

Underpotential and overpotential deposition of Al onto Cu(111) from the AlCl_3 –EtMeImCl room temperature molten salt

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Abstract: The processes of underpotential (UPD) and overpotential (OPD) deposition of Al onto Cu(111), from the room temperature molten salt AlCl_3 –EtMeImCl of different compositions, has been investigated by the cyclic voltammetry (CV) and potentiostatic pulse techniques. It was shown that the CVs of the UPD are characterized by two sharp peaks, while the potentiostatic cathodic and anodic j – t -transients of this process are characterized by two waves, indicating that the UPD of Al results in the formation of two structures. The first, less dense one, most probably the $(\sqrt{3} \times \sqrt{3})R30^\circ$ ordered structure of Al, is formed at a more positive potential of about 200 mV vs. Al, while the second one, a complete monolayer of Al, is formed at about 20 mV vs. Al, just before the reversible potential of Al in these melts (–20 mV vs. Al). The OPD of Al was detected at potentials more negative than –30 mV vs. Al, occurring through the progressive 3D nucleation and growth mechanism. Slow surface alloying of Al with Cu was found to occur at a potential close to the reversible potential of Al.

Keywords: AlCl_3 –EtMeImCl, room temperature molten salt, UPD and OPD, Cu(111), $(\sqrt{3} \times \sqrt{3})R30^\circ$, progressive 3D nucleation and growth, Al–Cu surface alloying.

INTRODUCTION

It has been shown that Ag–Cd alloys are thermodynamically stable in the UPD region ($0 < \Delta E = E - E_r < 70$ mV) at elevated temperatures in molten salts¹ and in aqueous solutions.^{2,3} This statement was proved by the results of Schmidt *et al.*,⁴ obtained on a polycrystalline silver electrode, and the results of Bort *et al.*⁵ and Jović *et al.*,⁶ obtained on single crystal silver electrodes. For the systems Al–Au and Al–Pt, this phenomenon has been demonstrated in inorganic chloroaluminate molten salts.⁷ It was shown that the UPD of Al onto an Au electrode starts at potentials about 0.4 V more positive than the reversible potential of Al in an equimolar AlCl_3 –NaCl molten salt at the temperature of 250 °C. Several intermetallic compounds, such as Al_2Au , AlAu_2 and Al_2Au_5 , obtained by holding the potential of the Au electrode in the UPD region of Al deposition, were detected by an X-ray investigation of the deposited samples.⁸ A similar phenomenon, occurring in the potential region between 0.6 V and 0.0 V vs. Al,

has been demonstrated for the system Ni–Al in a $2\text{AlCl}_3\text{--NaCl}$ molten salt and Ni–Al alloys of different compositions were successfully deposited from this molten salt containing 0.17 M Ni(II) ions.⁹ The disadvantage of the use of alkali-chloride based chloroaluminates is the substantial vapor pressure of Al_2Cl_6 associated with the acidic composition region of these molten salts.

By introducing organic chloroaluminates,¹⁰ such as 1-(1-butyl)pyridinium chloride (BupyCl), or 1-methyl-3-ethylimidazolium chloride (EtMeImCl), mixtures with AlCl_3 , known as room temperature molten salts, it was possible to deposit different Al alloys by dissolution of small amounts of metal ions (Ni^{2+} , Co^{2+} , Cu^+) in the $\text{AlCl}_3\text{--BupyCl}$ ^{11,12} or $\text{AlCl}_3\text{--EtMeImCl}$ ^{13–15} molten salts at the room temperature. In all cases, alloy formation was observed at potentials more positive than the reversible potential of Al in these molten salts, which was ascribed to UPD of Al onto the deposited metal (Ni, Co, Cu).

In the case of Cu–Al alloys, it was found that Al UPD commences at about 0.3 V vs. Al and that the maximum content of Al deposited in the potential region between 0.3 V and 0.0 V can reach 43 at. %. X-Ray diffraction studies indicated that the deposit containing 12.8 at. % of Al represents a two phase region, being characterized by the presence of a fcc copper structure and a martensitic β' - Cu_3Al bcc structure.¹⁵

The process of Al UPD onto a Au electrode from a 60 mol. % AlCl_3 – 40 mol. % EtMeImCl room temperature molten salt has recently been investigated by cyclic voltammetry.¹⁶ It was shown that this process is characterized by two well defined and separate peaks, with the total amount of deposited Al being consistent with the value for a monolayer of Al. A phase transformation of a less stable into a more stable Au–Al alloy has been detected by holding a Au electrode at a potential slightly negative (–10 mV) with respect to the reversible potential of Al in this molten salt. In a very recent work in this field,¹⁷ it was shown that for metals less sensitive to the presence of oxygen, such as Au, experiments performed under ultrahigh vacuum (UHV) were identical to those recorded in a glove box, while for the far more reactive W surface, it was necessary to perform the experiments in an UHV environment.

