



Full Length Article

Characterization of the electrochemical deposition of aluminum from an AlCl_3 :*N*-methylacetamide eutectic solvent modified with nicotinamide

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ARTICLE INFO

Keywords:

Electrodeposition

Aluminum

AlCl_3 :*N*-methylacetamide deep eutectic solvent

Additives

ABSTRACT

Aluminum currently sees extensive use in a wide range of applications that include cars, the aviation industry, consumer appliances, container vessels, and electronics. Aluminum electroplating is typically carried out using conventional ionic liquids, but these are typically toxic, costly, and relatively sensitive to air. This research will investigate the electrodeposition of aluminum for the first time from a (1:1 M ratio of) AlCl_3 :*N*-methylacetamide-based eutectic solvent on different substrates at room temperature in the presence and absence of nicotinamide as an additive. The electrochemical behavior of the aluminum in *N*-methylacetamide electrolyte was studied via chronocoulometry and cyclic voltammetry. The redox peak current was found to decrease relative to the pure Al solution when nicotinamide is added. The surface morphologies and composition of any aluminum films produced have been investigated via SEM/EDX, while the crystal structures of the products and their roughnesses were examined using XRD and AFM, respectively. The roughness of the Al film produced from the bath containing 0.02 M nicotinamide decreased to approximately 312 nm. The corrosion resistance of the aluminum coatings obtained from the systems containing 0.1 M and 0.2 M nicotinamide were found to be improved.

1. Introduction

Aluminum coatings have, quite understandably, been of considerable historic interest due to their resistance to corrosion, lack of toxicity, and relatively low densities, [1] with coatings typically being produced using such methods such as hot dipping, thermal spraying, vapor deposition, sputter deposition, and electrodeposition [2–6]. Of these, electrochemical deposition has been found to have particularly favorable characteristics such as low energy consumption, high reaction efficiency, ease of control over the resultant aluminum structures, and a requirement for, in general, only moderate experimental conditions to

produce such coatings [6,7]. Unfortunately, aluminum is amongst a number of active metals whose electrodeposition from aqueous solution has proved impossible owing to the evolution of hydrogen gas at the relevant electrode prior to the aluminum deposit even being produced. The various liquid salts – more commonly referred to as ionic liquids – utilized in metal electroplating have been shown to have numerous benefits over deposition from aqueous solution, most notably due to their high chemical stability and superior electrochemical properties [6,8,9].

Aluminum deposition from an ionic liquid was first reported by Hurley and Weir in 1951 [10]. They prepared an ionic liquid from *N*-

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ethylpyridinium chloride incorporated with aluminum chloride, which led to a number of studies looking at electrodeposition of aluminum and alloys of aluminum from ionic liquids. These studies showed that deposition from ionic liquids invariably improved the properties of the aluminum deposits formed, with the resultant films showing high conductivities and broad electrochemical windows. Many of these systems are based on chloroaluminate ionic liquids, which are synthesized by incorporating organic chloride salts with aluminum chloride [11]. One can control Lewis's acidity by adjusting the molar proportion of AlCl_3 , with aluminum being deposited when this ratio exceeds 50 %. The $[\text{Al}_2\text{Cl}_7]^-$ anion formed in the mixture is responsible for the deposition and common counterions include alkyl imidazole, alkyl pyridine, and quaternary ammonium cations [12]. Alkyl imidazole cations are often preferred because of the good electrical conductivity, high stability, and decreased viscosity of the ionic liquid so produced, with 1-ethyl-3-methylimidazolium ($[\text{Emim}]^+$) being the most commonly used [10,11]. However, their application is limited due to their high cost and hygroscopic nature, so the development of new systems based on neutral ligands and facilely obtainable hydrophobic is clearly of interest.

Abbott and co-workers [13,14] recently produced eutectic aluminum solvents through interacting AlCl_3 with either urea or acetamide. Whilst the complexes thus produced were fluid at room temperature, they were found to have high viscosities and decreased conductivities in comparison with the imidazolium chloroaluminate systems used; moreover, the aluminum films they deposited need considerable subsequent optimization. More recently, researchers have become increasingly interested in the metals electroplating and their alloys from deep eutectic solvents [9,15–22] which, despite being similar to room temperature ionic liquids RTILs, have much more desirable properties in that they are extremely cheap to produce and have wide potential windows.

Liu et al. [23] prepared a number of ionic liquids containing amide- AlCl_3 using different-structured amides (*N*-methylacetamide, acetamide, and *N,N*-dimethylacetamide) as donor molecules. Each amide was found to alter the proportions of the species in the liquid because of differences between the amide coordinating site and aluminum chloride.

Abbott et al. [24] investigated the influences of toluene and LiCl on the morphologies of the aluminum deposits prepared from a [1-Butyl-3-methylimidazolium] Cl/AlCl_3 ionic liquid, from which an aluminum mirror coating was obtained on addition of toluene to the plating solution, whilst LiCl addition resulted in a dark grey aluminum deposit. Caporali et al. investigated the influence of phenanthroline on the electroplating of aluminum from $[\text{Bmim}]\text{Cl}/\text{AlCl}_3$, obtaining bright aluminum deposits that were highly resistant to corrosion [25]. More recently, Zhang et al. [12] have shown that uniform, mirror aluminum deposits can be achieved when methyl nicotinate or nicotinic acid additives are present.

In this work, aluminum electrodeposition from (1:1) AlCl_3 :*N*-methylacetamide has, for the first time, been achieved on various substrates using nicotinamide as an additive. The advantages of this system of ionic liquids are that they are inexpensive compared to classical ionic liquids, and are considerably less sensitive to moisture. *N*-methylacetamide is inexpensive compared with quaternary ammonium halides, additionally, *Al-N*-methylacetamide eutectic solvents are relatively insensitive to water. Moreover, it has been found that the characteristics of this eutectic solvent show the same behaviours as those of popular ionic liquids. The electrochemical properties of this new aluminum liquid are studied herein via cyclic voltammetry, whilst the resultant surface morphologies, roughnesses, and crystal structures of the associated aluminum coating have been revealed by SEM/EDX, AFM, and XRD. In addition, the corrosion characteristics of the aluminum deposit in brine have been measured.

