STM STUDY OF 2D AND 3D PHASE FORMATION OF NI AND NI-AL ALLOYS DURING ELECTRODEPOSITION FROM A CHLOROALUMINATE MOLTEN SALT

C.A. Zell and W. Freyland

Institute of Physical Chemistry
University of Karlsruhe (TH)
Kaiserstrasse 12
D-76128 Karlsruhe, Germany

ABSTRACT

The electrodeposition of Ni and Ni-Al alloys from the Lewis acid ionic liquid AlCl₃/I-butyl-3-methylimidazolium chloride on Au(111) has been studied by STM. Phase formation of pure nickel close to its equilibrium potential is characterized by 2D layer-by-layer growth, whereas at more negative potentials a transition to 3D cluster growth is observed, which occurs almost exclusively along the substrate steps. At potentials below -0.25 V vs. Ni/Ni(II) simultaneous deposition of Al sets in leading to formation of Ni-Al alloy deposits. The structure of these alloy films depends strongly on their aluminium content. Voltage tunneling spectroscopy has been performed at the electrode/electrolyte interface in order to determine effective tunneling barriers at various potentials. The barrier height decreases with increasing aluminium content of the electrodeposit within the range of 1.0 eV to 0.3 eV.

INTRODUCTION

Scanning Tunneling Microscopy (STM) and its application to in situ studies of electrocrystallization has provided a completely new insight into interfacial electrochemistry on a nanometer scale (1,2). Details of the first stages of electrocrystallization, in particular of nucleation or 2D and 3D growth processes, can be imaged in real space by electrochemical scanning probe techniques (3). Thus, for example Ni deposition from aqueous electrolytes has been studied in detail on single crystal surfaces of various orientation such as Au(111) and Au(100) (4,5). These experiments showed that both substrate morphology and electrolyte composition strongly influence the equilibrium potential and the growth mechanism (6). In addition, because of the low reduction potential of nickel, hydrogen evolution occurs simultaneously with metal deposition, which is also expected to affect the electrodeposition process (4). Using molten salt electrolytes, complications due to the restricted electrochemical window of the solvent can be circumvented, because ionic liquids usually exhibit a significantly enhanced potential range for electrodeposition of elements and alloys, metals or semiconductors (7).

Lewis acidic (AlCl₃-rich) chloroaluminate molten salts such as AlCl₃/I-butyl-3-methylimidazolium chloride (BMIC) have been shown in numerous studies to be useful
solvents for the electrodeposition of transition metal-aluminium alloys, for example of Ni-Al (8), or Ag-Al (9). The main advantage of these ionic solvents is the fact, that they provide a concentrated reservoir of easily reducible aluminium-species, such as Al₂Cl₇⁻. In many cases, codeposition of aluminium with the respective transition metal is observed at potentials considerably higher than the equilibrium potential of pure aluminium (9). This behaviour has been ascribed to the free energy gain resulting from alloy formation (10). However, up to now little is known about the initial stages of electrocrystallization and growth in these systems. This is where STM experiments can provide interesting new information.

Recently we have published some first results of an STM and STS study of Ni and NiₓAlₙ₋ₓ electrodeposition from an AlCl₃/BMIC mixture in the molar ratio of 58:42 (11). At potentials close to its equilibrium value Ni exhibits a layer-by-layer growth, whereas formation of three dimensional clusters can be observed at lower potentials. This 3D growth seems to be favored at defects of the underlying Au substrate, especially along monoatomic steps. From tunneling spectroscopy it is possible to determine effective tunneling barriers at the electrode/electrolyte interface, which show qualitatively the same relative reduction with increasing aluminium content as for the vacuum interface (11). In this paper, we want to discuss the electrodeposition of Ni and Ni-Al alloys in more detail. Furthermore, we will show that the relative changes of the effective tunneling barrier can be related qualitatively to the composition of the electrodeposited alloy films.