In this paper the results of an investigation of the UPD and the OPD of Al onto Cu(111) from $\text{AlCl}_3\text{--EtMeImCl}$ molten salts of different compositions are presented and discussed.

EXPERIMENTAL

Preparation and purification of the $\text{AlCl}_3\text{--EtMeImCl}$ molten salt

EtMeImCl was synthesized from ethyl chloride and 1-methylimidazole (Aldrich 99 %) and recrystallized from acetonitrile–ethyl acetate mixtures as described in the literature.¹⁸ AlCl_3 (Fluka, puriss) was sublimed a minimum of three times under vacuum before use. In order to avoid the codeposition of hydrogen with aluminum, all traces of protonic impurities were removed from the molten salt by pre-electrolyzing the molten salt between two aluminum electrodes (Alfa Aesar, puratronic 99.999 %) for several days under stirring. The molten salt was filtered through a medium-porosity glass frit to remove any aluminum debris that may have been detached from the cathode during the electrolysis step, and then evacuated to 1.3×10^{-3} Pa for 24 h.

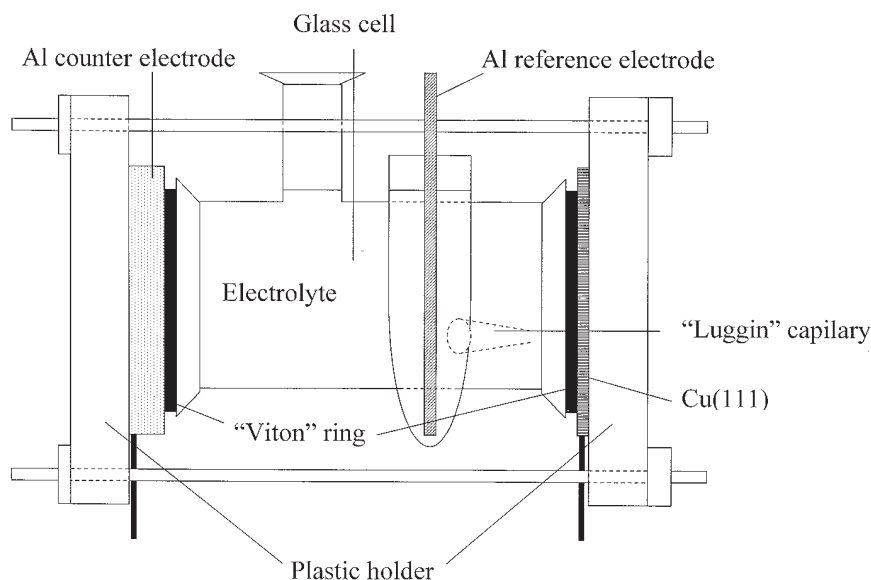


Fig. 1. Schematic representation of the experimental cell.

Instrumentation and the cell

All experiments were performed in an argon-filled glove box in which the content of oxygen was lower than 0.3 ppm. A small Pyrex glass electrochemical cell with an electrolyte volume of about 10 ml was used for all experiments at room temperature. The schematic representation of the cell indicating position of the single crystal electrode, reference electrode and counter electrode is shown in Fig. 1. High purity (Alfa Aesar, puratronic 99.999 %) aluminum wire ($d = 1$ mm) was used as the reference electrode, while an Al plate of the same quality, positioned parallel to the working electrode, was used as the counter electrode. Cyclic voltammetry experiments were performed using a universal programmer PAR M-175, potentiostat PAR M-173 and an X-Y recorder (Houston Instrument 2000R). Potentiostatic $j-t$ transients were recorded on a digital oscilloscope (Nicolet 4094A) and transferred to the X-Y recorder.

Preparation of the counter and working electrodes

The aluminum electrodes were etched for 1 min in a solution consisting of a 1:1 mixture (HF:alcohol) containing 15 vol.% H_2O_2 , washed with alcohol and dried under vacuum before being transferred to the glove box. The copper single crystal, orientation (111), (Monocrystals Comp.) was mechanically polished on fine grade emery papers (1200, 2400 and 4000) with subsequent polishing with polishing clothes impregnated with a suspension of polishing alumina with particles dimension of 1 μm , 0.3 μm and 0.05 μm . After mechanical polishing, the copper single crystal was electrochemically polished in a solution of 85 % phosphoric acid at a constant voltage of 1.7 V (vs. Pt counter electrode) until the current density dropped to a value of about 18 mA cm^{-2} . The electrode was then thoroughly washed with pure water (Barnstead - EASY pure UV). The water was removed from the electrode surface by a stream of nitrogen. The electrode was mounted on the cell (schematically presented in Fig. 1) under a stream of nitrogen and transferred into the glove box. The diameter of the working area of the single crystal was determined by a 19 mm diameter viton o-ring, *i.e.*, the surface area was 2.835 cm^2 .