2. Experimental

N-methylacetamide (NMA) (Fisher, $\geq 99\%$) was used as received without further purification. Analogous liquids were prepared in a

glovebox under an inert N_2 atmosphere in a 1:1 M ratio. The NMA/ AlCl_3 -based eutectic liquid was synthesized by slowly adding *N*-methylacetamide to anhydrous AlCl_3 . Anhydrous AlCl_3 was placed in the flask, to which *N*-methylacetamide was slowly added with stirring for 45 min. Under dry nitrogen gas in a 1:1 M ratio. The solids reacted immediately without external heating, reaching a temperature of ca. 75 °C. The reaction was complete after 4 h. The analogous liquids formed were homogenous, and were stored in a glovebox. The conductivity and viscosity of the (1:1) *N*-methylacetamide- AlCl_3 -based liquid was measured as shown in Fig. S1. Electrochemical data (cyclic voltammetry, chronocoulometry) was obtained using an Autolab potentiostat. Three types of electrodes were involved in the electrochemical cell: a Pt working electrode (1 mm dia.), a Pt foil counter electrode, and a reference electrode of silver wire. Ag wire was used as a pseudo-reference electrode directly immersed in the (1:1) *N*-methylacetamide- AlCl_3 -based liquid as Ag/AgCl RE is not suitable for use in DESs as it can cause problems when silver ions leach from the reference electrode. Platinum was used as a noble metal with which to study the intrinsic electrochemical properties of the liquid electrolyte. However, electroplating processes are often conducted at the surfaces of more reactive metals such as copper, brass, and steel. Cyclic voltammetry was run using a +1.0 to -1.0 V potential window for aluminum liquids at 25 °C. The chronocoulometry measurements were performed using the same electrodes at an applied potential of -0.4 V. Data from both techniques was collected at the same temperature, concentration, and using the same electrodes. Nucleation of Al deposition in the 1 AlCl_3 : 1 *N*-methylacetamide eutectic solvent was studied via the chronoamperometry method, as shown in Fig. S3.

Electrodeposition of aluminum was achieved from (a 1:1 ratio of) *N*-methylacetamide- AlCl_3 -based liquid with and without nicotinamide in the plating bath using copper, brass, and mild steel as the substrates. This was performed at 25 °C for 1 h at a CA of 3 mA cm^{-2} . The area of the aluminum anode was three times larger than that of the cathode, and the electrodes were separated by a distance of 2 cm. The anode electrode was polished by immersing it in cleaning solution (10 % acetic acid, 2 % HNO_3 , 60 % H_3PO_4 and 28 % H_2O), and then washing with deionized water followed by acetone. A protective layer of decane was floated on top of the Al solution to avoid any interaction between the liquid and air, as demonstrated in Fig. 1, due to the Al solution involved in this work being both air-and water sensitive.

The morphologies of the Al deposits were determined via the SEM/EDX technique. The surface roughnesses of Aluminum coatings were measured via AFM. The crystal structures of the Al coatings were recorded via the XRD technique.

The corrosion resistance of the various aluminum deposits produced were determined through data derived from Tafel plots. The tests were run using an Autolab PGSTAT20 potentiostat, a three-electrode cell with a Pt as CE that had an area similar to that of the WE (0.885 cm^{-2}), and an Ag/AgCl RE. The coatings were placed in a 0.1 M NaNO_3 solution to examine their corrosion resistance. The experiments employed a potential window of -0.25 V to 0.25 V at a scan rate of 10 mV s^{-1} with respect to the open circuit potential (OCP).

3. Results and discussion

3.1. Cyclic voltammetric studies

The new aluminum deep eutectic solvent prepared in this work was AlCl_3 :*N*-methylacetamide in a 1:1 M ratio. Consequently, it would be of interest to examine the redox behavior of aluminum in this liquid.

Fig. 2 (a) shows cyclic voltammograms of the aluminum deposition from the (1:1) *N*-methylacetamide- AlCl_3 -based liquid, recorded at room temperature using a platinum electrode vs. Ag wire. The redox reaction was recorded involving a potential windows of +1 V to -2.5 V at 25 °C, in which two distinct processes were detected that correspond to the deposition and dissolution of aluminum. The peak shapes are typical of

