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MEETING POINT OF THE SCIENCE AND PRACTICE IN THE FIELDS OF CORROSION, MATERIALS AND ENVIRONMENTAL PROTECTION

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Aluminium electrodeposition onto glassy carbon from deep eutectic system made of $AlCl_3$+urea

Elektrohemijsko taloženje aluminijuma na staklastom ugljeniku iz eutektičke smeše $AlCl_3$+urea

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Abstract

Electrochemical deposition of aluminium onto glassy carbon from deep eutectic solvent (DES), made of the $AlCl_3$+urea, at 25-50°C have been investigated. The deposition was performed in potentiostatic mode. The morphology of the obtained deposits were characterized using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Critical overpotential of aluminium deposition decreased from around – 0.150 V at 25°C to around – 0.100 V at 50°C. All recorded currents were small but would substantially increase with increasing working temperature (from 0.01 mA cm^{-2} up to 0.25 mA cm^{-2}). The deposits obtained showed variety of morphological shapes depending on the working temperature and potential applied. All the deposits were made of very small crystallites grouped randomly into more or less separate agglomerates. Density of the crystallites distribution over the substrate and complicity of the crystal forms increased with the potential applied.

Electrodeposition/dissolution of aluminium in used electrolyte onto used substrate obviously promises positive results if research aiming at reversible systems of such composition working at temperatures very close to room temperature.

***Keywords**: glassy carbon, aluminium deposition/dissolution, deep eutectic system, urea*

Izvod

Ispitivano je elektrohemijsko taloženje aluminijuma na staklastom ugljeniku iz eutektičke smeše (DES), $AlCl_3$+urea, na temperaturama od 25-50°C. Elektrotaloženje je izvođeno potenciostatski. Morfologija dobijenih taloga je analizirana skenirajućom elektronskom mikroskopijom (SEM) i energetsko disperzivnom spektroskopijom (EDS). Kritične prenapetosti elektrotaloženja aluminijuma kretale su se od oko – 0.150 V pri 25°C do oko – 0.100 V pri 50°C. Zabeležene gustine struje bile su male, ali su njihove vrednosti značajno rasle sa povećanjem radne temperature (od 0.01 mA cm^{-2} do 0.25 mA cm^{-2} uz povećanje temperature od 25°C do 50°C). Dobijeni talozi pokazali su raznovrsne morfološke oblike što je zavisilo od primenjene temperature i potencijala. Svi talozi sastojali su se od veoma malih kristala objedinjenih u aglomerate koji su bili nasumično raspoređeni po površini radne electrode. Gustina rasporeda kristalita po površini elektrode i njihova pojedinačna raznovrsnost po obliku rasle su sa povećanjem primenjenog potencijala.

Elektrohemijsko taloženje/rastvaranje aluminijuma u upotrebljenom elektrolitu i na upotrebljenoj podlozi obećava pozitivne rezultate u istraživanjima usmerenim na reverzibilne sisteme istog ili sličnog sastava koji bi trebalo da rade na temperaturama veoma bliskim sobnoj.

Ključne reči: *staklasti ugljenik, elektrohemijsko taloženje/rastvaranje aluminijuma, eutektička smeša, urea*

Introduction

The importance of aluminium and its alloys derives from their high level of corrosion resistance, electric conductivity, low density, high elastic modulus. These makes them promising materials for application in aerospace, military, automobile industry [1]. Different methods have been developed for Al coatings for corrodible materials, and besides hot dipping [2], vapour deposition, electroless plating, etc. [2], electrodeposition proved to be very promising way to obtain metal deposit at the micro or nano scale under controlled conditions. However, aluminium electrodeposition has to be done from non-aqueous electrolytes. In aqueous solutions aluminium deposition is preceded by hydrogen evolution due to very negative reduction potential of aluminium (-1.662 V vs. SHE). Numerous research efforts have been put into quest for non-aqueous electrolyte suitable for aluminium electrodeposition at low temperatures.