RESULTS

UPD and OPD of Al onto Cu(111) have been investigated in a room-temperature molten salt $\text{AlCl}_3\text{-EtMeImCl}$ of three different compositions: 55 mol.% AlCl_3 - 45

mol.% EtMeImCl, 60 mol.% AlCl₃ – 40 mol.% EtMeImCl and 66.7 mol.% AlCl₃ – 33.3 mol.% EtMeImCl. Negligible differences of the CVs and potentiostatic $j-t$ transients recorded in these molten salts were detected and, accordingly, the results presented for one melt composition are almost identical to those of the other two compositions.

CV Results

The CVs recorded in the molten salt 55 mol.% AlCl₃ – 45 mol.% EtMeImCl at a sweep rate of 20 mV s⁻¹ onto Cu(111) at two cathodic limit potentials (200 mV vs. Al – dotted line and –20 mV vs. Al – solid line) are shown in Fig. 2. As can be seen, the UPD process is characterized by two sharp and separate peaks. When the cathodic limit was set at 200 mV vs. Al, a very sharp anodic peak (1_a) was obtained and the shape of the cathodic and anodic part of the CV were identical, characterized by one very sharp pair of peaks (1_a and 1_c). At a potential of about 20 mV vs. Al, another sharp cathodic peak (2_c) with its counter part in the anodic branch (2_a) appeared on the CV. It is interesting to note that after cycling the electrode in the potential region of peaks 2_c and 2_a, the anodic peak 1_a became less sharp, while the shoulder 1_a' transformed into a broad peak.

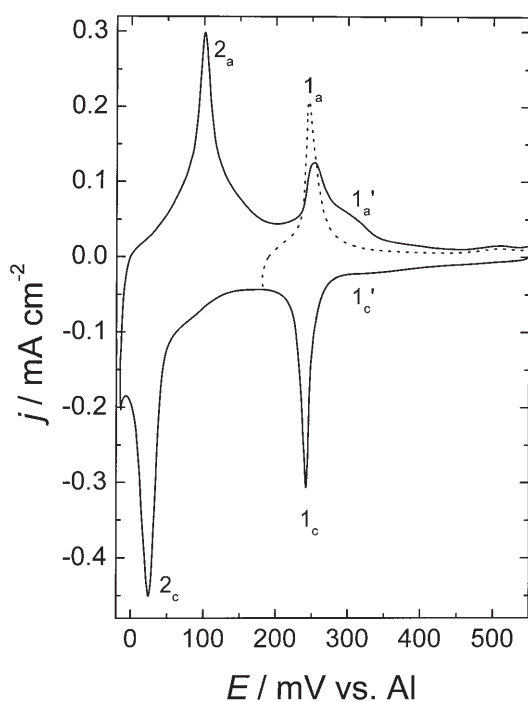


Fig. 2. CVs Recorded in the molten salt 55 mol.% AlCl₃ – 45 mol.% EtMeImCl at a sweep rate of 20 mV s⁻¹ onto Cu(111), recorded at two cathodic limit potentials (200 mV vs. Al – dotted line and –20 mV vs. Al – solid line).

The peak of the OPD of Al (3_c) appeared at about –50 mV vs. Al at a sweep rate of 50 mV s⁻¹, as can be seen in Fig. 3. This process is characterized by the presence of a typical "nucleation loop". The shape of the anodic part of the CV changed significantly after OPD of Al (dotted line). The peak of bulk dissolution of

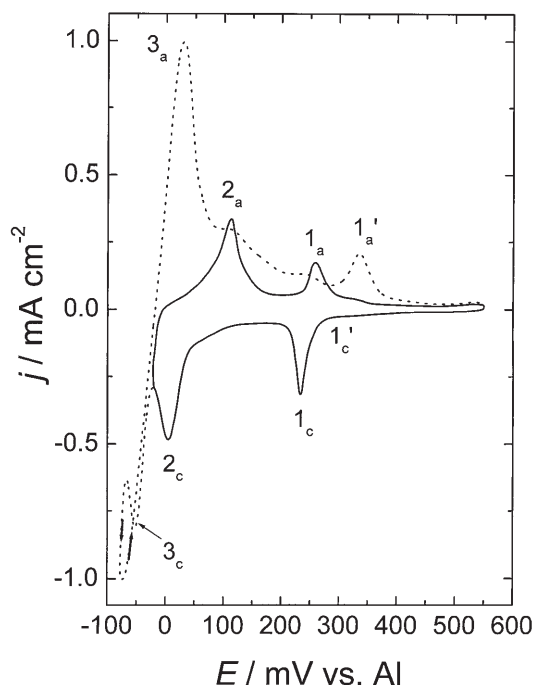


Fig. 3. CVs Recorded in the molten salt 55 mol.% AlCl_3 – 45 mol.% EtMeImCl at a sweep rate of 50 mV s^{-1} onto Cu(111), recorded at two cathodic limit potentials (-70 mV vs. Al – dotted line and -20 mV vs. Al – solid line).