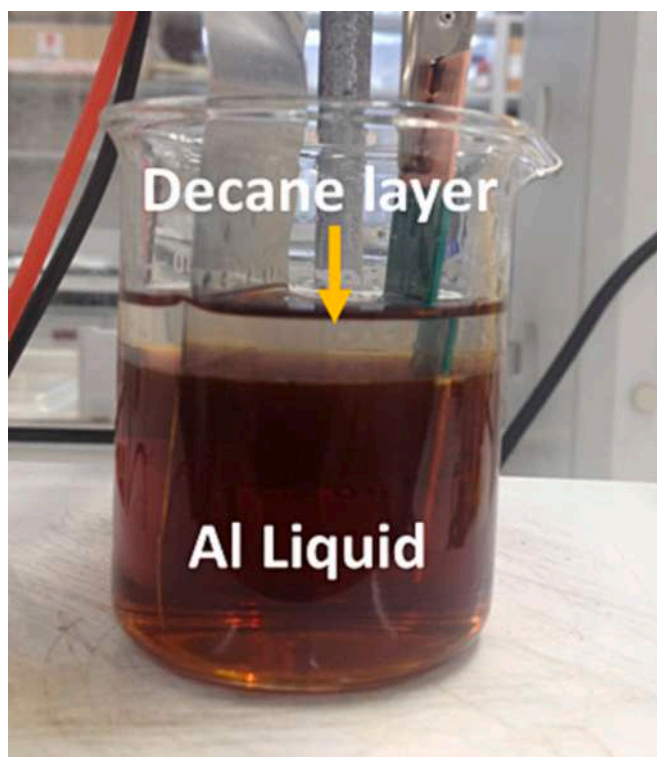
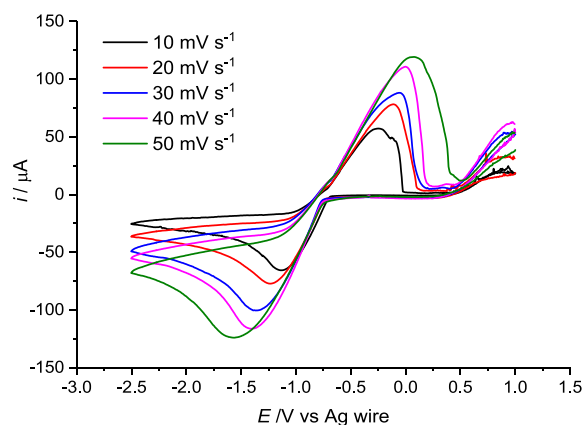


Fig. 1. The plating bath used to deposit aluminum on the copper substrate under specific conditions (room temperature and at 3 mA cm^{-2}).

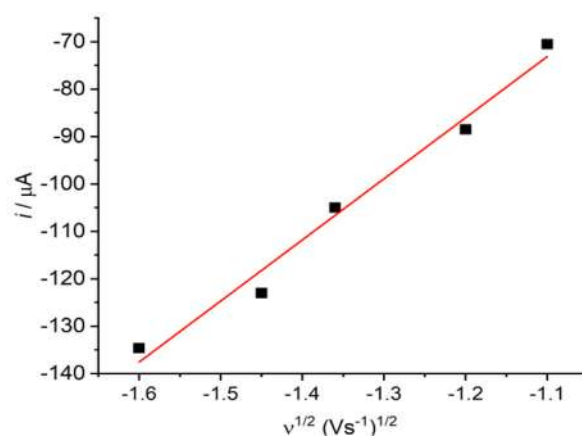
the aluminum reduction described for other ILs [26–28]. The underpotential deposition of aluminum was noted to occur $+0.35 \text{ V}$, while aluminum reduction occurred at -0.78 V . The oxidation of the pure aluminum that had been deposited on the Pt surface was found to occur at about -0.25 V .

Fig. 2 b), shows good linearity, this indicates that electrodeposition of aluminum from (1:1) AlCl_3 :*N*-methylacetamide eutectic solvent is mostly affected by mass diffusion and certain kinetic limitations.

There are a number of observations that can be made by examining the data presented in Fig. 2 (a) and (b).



(a)

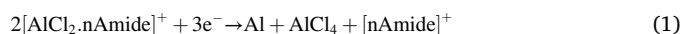


(b)

Fig. 2. a) Cyclic voltammograms of aluminum in the (1:1) AlCl_3 :*N*-methylacetamide-eutectic solvent performed using a Pt WE vs. Ag wire at 25°C at different scan rates, and b) deposition current peaks for the (1:1) AlCl_3 :*N*-methylacetamide eutectic solvent as a function of the square root of scan rate.

- (i) The increase in the cathodic peak current, I_{pc} , and the anodic peak current, I_{pa} , are directly proportional to the square root of scan rate ($v^{1/2}$);
- (ii) The increase in scan rate developed according to the ratio I_{pa}/I_{pc} (becomes greater than unity, and tends towards unity)
- (iii) E_{pc} shifted towards the cathodic with enhancing rate of scan.

These points reinforce the findings of Brown and Large, [29] that the oxidation and reduction of aluminum from the *N*-methylacetamide/ AlCl_3 -based liquid at room temperature fit the criteria that define a quasi-reversible charge transfer mechanism. Generally speaking, one can characterize the redox process at an electrode surface according to two processes in electrochemical reactions: a charge transfer process ($\text{O} + n\text{e}^- = \text{R}$), and a mass transfer (diffusion) of electroactive species. Charge transfer and diffusion of the electroactive species might both be important, however, which is considered a *quasi-reversible reaction*. In this work, the cathodic charge transfer reaction of aluminum from an *N*-methylacetamide/ AlCl_3 is indicative of Eq. (1). The given mechanism is not intended to indicate a concerted 3-electron transfer mechanism but is a summary of the overall process and in particular, indicative of the ligand exchange [30].



However, it should be noted that the actual process can be either more or less complex than implied in this representation. The given mechanism is not intended to indicate a concerted three-electron transfer mechanism but is a summary of the overall process and, in particular, indicative of the ligand exchange. In a quasi-reversible process, the reduction rate is concluded by the diffusion process [28,31–35] and so the current function, $I_p/v^{1/2}$, should be essentially (though not entirely) independent of scan rate [28,29]. Cyclic voltammograms of a 1 AlCl_3 :1 *N*-methylacetamide eutectic solvent using an Al working electrode vs. Ag wire and Al counter electrode with and without 0.01 M nicotinamide at a scan rate of $50 \text{ mV} \cdot \text{s}^{-1}$ were recorded, as shown in Fig. S2. The conductivity of the AlCl_3 :*N*-methylacetamide-based eutectic solvent was measured and found to be 1.416 mS cm^{-1} , as shown in Fig. S1. A complex between aluminum and oxygen and nitrogen atoms is formed in the liquid due to methyl group can be formed via the nitrogen atoms [23], as demonstrated in the structure of *N*-methylacetamide (Fig. 3).