**EXPERIMENTAL**

The method used to synthesize 1-butyl-3-methylimidazolium chloride (BMIC) from 1-chlorobutane and 1-methylimidazole (Merck) and the purification by recrystallization from acetonitrile have been described previously (12). Anhydrous AlCl₃ (Fluka, p.a. >99%) was purified several times by sublimation in an evacuated quartz ampulla (11). In an argon-filled glove box (O₂ and H₂O < 2ppm) AlCl₃ crystals were mixed with BMIC in a molar ratio of 58:42 yielding a colourless liquid. A solution of Ni(II) in the melt was prepared by controlled-potential coulometric anodization of a Ni wire (Alfa, 99.9945%, 0.5 mm diam.) at a potential of 0.25 V vs. a Ni/Ni(II) reference electrode up to a concentration of 5 mmol/l following the description in (8). The resulting liquid was slightly salmon coloured.

STM experiments were carried out with a home-built STM (13) driven by a Digital Instruments Nanoscope E controller. During the experiments the setup was placed into an argon-filled vacuum tight recipient which provided a clean and dry atmosphere allowing measurements for the duration of several days. The I-U-curves were taken in the current imaging spectroscopy (CITS) mode (11). With this method STM pictures and corresponding STS spectra can be taken simultaneously by acquiring the I-U curves rapidly (~200 µs) compared to the scan speed of the tip (~5 lines/s) (11). The STM tips were etched electrochemically from tungsten wire (Alfa, >99.98%, 0.25 mm diam.) in a 2M solution of NaOH (14) and coated with an epoxide electropaint (BASF, ZQ 84-3225 0201). The Au(111) samples consisted of Au films of 200-300 nm thickness deposited on quartz glass (Berliner Glas KG). The samples were annealed under vacuum for several hours up to 600 °C and kept under argon atmosphere afterwards in order to obtain...
extended terraces exhibiting hexagonal orientation of the surface atoms. Prior to use the substrates were heated to slightly red glow for some minutes in a hydrogen flame and cooled down again to room temperature in a nitrogen stream (15). A Teflon cell was sealed to the gold substrate via a Viton O-ring. A Ni ring electrode fixed at the wall of the Teflon cell and a Ni wire (Alfa, 99.9945%, 0.5 mm diam.) dipping into the melt served as reference and counter electrode, respectively. For details of assembling the cell and sealing under argon cf. ref. (16).

Deposition of Pure Nickel

An overview of the redox processes occurring during Ni electrodeposition from AlCl₃/BMIC (58:42) on Au(111) can be derived from cyclic voltammetry measurements. Figure 1 shows several typical cyclic voltammograms of this system with different switching potentials. At 1.0 V vs. Ni/Ni(H) oxidation of the Au bulk phase starts (process A) constituting the anodic limit of the electrochemical window in this system. The redox couple B/B’ at 0.8 V has already been observed during earlier studies of Ag and Al deposition on Au(111) in the same electrolyte (12). From STM pictures it could be shown, that at this potential reversible oxidation of the topmost Au layers is starting from the substrate steps. At 0.21 V a reduction wave, C, occurs. The respective dissolution peak is located at 0.35 V. After crossing the equilibrium potential the current starts to rise again corresponding to an additional reduction process at -0.15 V, which is labeled by D. From the cyclic voltammogram with a switching potential of -0.2 V in Figure 1 it can be seen, that process D corresponds to the dissolution peak C’, too. However, when the potential is decreased further, the reduction current does not decrease to give a minimum, but rises significantly yielding another peak at -0.47 V (E). A corresponding stripping wave at 0.11 V (E’) is observed, when the potential is swept backwards. At -0.7 V the equilibrium potential of Al is reached leading to a strong increase of the reduction current. The behaviour in the overpotential range nicely corresponds to the observations made by Moffat (10) and Pittner et al. (11) in AlCl₃/NaCl and AlCl₃/1-ethyl-3-methylimidazolium chloride, respectively: According to their results and in agreement with our STM observations, which will be described below, we assign process D to the bulk deposition of pure nickel, whereas process E/E’ corresponds to the simultaneous deposition of nickel and aluminium.

