ELECTRODEPOSITION OF METALS FROM MOLTEN SALTS

Ana María Martínez a, Geir Martin Haarberg b, Yolanda Castrillejo c, Børre Børresen a and Reidar Tunold a.

(a) Department of Materials Technology and Electrochemistry, NTNU, 7491-Trondheim, Norway

(b) SINTEF Materials Technology, Trondheim, Norway.

(c) Departamento de Química Analítica, Facultad de Ciencias, Universidad de Valladolid, 47005-Valladolid, Spain

ABSTRACT

Kinetics and nucleation phenomena of the electrodeposition processes for tantalum and magnesium have been studied. In both cases molten chlorides (CaCl2-NaCl and NaCl-KCl) were used as reaction media.

Electroreduction of K2TaF7 in CaCl2-NaCl at 550°C involves a single quasi-reversible five-electron step (Ta(V)+5e<->Ta). The influence of oxide ions has also been studied, showing that the presence of even small amounts of oxides in the melt complicates the electroreduction process. Another electrochemical signal at more cathodic potentials can then be found, which seems to be associated to the reduction/oxidation of Ta oxohalides presumably of the type TaOClxFy2- (z=x+y-3).

In the case of Mg electrodeposition, two equimolar melts were compared: CaCl2-NaCl (dilute MgCl2 system) and NaCl-KCl (5mol% MgCl2) at working temperatures of 550°C and 727°C respectively. In these melts electroreduction of Mg2+ showed different characteristics, especially concerning nucleation phenomena.

INTRODUCTION

Electrodeposition processes of metals (electrowinning, electrorefining, electroplating and electroforming) in molten salts media, have extensively been proved to be more advantageous than those carried out in aqueous solution. Higher efficiency of the electrolysis (one order of magnitude), often high electrodeposition rates and much better characteristics of the obtained deposits (1) can be pointed out as some of the main advantages. Moreover molten salts are the only media from where refractory and light metals can be obtained (with the exception of chromium). It has been reported that especially molten fluorides are suitable in the production of refractory metals by electrolysis. When using fluoride melts the formed deposits have better characteristics, i.e. adherent, compact and uniform (2). In addition it has been proved that fluoride melts stabilize the high oxidation states of the elements thus decreasing the stability of species.
in the lower ones. Then reactions that involve intermediate valence state compounds are less probable. However, molten fluorides have the big disadvantage of being very corrosive media. That is the main reason for which many studies have been carried out in order to investigate the possibilities of using molten chlorides instead.

This work deals with the electrodeposition studies of two metals that are commercially produced by electrolysis in molten salt media. Ta is produced in the solid state by the well-known Balke process (3), and Mg as an example of metal obtained in liquid state, which is industrially produced from molten chloride media (i.e. 4).

The studies of tantalum electrodeposition have become more important in the last years due to the necessity of finding new processes for tantalum electrolyplating baths. The replacement of solid tantalum anodes for ordinary substrates with a thin Ta coating could give substantial savings of the strategic raw material.

A literature review about the electrochemical reduction of tantalum in alkali chlorides indicates that the mechanism is not completely clear. This is due to the complexity of the electrochemical reaction because of the variety of oxidation states of tantalum stable in the molten baths, existence of subhalide cluster complexes and formation of tantalum rich oxides that complicate the electroreduction process. Some authors claim that the electroreduction of tantalum in pure chloride melts (5,6) and in mixed fluorochloride systems (2,7,8) involves a two step process, whereas many others advocate that the reduction pathway in fluorochloride mixtures goes straight through a single step (9-15).

The extreme sensitivity of Ta electrodeposition melts to impurities has been shown previously (10,15,16). As it is well known, oxides are some of the most important impurities in the production process of metals in molten chlorides, mainly due to the fact that it is very difficult to eliminate such ions completely from the bath. Particularly, this becomes an important problem in the tantalum electrolyplating baths, due to the high sensitivity of tantalum to oxygen (17) causing formation of o xo-complexes which degrade the quality of the obtained deposits.

Despite the many improvements of thermal methods, electrolysis is the main technique for the industrial production of magnesium. A typical electrolytic bath is a mixture containing mainly sodium chloride and calcium chloride: CaCl₂ (30-40%), NaCl (25-45%), MgCl₂ (8-16%) and KCl (0-10%) (weigh percent) (18) at a working temperature of 700°C. The formation of stable Mg droplets that are growing to a desired size before detaching from the cathode surface is a pre-requisite for the successful harvesting of the metal. The necessity for optimization of the process has led to a considerable amount of investigations about the electrodeposition process of Mg in molten chlorides. In this respect the mechanism of the cathode process, including mass transfer and phase formation processes, has been found to be highly dependent on the presence of oxides and other impurities (i.e. 18-21).