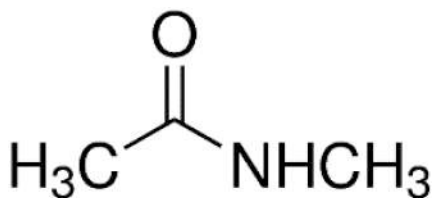


Fig. 3. Structure of *N*-methylacetamide.

3.2. Effect of nicotinamide on the CVs of aluminum in the (1:1) AlCl_3 :*N*-methylacetamide eutectic solvent

The effects of nicotinamide (NA) on the electrochemical behavior of aluminum in the (1:1) AlCl_3 :*N*-methylacetamide ionic liquid were studied, as illustrated in Fig. 4. Cyclic voltammograms of aluminum were measured at scan rates of 30 mV s^{-1} and at 25°C in all experiments. The CVs show two reduction and one anodic peak, with the deposition peak at -1.5 V corresponding to the bulk reduction of aluminum. NA has been shown to significantly affect the CVs of aluminum, with a decrease in the intensities of the stripping peaks of aluminum being observed with increasing amounts of NA in the aluminum liquid, as shown in Fig. 4. A negative shift in the deposition positional of aluminum was also observed as a result of introducing NA to the aluminum solution. It can be said that the changes in the CVs of aluminum in the (1:1) AlCl_3 :*N*-methylacetamide ionic liquid in the presence of NA are related to the adsorption of the latter onto surface of the electrode by an electron pair and which blocks the active site of the substrate, as a consequence affecting the nucleation of the Al growth mechanism and impeding aluminum deposition. Two anodic peaks are obtained when the electrodeposition of Al is carried out in a bath of 30 mM NA, as shown in Fig. 4. It is believed that the presence of two anodic processes could be identifiably attributed to two different crystal lattices being deposited. It is notable that the addition of NA substantially decreases the anodic current response. This could be due to the reduced amount of deposition arising when the NA is added gradually.

The additives can work in two ways: 1) they can present as a ligand, which can coordinate to the metal ions; or 2) the additives can adsorb on surface of cathode electrode and inhibit growth metal deposition [36]. Here, in this work, no change in the color of Al solution was noted when nicotinamide was added to the plating bath, so it was suggested that nicotinamide adsorbed onto the electrode surface and hindered the growth of the Al [37].

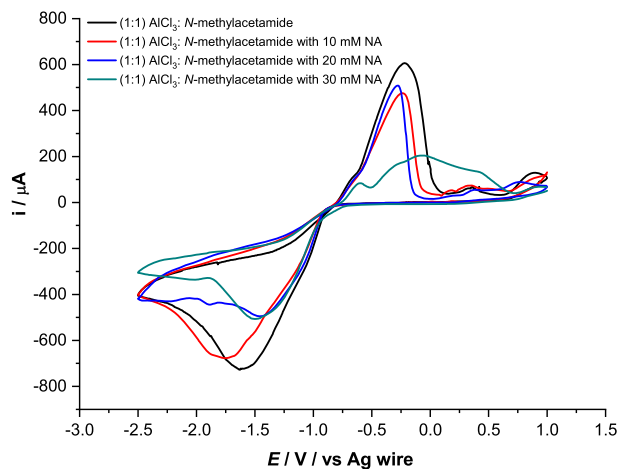


Fig. 4. Cyclic voltammograms of aluminum in (1:1) AlCl_3 :*N*-methylacetamide with and without NA at a scan rate of 30 mV s^{-1} and at 25°C .

3.3. Chronocoulometry

Chronocoulometry is considered a classical electrochemical method that can be used to evaluate whether a process is undergoing kinetic or mass transport control through the measurement of charge as a function of time. In this study, all chronocoulometry experiments for the electrodeposition of aluminum in (1:1) AlCl_3 :*N*-methylacetamide with various concentrations of NA as an additive were performed using a Pt electrode at 25°C , as shown in Fig. 5. The potential range was between 0.0 (10 s held) and -1.3 V over 15 min. The results in Fig. 5 show non-linear curves for plots of charge vs. $t^{1/2}$, indicating that the electrochemical reactions studied in these experiments are not diffusion controlled. These data are analogous to those reported in previous studies that also indicate that the nickel and zinc coatings from DESs were not diffusion controlled [20,38]. It can be observed that the charge associated with aluminum deposits rises steadily over time and the electrochemical process of aluminum deposition for the system without NA is faster than when this additive has been added to the electrolyte. In addition, the amount of charge for aluminum deposits decreased with increasing amounts of additive (NA) in the electroplating bath. These findings match the interpretation of results from the cyclic voltammetry discussed in the previous section. In accordance with Faraday's law ($Q = nFN$), the measured charge is directly proportional to the number of moles (N) of the deposited species. Therefore, the current efficiency of aluminum deposition from (1:1) AlCl_3 :*N*-methylacetamide decreases with increasing concentration of additive, and is lower than the efficiency of the same metal from an additive-free electrolyte.

3.4. Electrodeposition of aluminum from an AlCl_3 :*N*-methylacetamide-based liquid

The morphology of the surfaces of the aluminum deposited from the AlCl_3 :*N*-methylacetamide solvent without NA at 25°C and a current density of 3 mA cm^{-2} for 1 h on mild steel substrates was first investigated in this study via scanning electron microscopy (SEM). Fig. 6 (a) shows a grey layer of aluminum completely covering the surface of mild steel substrate at the end of the electrodeposition. The surface morphology seen in Fig. 6 (b) indicates a homogenous structure and large uneven crystallites with some aggregations of aluminum deposits. These findings are in agreement with those described in previous work [12,39]. In addition, the presence of elemental aluminum on the surface of the mild steel substrate after electrodeposition was confirmed via EDX analysis, which showed a larger sharp peak corresponding to aluminum located at 1.5 eV , as illustrated in Fig. 6 (c).

