits. In Fig. 3 typical composition of the deposits obtained with the rotating disk electrode are also shown. By comparing these results with the deposits without the electrolyte flow, it is clear that the partial current densities for the chromium deposition becomes high with rotating the electrode. On the other hand, the partial current densities for aluminum deposition vary little, because of the high concentration of Al$_2$Cl$_7^-$ ion in the acidic melt. We may, therefore, reasonably conclude that the composition of the Al–Cr deposit can be controlled by the flow rate of the melt. Moreover, the use of the rotating disk electrode improves the surface morphology of deposits. The effect of the chromium content in the deposit on the corrosion–resistance is now studied.

CONCLUSION

The aluminum–chromium alloy can be electroplated from the AlCl$_3$–EMICl melt containing CrCl$_2$, although no pure chromium can be obtained. The deposition of chromium is preferred at low overpotential, which relates to the cathodic shift of the deposition potential of aluminum. The chromium content in the deposit can be controlled by an increase in the flow rate of the melt.

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Fig. 1 Differential pulse polarograms on a vitreous carbon electrode (0.07 cm²) at 308 K for the melt (a) with 8.1 mmol/kg CrCl₂ and (b) without CrCl₂.

Fig. 2 Composition of the deposits and coulumbic efficiency by potentiostatic method.

Fig. 3 Effects of electrolyte flow on the partial current densities.