The observation of process C/C’ is surprising at a first sight, as no underpotential deposition (UPD) of nickel on gold is expected. In general, UPD occurs when the interaction of the depositing metal with the foreign substrate is enhanced compared to deposition on a substrate of the same metal. To a first (and crude) approximation this occurs when the electronic work function of the deposited metal is lower than the corresponding work function of the substrate (17). For the deposition of nickel on gold this condition is not fulfilled with reference to the work functions of the metal/vacuum interface (18). Experiments in aqueous electrolytes, however, showed that underpotential deposition of Ni on Au(111) can occur depending on the nature of anions present in the solution (6). From more detailed theoretical considerations, including adsorption and desorption energies of the various species involved in the deposition process as well as the role of specific adsorption of anions, it follows, that the work function difference is not necessarily the only parameter which determines the behaviour of a UPD system. Instead, the transport processes governing monolayer formation and the adsorption of solvent species can contribute significantly to the UPD shift (19).
Figure 1. Cyclic voltammograms of the system Ni$^{2+}$/Au(111) in the AlCl$_3$/BMIC ionic liquid with different switching potentials, sweep rate $\nu = 0.1$ V/s, electrode area: 0.38 cm$^2$; arrows show the potentials at which tunneling spectra were taken.

The interpretation of process C/C' as Ni deposition in the underpotential region is confirmed by the results of STM measurements. When the electrode potential is decreased from 0.5 V to 0.1 V, formation of a hexagonal superstructure with a nearest neighbour distance of 23 ± 1 Å and a modulation amplitude of ~ 0.5 to 0.6 Å can be observed as shown in Figure 2.a. This pattern does not occur immediately after switching the potential to the lower value, but only after several minutes. Chronoamperometric data have been taken simultaneously with the STM pictures. Integration of the current transient corresponding to a potential step from 0.5 V to 0.1 V (see Figure 2.b) yields a charge of 530 μC/cm$^2$. This corresponds to the formation of 0.9 monolayers, if it is assumed that Ni reduction occurs via

$$\text{Ni}^{2+}({\text{solv}}) + 2e^- \rightarrow \text{Ni}$$  \[1\]

and that the Ni deposit forms a (111)-oriented film. This result is in good agreement with the STM observations and leads to the conclusion, that at 0.1 V already a complete monolayer of nickel forms. The origin of the hexagonal pattern observed in the STM pictures is the incommensurability between the adsorbed layer and the lattice of the underlying substrate ($d_{\text{Ni}} = 2.49$ Å, $d_{\text{Au}} = 2.885$ Å (18)). Such a so called Moiré pattern with a nearest neighbour spacing of 18 to 21 Å is also observed during Ni deposition from aqueous electrolytes on Au(111) and Ag(111) (5).
Figure 2. Ni deposition on Au(111) in the UPD range; (a) Moiré pattern occurring after formation of the first Ni monolayer, $E$: 0.1 V, $E_{\text{tip}}$: 0.2 V, $I_{\text{ tun}}$: 3 nA; (b) Corresponding current time transient taken at a potential step from 0.5 V to 0.1 V

Figure 3. Formation of a Ni bilayer and subsequent 3D cluster growth along the substrate steps after switching the potential from 0.5 V to -0.2 V, $E$: -0.2 V, $E_{\text{tip}}$: 0.1 V, $I_{\text{ tun}}$: 4 nA

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When the potential is decreased further, nickel growth is dominated by a layer-by-layer growth until the equilibrium potential is reached. This behaviour is described in detail in ref. (16) and (11). The STM pictures in figure 3 summarize the two and three dimensional growth behaviour of pure nickel caused by applying a potential step from 0.5 V, where no deposition occurs, to -0.2 V corresponding to process D in the cyclic voltammogram. White arrows show the direction of the slow scan axis. The completion of each STM picture took about two minutes, so that a certain time resolution is found in the pictures. In the middle of Figure 3.a the potential was switched to the lower value. Immediately the formation of two Ni monolayers can be observed. Until the upper end of the STM picture these layers are nearly complete and almost free of defects. In Figure 3.b the onset of three dimensional growth is observed. Obviously, nucleation of 3D Ni clusters occurs almost exclusively along the monoatomic steps of the underlying Au substrate. Only a few nuclei are formed on the extended terraces. With time these clusters grow further, forming “columns” exhibiting rather uniform heights and diameters (Figure 3.c). A similar behaviour has been described for the electrodeposition of nickel both on Ag(111) (20) and on Au(111) (4) from an aqueous electrolyte.