Al (3_a) became well defined, peaks 2_a and 1_a transformed into shoulders, while the shoulder $1_a'$ became a well-defined peak.

A common feature of the CVs is the fact that the charge under the cathodic peaks is higher than that under the anodic ones. This could be the consequence of either simultaneous proton reduction or fast surface alloying of Cu with Al in the UPD region. Alloying of Cu with Al was detected in the potential region of a second UPD peak (2_c). The Cu(111) electrode was held at a potential of 20 mV vs. Al (potential of the peak 2_c) for different time intervals ($0 - 20 \text{ min}$) and the corresponding anodic CVs were recorded. As can be seen in Fig. 4a, the shape of the anodic CV changes with the holding of the electrode at a given potential, with the shoulder $1_a'$ becoming a more pronounced and well defined peak at longer holding times, with increasing the total charge under the CVs. The dependence of the charge excess, Δq , defined as the difference between the anodic charge recorded after holding the electrode (q_t) and the one corresponding to the CV obtained without holding the electrode at a given potential (q_0), vs. $t^{1/2}$ is shown in Fig. 4b, indicating slow alloying of Cu(111) with Al.

Of course, the possibility of a proton reduction reaction onto Cu(111) in the UPD region cannot be neglected. The appearance of a small gas bubble (1 mm in diameter) in the vicinity of the working electrode surface at the upper part of the cell, which was detected during experimental investigations lasting more than 5 h , might be the consequence of a simultaneous proton reduction and hydrogen evolution. As a consequence of such a reaction, it could be expected that the charge un-

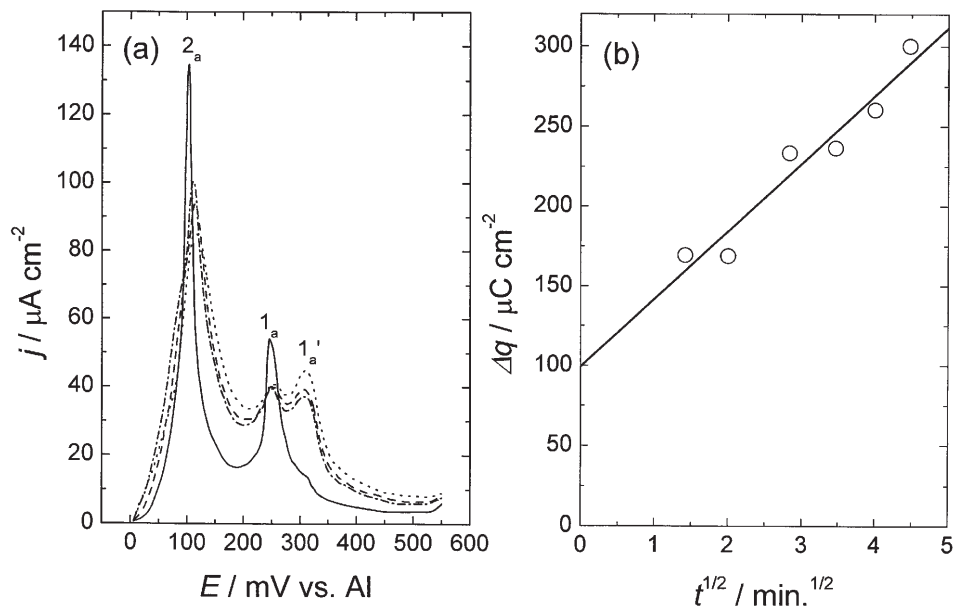


Fig. 4. (a) Anodic CVs recorded in the molten salt 55 mol.% AlCl_3 – 45 mol.% EtMeImCl at a sweep rate of 20 mV s^{-1} onto Cu(111), recorded after holding the electrode at the potential of the peak 2_c (20 mV vs. Al) for different times (solid line – 2 min, dash-dotted line – 8 min, dashed line – 16 min and dotted line – 20 min). (b) Δq vs. $t^{1/2}$ dependence obtained by analysis of the charge under the CVs shown in Fig. 4a.