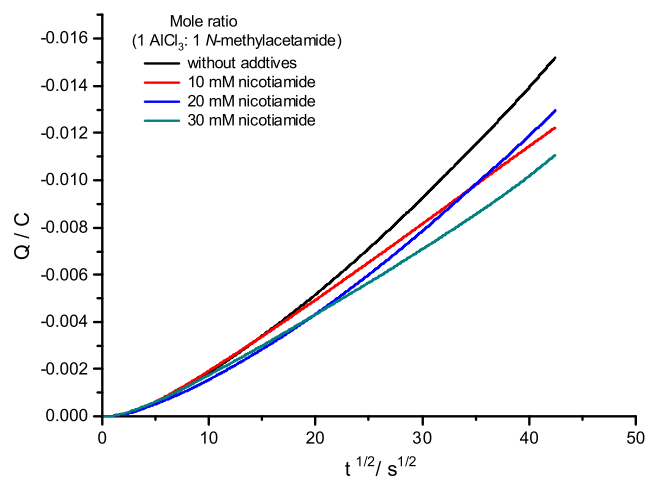


Fig. 5. Chronocoulometry of aluminum in (1:1) AlCl_3 :*N*-methylacetamide at various concentrations of NA deposited on a Pt electrode (dia. 1 mm^2) at a voltage of -1.3 V for a duration of 1200 s and at 25°C .

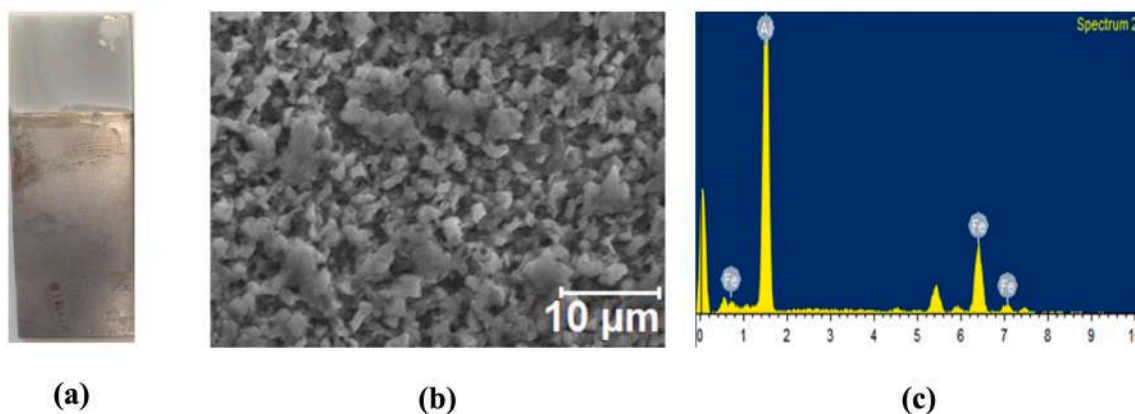


Fig. 6. Illustrations of the (a) image, (b) SEM, and (c) EDX of the aluminum coating achieved in the AlCl_3 :*N*-methylacetamide solvent without the NA additive. The deposition process was carried out for 1 h at a current density of 3 mA cm^{-2} on a steel plate at 25°C (sample width: 2 cm).

3.5. Electrodeposition of aluminum from an AlCl_3 :*N*-methylacetamide-based liquid on different substrates

The substrate material has a significant influence on the surface morphology and grain size of the metal deposited during electroplating, so a suitable substrate material is required to obtain a smooth and bright surface morphology. In order to select the optimum substrate substance for the electroplating of aluminum, four typical substrate materials (copper, stainless steel, mild steel, and brass) were assessed, with the subsequent morphologies of the aluminum films obtained for each analyzed via SEM, as shown in Fig. 7. The nature of the electrode surface plays a significant role in the electroplating process (electron transfer). Different electrodes (copper, stainless steel, mild steel, and brass) were used in this work to study the influence of the type of the electrode on the surface properties of the Al coating produced, such as roughness and morphology.

Herein, the electroplating process was carried out in AlCl_3 :*N*-methylacetamide IL at a CD of 3 mA cm^{-2} at 25°C in all experiments. The surface morphology of the aluminum film deposited on the copper substrate is relatively homogenous in structure, with grains that are relatively uniform in size and pyramidal in shape, in addition to giving the brightest, smoothest, and more compact film than the other substrates.

The efficiency of the electrodepositions of aluminum from AlCl_3 :*N*-methylacetamide-based liquid on each of the substrates was calculated. The current efficiency of the electrodeposition on copper was found to be about 88 %, while that for aluminum deposited on mild steel was

about 61 %, on stainless steel about 56 %, and on brass about 81 %, indicating that the electrodeposition rate of aluminum on a copper substrate is faster and easier than the other substrates initially tested; therefore, the copper substrate was chosen for use in all subsequent experiments. Further SEM and EDX data are given in Fig. S4. Additional data on the effect of current density on the deposition Al are shown in Fig. S5.

3.6. Influence of nicotinamide on electrodeposition of aluminum coatings

The effect of the concentration of the NA additive on the aluminum deposits obtained from AlCl_3 :*N*-methylacetamide-based liquid was also investigated. Fig. 8 depicts optical images and the results of the SEM and AFM analysis for the electrodeposition of aluminum from *N*-methylacetamide in the presence and absence of various concentrations of NA. All of the aluminum electrodeposition experiments were carried out at a current density of 3 mA cm^{-2} , a time of 1 h, on a copper substrate, and at 25°C . As mentioned earlier in this study, the grain size and roughness of the deposited aluminum are increased when the electrodeposition is performed from *N*-methylacetamide that does not contain any NA additive (Fig. 8 (e) and (i)). However, it was found that the size of particles of the aluminum deposits reduced and their morphologies became much denser and smoother with increasing amounts of NA in the AlCl_3 :*N*-methylacetamide liquid until [NA] reached 0.02 M, as shown in Fig. 8 (f) and (g). It can therefore be concluded that important changes in the surface morphologies of the aluminum coatings occurred when the electrodeposition took place in the presence of an [NA] of 0.01–0.02 M