In this work, the molten binary equimolar chlorides, CaCl₂-NaCl or NaCl-KCl, have been used as reaction media. Kinetics of the electrodeposition of tantalum and magnesium have been determined and special attention has been devoted to the study of the nucleation processes. The results obtained could have some applications both in the
industrial preparation of tantalum coatings and in the improvement of the industrial process for magnesium production.

EXPERIMENTAL

The chloride mixtures were melted in a glassy carbon crucible placed in a quartz cell inside a furnace. A West 3300 or an Eurotherm Model 2404 programmable device controlled ±2°C the temperature of the furnace. The working temperature was measured with a thermocouple protected by an alumina tube inserted into the melt.

The experiments were carried out in an inert argon atmosphere, and in the case of the magnesium studies, inside a VAC Model HE-43-2 glove box.

The working electrodes consisted of 3 mm glassy carbon rods and tungsten (1 mm wires or 3 mm rods). Another tungsten wire or the glassy carbon crucible was used as counter electrode. The reference electrode consisted of a silver wire dipped into a solution of silver chloride in a CaCl₂-NaCl or NaCl-KCl molten mixture contained in a quartz or porous alumina tube.

After melting the salt and in the experiments carried out outside the glove box, HCl(g) was bubbled through the molten mixture for at least 30 min in order to purify it. The residual oxide ions will then react according to:

\[ \text{O}^{2-} + 2\text{HCl} (g) \leftrightarrow \text{H}_2\text{O} (g) + 2\text{Cl}^{-} \]  \[1\]

This procedure has been used previously (22), showing a good improvement in the purification of the melt.

The additions of the electroactive species in the melt were made by weighed amounts of anhydrous K₂TaF₇ (commercially available) and dehydrated MgCl₂ in the case of Ta and Mg electrodeposition respectively. The dehydration method of commercially available MgCl₂·6H₂O was described elsewhere (23).

RESULTS OBTAINED IN THE STUDIES OF Ta ELECTRODEPOSITION

Electrochemical studies of TaF₇²⁻ in the equimolar CaCl₂-NaCl melt at 550°C.

Figure 1 shows a series of voltammograms obtained in the equimolar melt CaCl₂-NaCl containing K₂TaF₇²⁻ when using a glassy carbon rod as working electrode.

The process is characterized by a cathodic peak, A, associated with the corresponding sharp re-oxidation peak, A', which shapes are characteristic of a soluble-insoluble system (24). The electroreduction of Ta(V) ions seems to take place in a single step, with the formation of metallic Ta (see Figure 2), according to the reaction:

\[ \text{Ta} (\text{V}) + 5\text{e} \leftrightarrow \text{Ta} (\text{s}) \]  \[2\]

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An electrochemical reaction involving simultaneous transfer of more than one electron is improbable (25). We can then consider the above reaction [2] as a multistep process thus only being possible to detect the slowest step in the usual time scale.

![Cyclic voltammograms obtained at glassy carbon electrode in molten CaCl₂-NaCl containing K₂TaF₇. Sweep rate 0.2 V s⁻¹.](image1)

Figure 1. Cyclic voltammograms obtained at glassy carbon electrode in molten CaCl₂-NaCl containing K₂TaF₇. Sweep rate 0.2 V s⁻¹.

![Voltammogram that proves the formation of a solid product (metallic Ta) at the glassy carbon surface.](image2)

Figure 2. Voltammogram that proves the formation of a solid product (metallic Ta) at the glassy carbon surface.

From Figure 1 it is also possible to see a small oxidation peak, labeled B', which as it will be discussed later, could be related to the formation of oxo-complexes due to traces of oxide ions present in the melt.
The fact that the small shoulder, labeled C', increases with the cathodic potential limit could indicate that it is related to Na electrodeposition.

The cathodic peak current was found to be proportional to the square root of the sweep rate, and from the slope it was possible to calculate the diffusion coefficient of the TaF$_7^-$ ions. The value was compared to the one obtained by semi-integration of the voltammetric curves (see Table I). The exact amount of tantalum dissolved was determined by ICP analysis of samples taken from the melt.

Table I. Kinetic parameters of Ta(V) ions in the equimolar CaCl$_2$-NaCl at 550°C.

| Method              | $D_{Ta(V)} / \text{cm}^2 \text{s}^{-1}$ | $\alpha$ | $\log k^o / \text{cm s}^{-1}$ |
|---------------------|----------------------------------------|----------|-------------------------------|
| VOLTAMMETRY         | 7x10$^{-7}$                            | -        | -                             |
| SEMI-INTEGRATION    | 6x10$^{-6}$                            | 0.3 ± 0.1| -4.0 ± 0.1                    |

The cathodic peak potential was found to be dependent on the logarithm of the sweep rate for values higher than 0.4 V s$^{-1}$, which means that at $v>0.4$ V s$^{-1}$, the rate of the diffusion step approaches the one of the electron-transfer. The values of the charge transfer rate constant, $k^o$, and the charge transfer coefficient, $\alpha$, of the Ta(V)/Ta(0) process were calculated from the logarithmic analysis of the convoluted curves obtained from the voltammograms, by applying the equation corresponding to a quasi-reversible reaction with formation of an insoluble product (see Table I) (26).