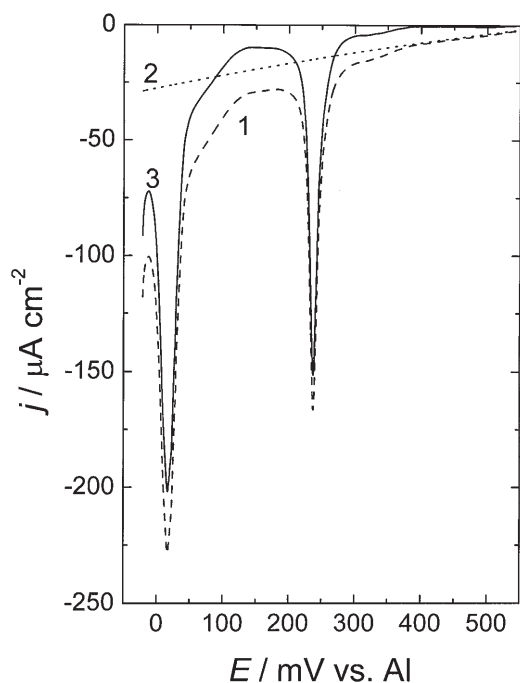


Fig. 5. Curve 1 – CV recorded in the molten salt 55 mol.% AlCl_3 – 45 mol.% EtMeImCl at a sweep rate of 20 mV s^{-1} onto Cu(111). Line 2 – CV corresponding to the proton reduction current. Curve 3 – CV obtained after subtraction of the proton reduction current (line 2) from curve 1.

der the cathodic part of the CV would be higher than that under the anodic one, which is the case for all the shown CVs. Since it is not possible to determine the value of this current, the cathodic current recorded in the potential region between 550 mV and 400 mV vs. Al of Fig. 2 was used (assuming its linear dependence on potential, Fig. 5 curve 1) and its value was subtracted from the experimentally recorded curve (curve 2 in Fig. 5) in order to obtain the “real” response for the UPD of Al onto Cu(111), presented by curve 3 in Fig. 5. It is interesting to note that the total charge under curve 3 amounts to about $720 \mu\text{C cm}^{-2}$ (a slightly higher value than the one needed for a completely discharged monolayer of Al, $Q_m = 677 \mu\text{C cm}^{-2}$), while the cathodic and anodic charges for the pair of peaks 1 (1_c and 1_a) amount to the same value of about $217 \mu\text{C cm}^{-2}$.

Potentiostatic pulse results

Potentiostatic $j-t$ transients of Al UPD onto Cu(111) recorded in 60 mol.% AlCl_3 – 40 mol.% EtMeImCl are shown in Fig. 6. The cathodic $j-t$ transients were obtained by stepping the potential in steps of 20 mV from 500 mV vs. Al (E_{in}) to the desired potential value, although only some of them are shown in the Figure, while the anodic $j-t$ transients represent the response of the system when the potential was stepped back to E_{in} . If the applied potential is positive with respect to the potential of peak 2_c (Fig. 2), the $j-t$ transients are characterized by one wave, while at potentials negative with respect to the potential of peak 2_c , two waves are present on both, the cathodic and anodic $j-t$ transients, indicating deposition and disso-

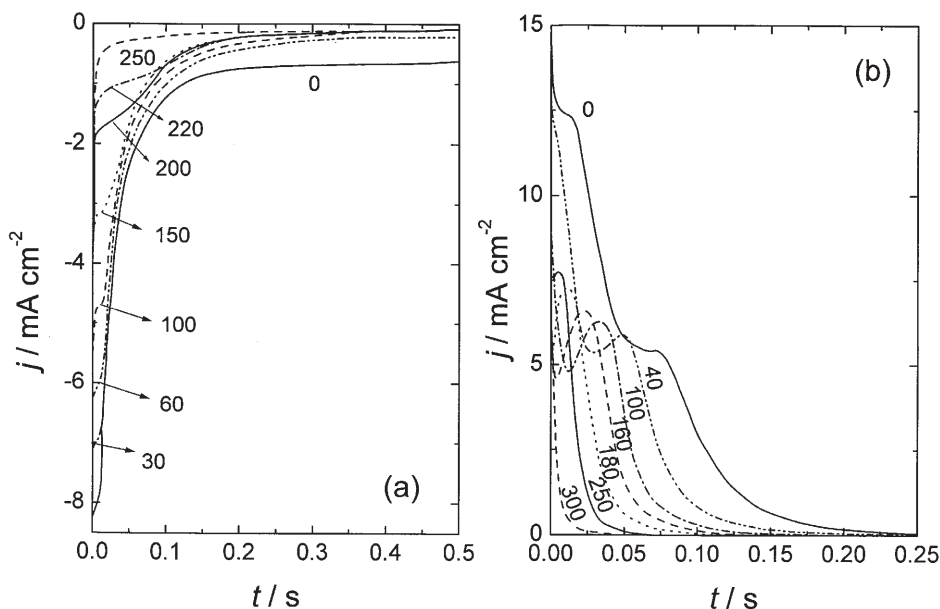


Fig. 6. Potentiostatic $j-t$ transients of Al UPD onto Cu(111) recorded in 60 mol.% AlCl_3 – 40 mol.% EtMeImCl: (a) cathodic transients; (b) the corresponding anodic transients (pulse potentials are marked in the Figure in mV vs. Al).