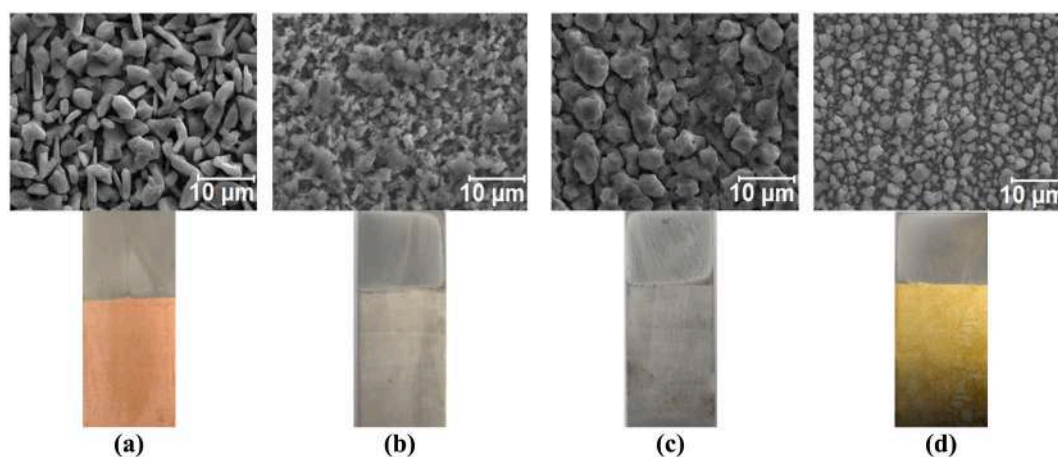


Fig. 7. Electrodeposition of aluminum from AlCl_3 :*N*-methylacetamide-based liquid on different substrates: a) copper, b) stainless steel, c) mild steel, and d) brass, all at a CD of 3 mA/cm^2 , at 25°C .

Optical images

SEM

AFM

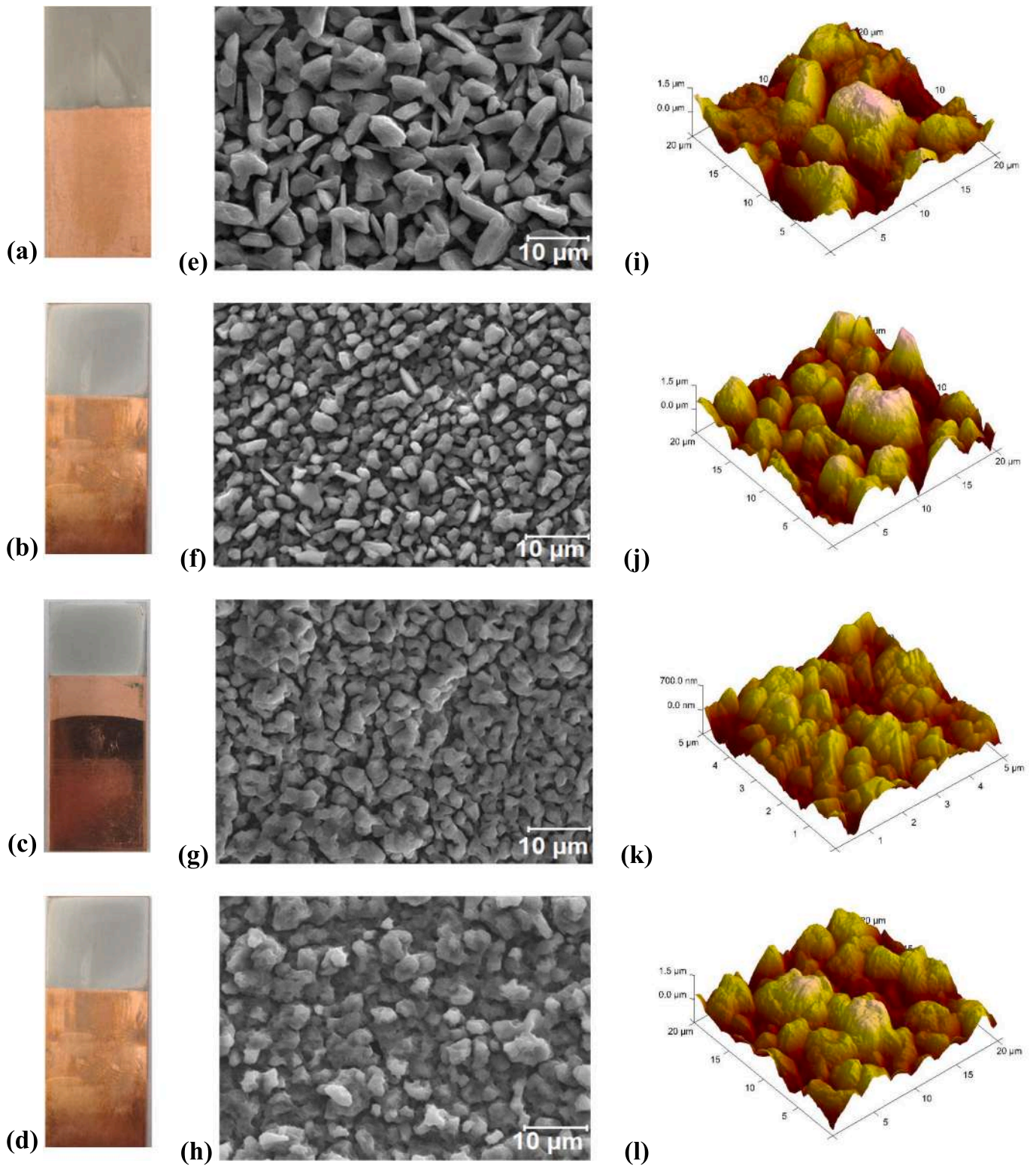


Fig. 8. Optical photographs (a-d), SEM morphologies (e-h), and AFM (i-l) of the Al electrodeposits obtained from $AlCl_3/N$ -methylacetamide on a copper substrate at 3 mA cm^{-2} and at $25 \text{ }^\circ\text{C}$ for 1 h with various concentrations of NA: samples (a, e, i) 0 M, (b, f, j) 0.01 M, (c, g, k) 0.02 M, and (d, h, l) 0.03 M.