A qualitative explanation of this growth mechanism can be given in terms of a simple model taking into account the interplay between a vertical component of the nucleation rate on top of the nickel clusters and the horizontal growth rate of Ni on the underlying substrate (20). When the first Ni monolayer is deposited on the Au substrate, a structural defect is induced along the admetal/substrate-boundary due to the height difference between a Au step (2.3 Å) and the first Ni monolayer (1.9 Å), which serves as a preferential nucleation centre. The second layer formed on top of this defect is distorted and therefore considerably strained. This lattice distortion remains also into the third and higher Ni layers, providing heterogeneous nucleation sites for multilayer growth. With increasing height the respective strain is decreasing due to lattice relaxation. This leads to a decreasing nucleation probability on top of the nickel cluster and thus to a decrease of the vertical component of the nucleation rate, which is in good agreement with our STM data (cf. ref. (16)).

Nickel-Aluminium Alloy Deposition

As can be derived from the cyclic voltammogram in Figure 1, at -0.25 V the reduction current increases strongly due to another reduction process labeled E, which has been assigned tentatively to the simultaneous deposition of nickel and aluminium. This interpretation is based mainly on classical electrochemical measurements of Gale et al. (21), Heerman and D’Olieslager (22) and Pitner et al. (8). From cyclic voltammetry measurements in AlCl₃/-ethyl-3-methylimidazolium chloride they determined the onset of nickel-aluminium codeposition at ~0.4 V vs. Al/Al(III). With different techniques, such as anodic linear sweep voltammetry (ALSV), scanning electron microscopy (SEM) electron dispersive spectroscopy (EDS) and X-ray diffraction (XRD) electrodeposited alloy films of mesoscopic thickness were analyzed (8).

The initial growth stages of such a Ni-Al alloy deposit at a potential of -0.4 V vs. Ni/Ni(II) are shown in Figure 4.a-c. After stepping to this potential, formation of 1-2 nm high clusters of ~10 nm diameter is observed (4.a). As is seen in Figure 4.b, their number is increasing quickly. At the same time they merge and form bigger agglomerations (4.c) leading to a “cauliflower” appearance of the deposit. The above mentioned SEM
measurements show that mesoscopic films have a similar structure consisting of nodules of the order of 10 to 30 μm in size which, again, are composed of much smaller nodules (8). Apparently, this structure is already determined by the first stages of nucleation and growth. The grain size observed in the STM pictures is in excellent agreement with the results of XRD-measurements at electrodeposited Ni-Al-alloy films of several μm thickness. From line width analysis a grain size of the order of 10 nm could be determined (8).

![Figure 4](image_url)

**Figure 4.** Ni-Al alloy deposition; (a)-(c) growth of an alloy deposit at E: -0.4 V, E_tip: -0.05 V, I_tun: 5 nA; (d) Onset of the Al bulk deposition at -0.7 V, E_tip: -0.05 V, I_tun: 5 nA

Figure 4.d shows the electrode surface after a further potential decrease to -0.7 V. Here the Al bulk deposition is the dominant process leading to the formation of significantly smaller clusters of Al (diameter ~ 2-3 nm) on top of the Ni_xAl_{1-x} deposit. In general, it could be observed in our studies, that with increasing Al content the grain size of the respective alloy film is decreasing.

Finally, the Ni-Al deposits have been analyzed by scanning tunneling spectroscopy (STS). This method provides insight into the electronic structure of the electrode/electrolyte interface. Furthermore, it is possible to derive from I-U-curves effective tunneling barriers and thus information about the chemical nature of the deposit. These measurements are carried out in the following way: For the duration of the
measurement, the STM tip is held at a constant z-position above the surface and the bias voltage is ramped linearly, while the response of the tunneling current is detected. Figure 5.a shows a typical I-U curve obtained in this manner on a Ni-Al film at a potential of -0.4 V vs. Ni/Ni(II). From these curves effective tunneling barriers can be determined. Applying a simple one dimensional tunneling model and assuming constant density of states for both sample and tip, the tunneling current is approximated by (23)

$$I = \text{const} \cdot \int_0^U \frac{1}{z} \exp \left( -\frac{\phi - eU}{2z} \right) dU$$

[2]

