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The effect of electrode surface modification and cathode overpotential on deposit characteristics in aluminum electrorefining using EMIC–$AlCl_3$ ionic liquid electrolyte

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ABSTRACT

Electrorefining of aluminum alloy was investigated using $AlCl_3$ and 1-ethyl-3-methyl-imidazolium chloride (EMIC) (molar ratio $AlCl_3$:EMIC = 1.65:1) ionic liquid electrolyte on copper and aluminum cathodes at temperature of $90 \pm 3\,^{\circ}C$ and cell voltage of 1.5 V. The effect of electrode surface modification and cathode overpotential on deposit characteristics of aluminum was investigated. The surface modification of electrodes reduced the dendritic depositions of aluminum. It was also observed that cathodic overpotentials obtained from experiments using modified electrodes are significantly lower than those of unmodified electrodes. A non-dendritic deposit of aluminum was observed even after prolonged electrorefining of 25 h. Pure aluminum deposits were obtained for all experiments with the current efficiencies in the range of 94–99%.

1. Introduction

Aluminum electrorefining/recycling from aluminum scrap using ionic liquid electrolyte is a technologically attractive process due to the unique chemical and physical properties of ionic liquids such as wide temperature range for the liquid phase, high thermal stability, negligible vapor pressure, low melting point and wide electrochemical window. In current scenario, two processes are used for aluminum electrorefining: three layer process (Hoope's process) and the segregation process. High temperature (800–950 °C) and high energy consumption (15–18 kW h/kg of aluminum) make three layer process less economical unless for very high-purity aluminum production [1]. In the segregation process, the purity of aluminum is not high enough (99.9%), which requires additional refining steps for high-purity aluminum production.

For this reason, extraction and refining of aluminum from low temperature or room temperature ionic liquid electrolytes is gaining interest. Many researchers have studied electrodeposition of aluminum using different ionic liquid melts [2–8]. But bulk electrodeposition and commercialization is yet to be established. In recent years, Reddy and co-workers [9–13] have reported bulk electrowinning and electrorefining of aluminum using low temperature chloroaluminate ionic liquid electrolytes, which yield high-purity aluminum deposits with zero pollutant emissions. Optimization of aluminum deposition from ionic liquid electrolytes was not fully investigated. In electrorefining cell, coarse grained, rough and adhesive deposits are required. As dendritic deposition is not adherent enough to endure handling before melting and casting into desirable shapes for further processing, they add additional cost for handling and processing. Dendrites sometimes short the flow of current between anodes and cathodes which is not desirable. Although there are number of experimental parameters such as electrolyte concentration, surface roughness of electrodes, addition of additives, impurities, stirring, temperature and deposition time to prevent the dendritic deposition, current density and cathode overpotential play the major role.

There are very few investigations reported in the literature on the deposition of aluminum on copper [3,9–13] and aluminum [14,15]. Aluminum deposition on aluminum or copper substrates can be divided into two steps: (a) a thin layer deposited on the substrate, (b) dendrites attaching to this thin layer. Adherence depends directly on the reactivity between the aluminum and cathode material. Formation of intermetallic compounds like Al_2Cu due to interdiffusion implies strong reactivity. The presence of an underlayer ensures good adherence of the dendrites. In the case of aluminum cathode, there is a low reactivity between the aluminum and the substrate. At the beginning of growth of layer, Budevski et al. have proposed models taking into account the binding energy of the electrodeposited metal (M), either on substrate (S), E_{MS} or on the pre-deposited metal E_{MM} [16,17]. When $E_{MS} \le E_{MM}$ (Volmer–Weber model), M becomes deposited on M rather than on S, leading to three-dimensional islands. This initial process favors

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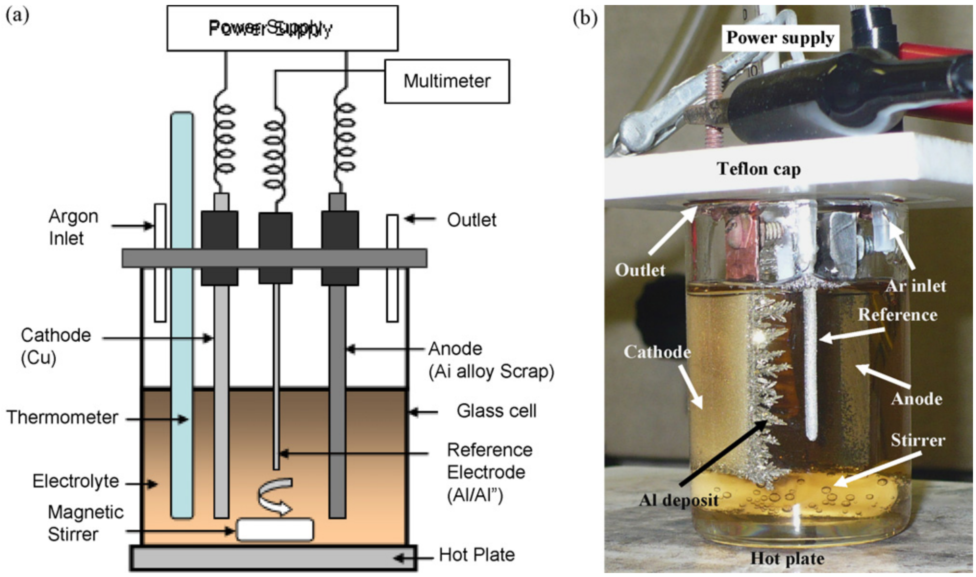