in the AlCl_3 :*N*-methylacetamide IL, indicating that NA plays an important role in refining the particle size of the deposit, and in particular leading to a smaller grain size and smoother morphology with brighter coatings, as shown in the optical images (Fig. 8 (b-d)).

In addition, AFM was used to further support the above conclusions, and for the characterization of the surface topographies and roughnesses of the aluminum films made from the AlCl_3 :*N*-methylacetamide at 25 °C, with and without various concentrations of NA additive, as illustrated in Fig. 8 (i-l). It is clear that increased roughness (~671 nm) with a bigger grain size were achieved in the aluminum electrodeposited from the additive-free electrolyte, while an increase in the concentrations of NA in the bath solution resulted in aluminum deposits that were less rough, more homogeneous, and of a smaller grain size. The roughness of the aluminum coatings decreased to 522 nm, and then 312 nm, for NA concentrations of 0.01 and 0.02 M in the electrolyte, respectively. These results provide further support for the hypothesis that the NA additive was strongly adsorbed onto the surface of the copper substrate, increasing the rate of nucleation and inhibiting the growth of aluminum nuclei during the electroplating process. The results of this research are in agreement with those reported in earlier works in this regard [12,40].

3.7. XRD analysis

3.7.1. Crystal structures of aluminum deposit

The XRD analyses of the aluminum coatings formed from (1:1) AlCl_3 :*N*-methylacetamide with various concentrations of NA additive were studied to explore the relationship between the crystal orientations of the aluminum deposits and their surface morphologies. In this study, all XRD patterns were determined from a copper at a CD of 3 mA cm^{-2} , deposited for 1 h with stirring at 25 °C. The XRD of the aluminum coated from (1:1) AlCl_3 :*N*-methylacetamide is essentially identical to the standard JCPDS card of aluminum [1,12], though the plane intensities of the aluminum deposits change with the concentration of NA. It can be observed from Fig. 9 that no significant differences were found in the positions of XRD peaks for aluminum samples deposited at various NA concentrations. Generally, their diffraction peaks were observed to emerge at $2\theta = 38.54^\circ$, 44.74° , 65.17° , and 78.34° , which can be attributed to the (111), (200), (220), and (311) planes, respectively as observed in earlier studies [1,12]. The low intensities of the associated XRD peaks can be attributed to the fact that the deposits themselves are extremely thin. It was observed that when increasing the concentration of NA additive in the electrolyte bath, there was some degree of enhancement in the peak intensities associated with the (200) and (220) planes of the deposited aluminum, whereas the (311) plane became weaker. This is due to changes in crystallite sizes of aluminum and their

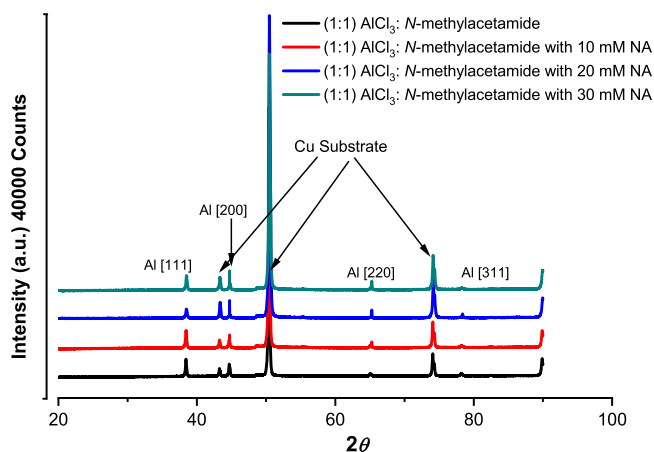


Fig. 9. The XRD data for the electrodeposition of aluminum performed from (1:1) AlCl_3 :*N*-methylacetamide on a copper substrate with and without of various amounts of NA additive.

orientations, suggesting the adsorption of the NA onto copper substrate during electrodeposition. It seems possible that these observations could also be due to the growth of aluminum in the presence of NA being slower than that found in additive-free electrolyte. Therefore, the smallest grain size of the crystallites and smoothest surface morphologies were obtained when the concentrations of NA were increased in the electrolyte bath, causing the resultant brightness of the associated coatings. The findings of this study are consistent with earlier research [20,41]. It can be concluded that the important changes in the brightness and surface morphology of aluminum deposits occurred due to the changes in the reduction of grain size and the crystal orientations during aluminum deposition with the additive, as shown by the SEM and AFM results.