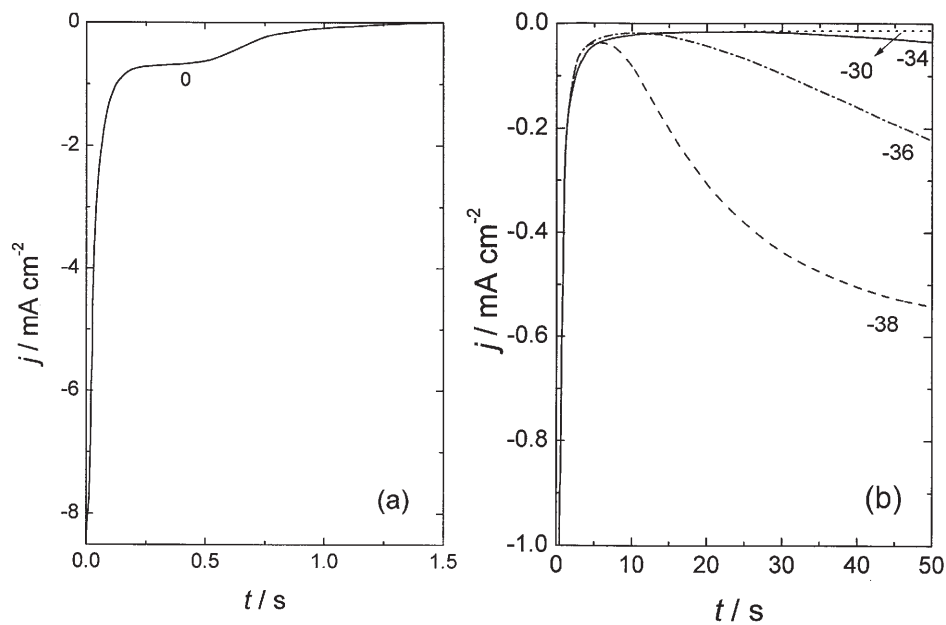


Fig. 7. (a) Potentiostatic j - t transient of Al UPD onto Cu(111) recorded in 60 mol.% AlCl₃ - 40 mol.% EtMeImCl at a potential of 0 mV vs. Al. (b) Potentiostatic j - t transients of Al OPD onto Cu(111) recorded in 60 mol.% AlCl₃ - 40 mol.% EtMeImCl at different potentials (marked in the Figure in mV vs. Al).

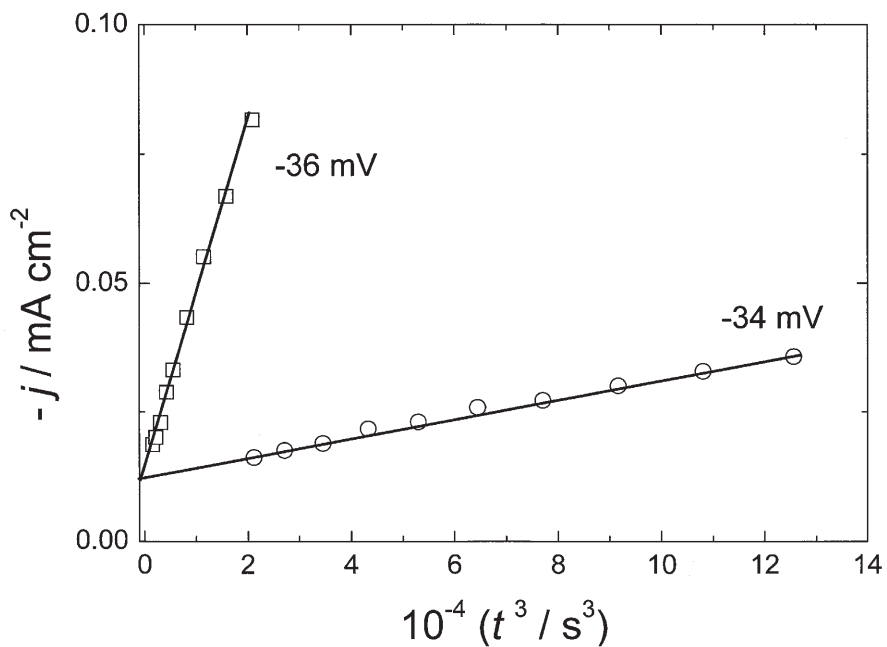


Fig. 8. j vs. t^3 Dependences obtained by analysis of the rising portion of the corresponding j - t transients shown in Fig. 7b.