Some success was recorded in inorganic molten salts, like chloroaluminates, electrolytes with working temperatures between 200°C and 500°C producing aluminium deposits of good quality and adherence [3]. Some time ago these have been joined with relatively new class of solvents, known as room temperature molten salts or ionic liquids (IL), to be used for electrodeposition of pure aluminium or aluminium alloys. Most of the research regarding aluminium electrodeposition was carried out from $AlCl_3$-1-ethyl-3methylimidazolium chloride [4]. Aluminium deposition from ionic liquids was observed only from acidic electrolyte, and aluminium deposited layer was reported to be relatively smooth with higher adhesive strength [4,5]. Recently, interest have been expanded to some aluminium chloride based electrolytes which in combination with some polarizable organic compounds produce nonaqueous solution near or close to room temperature. These systems are known as deep eutectic solvents (DESs) or solvate IL [4,6]. Due to their low cost and minimum environmental footprint these class of ionic liquids have been found to be of interest for electrodeposition of aluminium [7,8].

In this study, the synthesis of deep eutectic solvent based on $AlCl_3$+urea, and their use for aluminium electrodeposition was reported. Cyclic voltammetry (CV), Chronoamperometry, and polarization curves were used to study aluminium electroreduction and deposition on glassy carbon working electrode in $AlCl_3$+urea deep eutectic system.

Experimental

In a small glass container urea (p.a. used as received, Carlo Erba, France) was added to $AlCl_3$ (>99%, Aldrich Chemical Company, Inc.), molar ratio was 1:1.6, and slowly mixed under argon atmosphere inside glove box. It took several seconds to form a homogeneous, yellow colored liquid (deep eutectic solvent – DES) which then was left to cool gradually at room temperature. Finally, DES from the beaker was transferred to a sealed tree electrode electrochemical cell supplied with argon atmosphere. Electrochemical experiments in the cell were performed outside the glove box.

Two aluminium electrodes (99.99%, Alfa Products, Thiokol Ventron division, USA) were used: wire with 3mm diameter as a reference electrode and curved rectangular shovel with geometrical area = 15 cm^2 as a counter electrode. Cylindrical glassy carbon working electrode (GC) was placed in the centre of the cell, with surface area of 0.5 cm^2 exposed to ionic liquid electrolyte. Prior to every electrochemical measurement or electrodeposition process, aluminium electrodes were polished and etched as described elsewhere [9]. After being polished with 0.05 μm alumina powder (Merck) glassy

carbon working electrode was cleaned by sonification in Milli-Q water in several intervals for 5 min and finally rinsed with distilled water and absolute ethanol.
Cycling voltammetry (CV), Chronoamperometry and Chronopotentiometry were used to study aluminium deposition/dissolution from the DES under argon atmosphere, using EG&G PAR 273A Potentiostat/Galvanostat controlled by Power Suite software (Princeton Applied Research, USA).

Results and discussion

Voltammograms were recorded for the linear potential changes from the starting potential, E_i, 100-150 mV negative to the working electrode open circuit potential (1.400 V vs. Al^{3+}/Al) towards the negative end potential, E_f, and back using different scan rates. Typical examples of the voltammograms depicting Al deposition/dissolution on/from GC working electrode in the DES used are presented in Fig.1. Charges under deposition peaks are very close to the charges under dissolution peaks for all working temperatures used, which suggests good reversibility of the two processes. The reproducibly of the voltammograms recorded at the same conditions was very good. It was interesting to find that aluminium deposition and dissolution proceeds very well even at 25°C, although with rather small current densities. During experiments the electrolyte was not stirred.

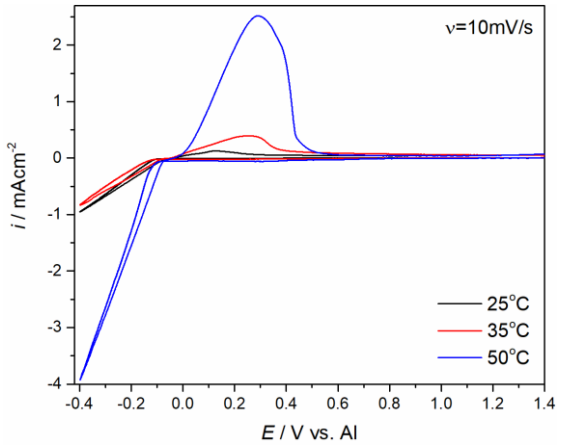


Figure 1. Voltammograms obtained on GC working electrode in DES used at three different temperatures.