3.8. Corrosion behavior of aluminum coating

The potentiodynamic polarizations of aluminum films were examined in a 0.1 M NaNO_3 electrolyte, as reported in Fig. 10 and Table 1. The investigations were performed at 25 °C, where the potential window was between -0.20 V and $+0.20 \text{ V}$ at a scan rate of 10 mVs^{-1} . The potentiodynamic polarization curves for the aluminum films obtained from AlCl_3 :*N*-methylacetamide-based liquid containing NA at concentrations of 0.01 M and 0.02 M, were shifted towards more positive potentials. This may correspond to the natural protection layer that forms on aluminum films when deposition is achieved from a solution containing NA, where the natural aluminum coating surface could be affected by the protection layers. In addition, the surface roughness of the aluminum coating strongly affected the corrosion rate. The deposit particle size on the surfaces of the aluminum coatings produced from the systems containing 0.01 M and 0.02 M NA were smaller than that generated from additive-free solution, where there is an increased roughness of the associated aluminum coating, as was earlier demonstrated via AFM. An enhanced roughness of the surface coating implies an increased surface area, and consequently an enhancement in the corrosion rate. Table 1 demonstrates the corrosion resistance of aluminum deposited from AlCl_3 :*N*-methylacetamide liquid containing NA as an additive. It can be seen from the data described in Table 1 that a reduction in the corrosion resistance of the aluminum film was noted when the coating was obtained from a solution containing NA. This could be due to the surface roughness of these coatings being smaller than that produced from the system without NA.

The mechanism of corrosion for the Al film in 0.1 M NaNO_3 electrolyte can be predicted to be the oxidation of Al, which leads to the

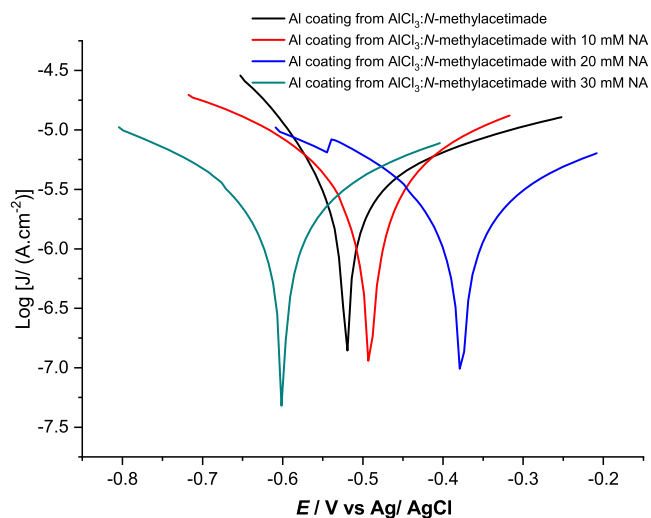


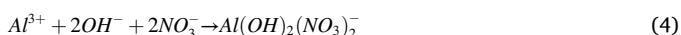
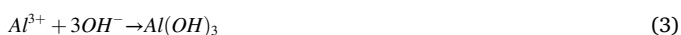
Fig. 10. Potentiodynamic polarization curves of the aluminum coatings obtained from AlCl_3 :*N*-methylacetamide with and without NA.

Table 1

Corrosion test, as achieved by polarization in a 0.1 M NaNO₃ solution, of aluminum films achieved from Al liquid.

Liquids	E _{corr} vs. Ag/AgCl/ V	i _{corr} /A cm ⁻²	Corrosion rate / mm year
Al coated from AlCl ₃ : N-methylacetamide	-0.512	5.52 × 10 ⁻⁶	1.26 × 10 ⁻¹
Al coated from AlCl ₃ : N-methylacetamide with 10 mM NA	-0.489	5.24 × 10 ⁻⁶	6.99 × 10 ⁻²
Al coated from AlCl ₃ : N-methylacetamide with 20 mM NA	-0.371	1.84 × 10 ⁻⁶	4.29 × 10 ⁻²
Al coated from AlCl ₃ : N-methylacetamide with 30 mM NA	-0.602	5.55 × 10 ⁻⁷	9.11 × 10 ⁻²

creation of Al(OH)₃ or Al(OH)₃(NO₃)₃⁻, as shown in Eqs. (2), (3), and (4), where these complexes could be converted to the Al₂O₃ layer [42]. In an sodium nitrate solution, the Na⁺ disperses towards the negative electrode, while NO₃⁻ diffuses to the anode, which holds dissolved Al.



4. Conclusion

This work reports the characterization of aluminum films deposited from an ionic liquid that is inexpensive, non-toxic, and that is relatively insensitive to moisture, namely (1:1) AlCl₃:N-methylacetamide eutectic liquid, on different substrates in the appearance and absenteeism of various concentrations of nicotinamide. Aluminum reduction in AlCl₃:N-methylacetamide liquid shifts further towards the negative with increasing concentration of NA, whilst redox current peaks reduced in intensity. A high current efficiency of 88 % was noted for the deposition of aluminum on copper plate. Bright, thick, and adherent aluminum coatings were achieved on copper substrates from aluminum liquid with an [NA] of 0.02 M. The SEM data demonstrated variations in the morphology of the aluminum coatings formed in liquid containing NA. The XRD patterns for aluminum coated from AlCl₃:N-methylacetamide-based liquids with and without NA were considered, which showed only very small changes in the comparative intensities of the aluminum crystals planes. However, the intensity of the (211) peak increased in the aluminum coating formed from AlCl₃:N-methylacetamide containing NA compared to the analogous systems without NA. Aluminum coatings derived from AlCl₃:N-dimethylacetamide liquid containing 0.02 M NA had a higher resistance to corrosion compared to those formed from AlCl₃:N-methylacetamide without the NA additive.

CRediT authorship contribution statement

Hasan F. Alesary: experimental work, writing the original draft of manuscript, and wrote supplementary information. **Hani K. Ismail:** writing the original draft of manuscript and editing. **Jalil H. Kareem** – measured SEM, AFM. **Idrees B. Qader:** Measured XRD and investigation. **Atheer Hameid Odda:** checked manuscript. **Ahmed F. Halbus:** software. **Zahraa H. Athab:** experimental work. **Ahmed Al-Yasari:** visualization. **Mark J. Watkins:** proofreading and editing. **Karl Ryder:** supervision, software, validation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

The authors wish to thank University of Kerbala and the Ministry of Higher Education and Scientific Research MHESR, Iraq, for the financial support.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.surfcoat.2023.130160>.

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