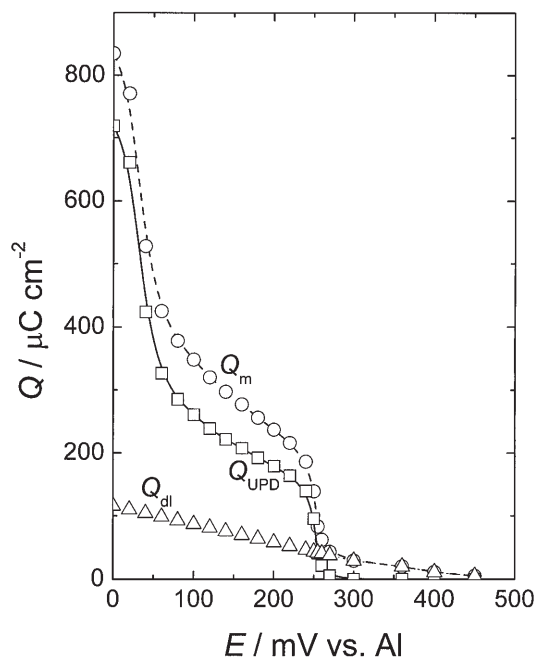


Fig. 9. Q vs. E Dependences obtained by analysis of the anodic $j-t$ transients shown in Fig. 6b: Q_m – measured values; Q_{dl} – charge corresponding to the double layer; Q_{UPD} – charge corresponding to the UPD process.

lution of two different structures. It should be mentioned here that all anodic responses were recorded after application of a 1.5 s cathodic pulse, the current density on the cathodic $j-t$ transients dropped to zero after 1.5 s, indicating that the UPD of Al was finished (see Fig. 7a).

A complete $j-t$ transient recorded onto the Cu(111) face at $E_p = 0$ mV vs. Al in 60 mol % $AlCl_3 - 40$ mol.% EtMeImCl molten salt is shown in Fig. 7a. As can be seen, the duration of the cathodic pulse must be 1.5 s for completion of a monolayer of Al. The potentiostatic $j-t$ transients for OPD of Al onto Cu(111) in the same molten salt are shown in Fig. 7b. As can be seen, a rising current on these transients can only be detected if the applied potential is more negative than -30 mV vs. Al, indicating that the cathodic peak 3_c in Fig. 3 corresponds to the beginning of the OPD of Al.

By analysis of the rising portion of the $j-t$ transients of OPD of Al recorded at -34 mV and -36 mV vs. Al (shown in Fig. 7b), linear j vs. t^3 dependences, shown in Fig. 8, were obtained, indicating the occurrence of a progressive 3D nucleation and growth mechanism of Al OPD onto Cu(111).¹⁹

The dependence of the charge recorded under the anodic $j-t$ transients as a function of the pulse potential is shown in Fig. 9, where Q_m represents the measured charge. As can be seen, in the potential region between 500 mV and 300 mV vs. Al, this dependence is linear and most likely represents double layer charging since there are no peaks on the CV. In this case, the contribution of the proton reduction current can be neglected, since only anodic responses were recorded. Hence, the values of Q_{dl} , represented by the linear dependence in Fig. 8 should be subtracted from the measured ones (Q_m) in order to ob-

tain “real” values for the charge corresponding to the process of UPD (Q_{UPD}) of Al onto Cu(111). As can be seen, a sharp increase in Q_{UPD} was recorded in the potential region between 300 mV and 350 mV vs. Al and between 50 mV and 0 mV vs. Al, which is in good accordance with the CV shown in Fig. 2.

DISCUSSION

The results presented in Fig. 4 clearly indicate slow surface alloying of Cu with Al in the UPD region.^{5,18,20} The appearance of a new anodic peak on the CV (peak 1_a'), as well as a linear dependence of Δq vs. $t^{1/2}$ can only be ascribed to a slow alloying of Cu(111) with Al.

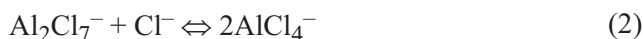
The third cathodic peak, recorded just before a “nucleation loop” (Fig. 3), corresponds to the commencement of OPD of Al. A common way of determining the reversible potential of the OPD in the case of a “nucleation loop” is the point at which the back-going sweep crosses the zero current line. By careful consideration of Fig. 3, it can be seen that this point amounts to about -20 mV vs. Al. This is also confirmed by the results presented in Figs. 7b and 8. Three dimensional growth of Al onto Cu(111), characterized by a rising portion on the $j-t$ transients, starts at pulse potentials more negative than -30 mV vs. Al, indicating that the nucleation overpotential for 3D nucleation and growth of Al is about -10 mV. By analysis of the rising portion of the $j-t$ transients (the part of the $j-t$ transients where individual nuclei can still grow without overlapping with their neighbors) recorded at -34 mV and -36 mV vs. Al, linear j vs. t^3 dependences, shown in Fig. 8, were obtained, indicating the occurrence of a progressive 3D nucleation and growth mechanism¹⁹ of Al OPD onto Cu(111). It should be mentioned here that these results are in good accordance with the results presented for 3D nucleation and growth of Al onto a glassy carbon electrode from $\text{AlCl}_3\text{-NaCl}$ molten salt.⁷