Examples of the current-time transients obtained by aluminium electrodeposition conducted under constant potential (– 0.120 V vs. Al^{3+}/Al) at three different temperatures: room temperature (25°C), 35°C and 50°C are presented in Fig.2. During aluminium deposition the electrolyte was not stirred.

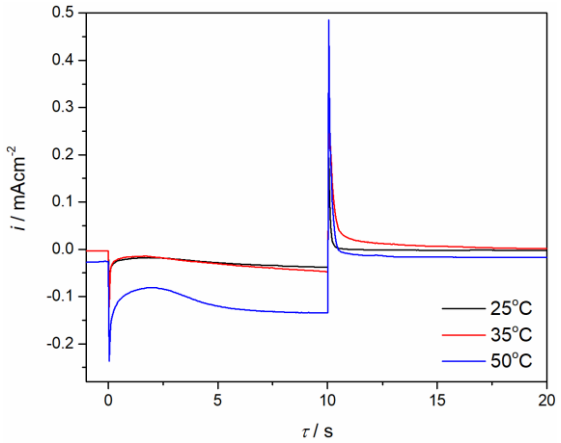
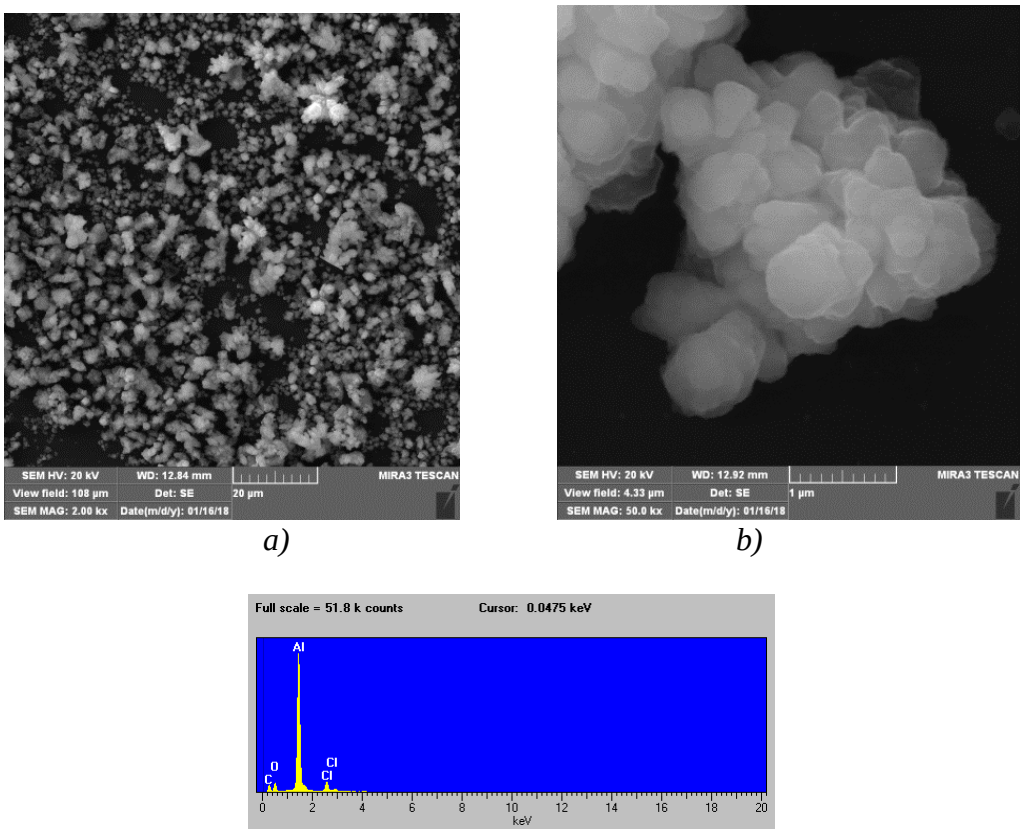


Figure 2. Current-time transients obtained with GS electrode in DES with cathodic overpotential of – 0.120 V (10 s duration) at three different temperatures.