Fig. 1. (a) Schematic diagram of the experimental cell and (b) electrorefining cell.

a rapid formation of axial dendrites on the cathode surface. In case of copper, a surface alloy is formed by metal interdiffusion with the underlayers of aluminum and dendrite formation occurs when the intermetallic layer is saturated. At this time E_{MM} is higher than $E_{M\text{-alloy}}$ which leads to the formation of 3D islands. During deposition growth, orthogonal needles result from diffusional phenomena favoring current at the top of the islands. The heterogeneity of the electrolyte layer at the interface with the cathode material causes a particular fluid motion which readily influences the morphology of the deposition. Fleury et al. [18,19] demonstrated that the depletion of cations near the cathode generates strong local electric fields. According to these authors, the electrolyte motion follows contra-rotative vortices at the tip of each needle, producing ramification at the edges.

In this article, we have investigated the effect of electrode surface modification and cathode overpotential on deposit morphology of aluminum using $AlCl_3$ and EMIC (molar ratio 1.65:1) electrolyte at 90 ± 3 °C.

2. Experimental

The electrorefining experiments were conducted in a 40 ml Pyrex® glass cell fitted with teflon cap. The schematic diagram and actual electrolytic cell are shown in Fig. 1(a) and (b), respectively. The anodes were prepared by cutting the aluminum alloy ingot material into 45 mm × 20 mm × 5 mm plate. Table 1 shows the compositional analysis of aluminum alloy. Copper and aluminum (99.999% pure, Alfa Aesar®) sheets with dimensions of 45 mm × 20 mm × 1 mm were used as cathodes. Pure aluminum wire (2 mm diameter, 99.999% pure, Alfa Aesar®) was used as reference electrode. $AlCl_3$ and 1-ethyl-3-methyl-imidazolium chloride (EMIC) (molar ratio 1.65:1) were used as is.

All electrodes were polished with a 320 grit SiC emery paper to expose fresh metal surface before electrorefining. Some of the anode and cathode back surfaces were masked with non-conductive tape (HP260®) and referred as "modified" in this investigation. The cathode area of deposition and anode working area were calculated from the exposed area of electrodes into the electrolyte. The purpose of reference electrode was only to measure the electrode potential of anode and cathode individually, using a multimeter (Keithley® 2000 Multimeter). The constant voltage power source (Kepco® ABC Programmable Power Supply) supplied the required voltage across anode and cathode. The electrolyte was stirred at a constant speed (60 rpm) using a magnetic stirrer. The temperature was controlled by placing the electrorefining cell on a hot plate. A thermometer was inserted through the teflon cap to monitor the temperature. The electrolyte was heated stepwise to the required temperature under a controlled atmosphere (argon). The electrolyte was then allowed to stand for at least 30 min at the final temperature for stabilization before starting the experiment.

In order to determine the effect of cathode overpotential on deposit morphology, a set of experiments were conducted with three-electrode system using EG&G PARC model 273A potentiostat/galvanostat® attached with *Power Suite®* software. Similar experimental setup (Fig. 1) as mentioned above was used for all experiments. Constant cathode potential ranging from −0.25 V to −0.65 V were supplied between modified aluminum sheet cathode (working electrode) and aluminum wire (reference electrode). Modified aluminum alloy anode with dimensions of 45 mm × 20 mm × 1 mm was used as counter electrode.

All experiments were conducted in a ventilated hood, under argon atmosphere at 90 ± 3 °C with duration of 5 h except one for 25 h. After experiments, thorough washing of electrodes were carried out with acetone and double distilled water to remove the electrolyte from the deposit before characterization.

The qualitative and quantitative analysis of the electrodeposited aluminum were carried out using Philips® XL30 scanning electron microscope (SEM) with energy dispersive spectroscope (EDS). The X-ray diffraction (XRD) analysis was performed using Philips® PW3830 X-ray diffractometer which uses a monochromatic CuK_α radiation (λ = 1.5406 Å).

Table 1
Elemental analysis of aluminum alloy anode.

Elements	Al	Si	Fe	Mn	Mg	Cu	Ti	+Cr	Ni	Zn
Wt%	74.25	25.07	0.08	0.008	0.345	0.02	0.13	0.002	0.007	0.03