Considering the CV obtained by setting the potential limit at 200 mV vs. Al, Fig. 2, it can be seen that the anodic and cathodic peaks are identical, indicating a reversible adsorption/desorption process. The fact that both peaks are composed of a sharp peak (1) with a shoulder (1') indicates that the nature of this process is complex. According to the charge under the cathodic peaks 1_c' and 1_c obtained after subtraction of the proton reduction current and the double layer charging current (curve 3 in Fig. 6), which amounts to 217 $\mu\text{C cm}^{-2}$, as well as according to the $Q_{\text{UPD}} - E$ dependence shown in Fig. 9, it is most likely that in the case of complete charge transfer, an ordered $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure of Al onto Cu(111) is formed. It should be emphasized here that the behavior of the $\text{Al}^{3+}/\text{Cu}(111)$ system in a room temperature $\text{AlCl}_3\text{-EtMeImCl}$ molten salt is almost identical to the behavior of $\text{Cd}^{2+}/\text{Ag}(111)$ ²⁰ and $\text{Cd}^{2+}/\text{Cu}(111)$ ²¹ systems in aqueous electrolytes, where slow alloying and $(\sqrt{3} \times \sqrt{3})R30^\circ$ structures were defined. However, one significant difference appears to exist in the shape of the $j-t$ responses of these systems. Thus, in the case of the $\text{Cd}^{2+}/\text{Ag}(111)$ ⁶ and $\text{Cd}^{2+}/\text{Cu}(111)$ ²⁰ systems in aqueous

electrolytes both the cathodic and anodic $j-t$ responses are composed of only one wave, although two different structures are formed, the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure and a full monolayer, while in the system $\text{Al}^{3+}/\text{Cu}(111)$ both $j-t$ responses are composed of two waves when the pulse potential is more negative than the peak potential of the formation of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure (about 230 mV vs. Al). This could be due to the fact that Al UPD from the acidic $\text{AlCl}_3\text{-EtMeImCl}$ molten salt can occur by the following electrochemical reaction¹²⁻¹⁶



During this reaction Cl^- ions are liberated and they react with Al_2Cl_7^- ions to form AlCl_4^-



Hence, first the AlCl_7^- complex is reduced and then AlCl_4^- complex is formed in the vicinity of the electrode surface. It is most likely that these two reactions influence the rate of the Al UPD process in both directions, cathodic and anodic, and, accordingly, cause two waves on the $j-t$ transients to appear, which is not the case for aqueous electrolytes in the systems $\text{Cd}^{2+}/\text{Ag}(111)$ ⁶ and $\text{Cd}^{2+}/\text{Cu}(111)$.²⁰

CONCLUSIONS

From the results presented in this paper, it can be concluded that the UPD of Al onto Cu(111), from the room temperature molten salt $\text{AlCl}_3\text{-EtMeImCl}$ of different compositions, takes place through two structures. The first, less dense one is most likely the $(\sqrt{3} \times \sqrt{3})R30^\circ$ ordered structure of Al, formed at more positive potentials of about 200 mV vs. Al and the second one is a complete monolayer of Al, formed at about 20 mV vs. Al, just before the reversible potential of Al in these melts (-20 mV vs. Al). OPD of Al was detected at potentials more negative than -30 mV vs. Al, which occurs through the progressive 3D nucleation and growth mechanism. Slow surface alloying of Al with Cu was found to occur at potentials close to the reversible potential of Al.

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ИЗВОД

ЕЛЕКТРОХЕМИЈСКО ТАЛОЖЕЊЕ АЛУМИНИЈУМА НА МОНОКРИСТАЛУ
БАКРА ОРИЈЕНТАЦИЈЕ (111) ПРИ ПОТЕНЦИЈАЛИМА ПОЗИТИВНИЈИМ И
НЕГАТИВНИЈИМ ОД РАВНОТЕЖНОГ ИЗ РАСТОПА СОЛИ $\text{AlCl}_3 - \text{EtMeImCl}$
НА СОБНОЈ ТЕМПЕРАТУРИ

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Процес електрохемијског таложења алуминијума на монокристалу бакра оријентације (111) из растопа соли $\text{AlCl}_3 - \text{EtMeImCl}$ на собној температуре испитиван је методама цикличне волтаметрије и потенциостатског пулса. Показано је да се при потенцијалима позитивнијим од равнотежног одиграва процес таложења монослоја алуминијума, који је окарактерисан са два оштра струјна врха на цикличним волтамограмима, одн. два јасно дефинисана катодна и анодна струјна таласа на потенциостатским струја–време одговорима, указујући на формирање две различите структуре: на потенцијалу од око 200 mV vs. Al највероватније се формира уређена структура алуминијума $(\sqrt{3} \times \sqrt{3})R30^\circ$, док се на потенцијалу од око 20 mV vs. Al формира монослој алуминијума. При потенцијалима негативнијим од равнотежног ($E < -30$ mV vs. Al) долази до тро-димензионалног таложења алуминијума које се одиграва путем постепене нуклеације и раста талога. Такође је показано да се у областима потенцијала блиским равнотежном одиграва процес спорог површинског легирања алуминијума са бавром.

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