It was found that overpotential of – 0.120 V was sufficient to initiate and sustain aluminium deposition even at room temperature. However, at 25°C recorded current densities were of the order of 0.01 mA cm^{-2}. Initial portions of the transients at all applied temperatures indicated continuous nucleation and growth of the aluminium deposited.
After deposition completed, the obtained samples were thoroughly rinsed with absolute ethanol to remove any residues of the electrolyte and left to dry in air before characterisation. The microstructures of the deposits were visualised using scanning electron microscope (SEM, TESCAN Digital Microscope; model VEGA3, Brno, Czech Republic) and composition of the deposit was analysed by energy dispersive spectroscopy (EDS-TESCAN), see Fig.3.



a) *b)*

c)

Figure 3. SEM and EDS analysis of GC working electrode after potentiostatically deposited aluminium at – 0.250 V for 30 min, temperature 25°C.

After 30 minutes of aluminium deposition at – 0.250 V at 25°C, GC working electrode becomes randomly covered with aluminium clusters, 2µm of average size, Fig.3a. Most of the clusters were composed of hexagonal flakes, Fig.3b, and the smallest once were pyramids and bipyramids of up to 200 nanometres in base. EDS analysis has shown that the deposit was aluminium.
The depositions made under all other conditions being the same but at elevated temperatures (namely 35°C and 50°C) produced incoherent (loos) aluminium deposits made of clusters which were of bigger average size. However, no compact and adherent aluminium deposit was obtained. The deposits obtained were of very high surface area and reach morphology which points to diffusion controlled aluminium electrodeposition. It appears that after nucleation the grains develop as pyramids (or bipyramids) which after achieving a certain size (a few hundred nanometres up to a micrometre, depending on the applied temperature) either stop growing or continue to grow only on a few of the irregularities active on a crystallographic planes. When this might be the case the growth includes constructions made of hexagonal flakes bound together, Fig.3a.

This initial results are not sufficient for serious analysis on the mechanisms governing formation of so elaborate and complex deposit morphology. Deposition current densities are very small, particularly at 25°C (of the order of 0.01 mA cm^{-2}), although they are not much greater at 35°C (around 0.05 $mAcm^{-2}$) and 50°C (of the order of 0.1 $mAcm^{-2}$). Such small currents could be attributed to very high electrolyte resistivity. No reliable value for diffusion limited deposition current density could have been determined. In several papers, published very recently [10,11], reporting on similar systems, no deeper discussion on the subject of similar deposit morphology had been opened. It is obvious that comprehensive specially designed experiments will be needed to unveil the roles of electrolyte resistance and aluminium ions diffusion control onto complex deposit morphologies observed.

Conclusion

Aluminium has been successfully deposited onto glassy carbon from deep eutectic solvent (DES), made of the AlCl3+urea, at 25, 35 and 50°C.
Deposition and dissolution processes were reversible and reproducible, even at 25°C. Both, potentiostatic deposition and dissolution were performed with rather low current densities (bellow 0.1 mA cm^{-2}).
Obtained deposits were made of individual randomly distributed aluminium clusters which were closer together and bigger as the deposition potential, deposition time and working temperature were increased. Although of high surface area, the deposits were not coherent and well adherent to the substrate.
The morphology of the obtained deposits was very complex and elaborate consisting of individual crystallites (pyramids, bipyramids), boulders with coral like additions and clusters made of hexagonal flakes.
How much the morphology was influenced by small current densities due to high electrolyte electric resistivity, and how much by possible diffusion controlled deposition at this initial stages of research was difficult to ascertain.

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