Figure 5. (a) Typical example of an STS measurement; experimentally determined I-U curve (dots) and fit (straight line) at -0.4 V, taken at the position marked by a cross on the respective STM picture (b) Comparison of effective barrier heights (full symbols) and literature data of alloy composition (open symbols)
with \( A = 2\hbar^2/(2m)^{3/2} \approx 1.025 \text{ eV}^{-1/2}\text{Å}^{-3} \). Here \( \phi \) is the effective barrier height, which depends on the electronic work functions of sample and tip. For example, for a trapezoid tunnel barrier \( \phi \) is given by \((\phi_s + \phi_j)/2\). From earlier distance tunneling measurements in the same electrolyte it has been estimated that at a setpoint of 5 nA the tip-to-surface distance is of the order of \( 6 \pm 1 \) Å. With a constant \( z \) value of 6 Å a consistent description of all I-U curves is achieved. A fit of equation [2] to the experimental data in Figure 5.a yields an effective tunneling barrier of 0.4 eV.

Additional measurements have been performed at the uncovered Au surface at a potential of 0.5 V, at -0.2 V, where 3D clusters of pure nickel are deposited along the substrate steps and at -0.7 V, the onset of aluminium bulk deposition. The resulting effective barrier heights are plotted in Figure 5.b as a function of the applied potential. The error bars are given by the scattering of the tunneling barriers determined from several I-U curves. For comparison literature data are shown, giving the alloy composition as a function of the working electrode potential. The potential scale is given versus an Al/Al(III) reference electrode. For convenience the respective potentials at which tunneling spectra have been measured are labeled by arrows in the cyclic voltammogram (Figure 1) in addition. From Figure 5.b it becomes clear, that the relative changes of the effective tunneling barrier heights are correlated with the aluminium content of the alloy deposit.

The values determined for the effective tunneling barriers of pure metals and alloys in this study lie between 1.0 and 0.3 eV. However, electronic work functions of metals are typically of the order of 3 to 5 eV. This significant decrease of the effective tunneling barrier at the electrode/molten salt interface becomes plausible, if the influence of an adsorbed species at the metal surface on the electronic work function is considered. Within the jellium model, the electron density \( \rho(\mathbf{r}) \) is described in the presence of a uniform positive charge density \( \rho^+(\mathbf{r}) \) caused by the ion cores. The electron density spills out over the interface into the vacuum, thus inducing a dipole layer, whose dipole moment points into the bulk metal. Adsorbed species from the molten salt electrolyte can reduce this surface dipole considerably, leading to a decrease of the electronic work function by several eV (24). However, apart from these qualitative considerations, to our knowledge so far a quantitative theoretical description of the electronic properties of the electrode/electrolyte interface does not exist.

Although the absolute values of \( \phi \) can show a considerable variation depending on the experimental conditions, especially on the tunneling parameters, their relative changes can be used to estimate the changes in aluminium content of a Ni-Al alloy deposit. For example, tunneling barriers determined at -0.4 V are significantly reduced compared to those at -0.2 V. This confirms the former assignment of reduction process E to codeposition of nickel and aluminium leading to the formation of a Ni-Al alloy film. Furthermore, as already indicated in Figure 5.a, STS spectra can be taken with relatively high spatial resolution. Thus, it should be possible to determine tunneling barriers of singular clusters. In this way, electronic structure differences of various clusters forming an alloy deposit could be detected.
CONCLUSIONS

Electrodeposition of Ni$_x$Al$_{1-x}$ alloys has been studied by scanning tunneling microscopy and spectroscopy within the limits of pure Ni underpotential deposition and Al bulk deposition from the chloroaluminate ionic liquid AlCl$_3$/BMIC (58:42). In the UPD range and close to the Ni/Ni(II) equilibrium potential deposition of pure Ni proceeds by 2D layer-by-layer growth, whereas at more negative potentials 3D cluster growth sets in almost exclusively along the steps of the underlying Au(111) substrate. At potentials below -0.25 V codeposition of nickel and aluminium occurs and Ni-Al alloy films are formed, whose structure is clearly dependent on the applied potential and, therefore, on their composition. In general, with increasing aluminium content the grain size decreases.

STS measurements were performed at the electrode/electrolyte interface. The respective effective tunneling barriers were found to be significantly reduced compared to typical vacuum values. However, a clear decrease of the barrier height can be observed with increasing aluminium content of the corresponding deposit. In particular for investigations of alloy deposition the variation of $\phi$ can provide valuable information about the electronic structure at the interface.

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