Figure 3. Voltammograms and their corresponding convoluted curves. Scan rates shown in the plot.
Influence of the presence of oxide ions.

When oxides were present, a peak appeared during the cathodic sweep (B), which is associated to an oxidation peak B'. System B/B' is more pronounced when using tungsten wires as working electrodes (see Figure 4).

![Figure 4.- Voltammogram corresponding to the reduction of K2TaF7 in CaCl2-NaCl on a tungsten electrode in the presence of oxide ions (added as solid sodium carbonate, 0.01 mol kg⁻¹). V=0.2 V s⁻¹.](image)

The results could be explained in terms of the formation of oxyhalide complexes of Ta(V) of the type TaOClₓFᵧ⁺, where z=x+y−3, as it has been shown by other authors (10,15). According to Figure 4 the oxyhalide complexes are reduced at more negative potentials (are more stable) than the oxygen-free complexes.

RESULTS OBTAINED IN THE STUDIES OF Mg ELECTRODEPOSITION

Dilute solutions of MgCl₂ in the equimolar CaCl₂-NaCl melt at 550°C.

The electrochemical properties of dilute solutions of Mg²⁺ ions in the equimolar CaCl₂-NaCl at 550°C have been studied by voltammetry, semi-integration, chronomperometry and chronopotentiometry (23). A tungsten wire was the only substrate used. It was not possible to use glassy carbon in this very dilute melt due to formation of Na-C compounds.

Figure 5 shows a typical voltammogram of the melt. The electroreduction takes place in a single step characterised by a cathodic wave A associated to the re-oxidation peak A', which shape is characteristic of the formation of a product that remains adhered to the electrode. Peaks B, C and D are most likely due to the formation of various Mg-Na alloys formed on the W surface (27).

The kinetics of the system were investigated (23) by different electrochemical techniques, showing that the mechanism of Mg²⁺ reduction proceeds according to the following path:
The kinetic parameters of mass and charge transfer were calculated and the values gathered in Table II.

![Voltammogram](image)

Figure 5.- Voltammogram obtained on a tungsten wire. V=0.2 V s⁻¹, MgCl₂ concentration 0.1137 mol kg⁻¹ (less than 1 mol%) in the equimolar CaCl₂-NaCl melt. The voltammogram is also compared to the one obtained in the melt without MgCl₂ (-----).

| Table II. Kinetic parameters of Mg(II) ions in the equimolar CaCl₂-NaCl at 550°C. |
|---------------------------------|-----|-----|
| DMg(II) / cm² s⁻¹ | α | log k⁰ / cm s⁻¹ |
| VOLTMETRY | 7x10⁻⁵ | ----- | ----- |
| SEMI-INTEGRATION | 1x10⁻⁵ | 0.7 ± 0.1 | -3.9 ± 0.8 |
| CHRONOPOTENTIOMETRY | 8x10⁻⁵ | ----- | ----- |

The electrochemical nucleation of Mg on tungsten substrates was investigated by chronoamperometry over a wide potential range (23). In no case any evidence of nucleation or growth phenomena was found.

Results obtained in the equimolar NaCl-KCl containing 5mol% MgCl₂ melts at 727°C.

Electrochemical deposition of Mg was studied in the equimolar NaCl-KCl mixture containing 5 mol% (=7 wt%, 0.74 mol kg⁻¹) MgCl₂ at 727°C, using glassy carbon and tungsten (3 mm rods) substrates.
Figure 6 shows a typical voltammogram obtained on glassy carbon. The cathodic wave A is related to the electrodeposition of both metallic Mg and underpotential deposition of Na. B, which is associated with B', has the characteristic habit of the formation of a new phase, that is metallic Mg. The anodic wave C' is probably related to the presence of residual oxides in the melt. D' is chlorine evolution.

![Voltammogram](image)

*Figure 6.* Voltammograms obtained in the equimolar NaCl-KCl + 5 mol% or 0.74 mol kg\(^{-1}\) MgCl\(_2\) (---) and in the pure equimolar NaCl-KCl (-----) at 727°C. Glassy carbon substrate. V=0.2 V s\(^{-1}\).

The current efficiency in the Mg electrodeposition process was determined by calculating the ratio between the cathodic and the anodic charge obtained during double potential step measurements. The ratios are always rather low (lower than 45%) which could be explained by Na co-deposition that can remain strongly bounded in the carbon structure and/or losses by metallic dissolution (both Mg and especially Na).

![Voltammogram](image)

*Figure 7.* Voltammograms obtained in the equimolar NaCl-KCl + 5 mol% MgCl\(_2\) (---) and in the pure equimolar NaCl-KCl (-----) at 727°C. Tungsten rod electrode. V=0.2 V s\(^{-1}\).
Voltammograms obtained at a tungsten rod electrode showed different features (see Figure 7). In this case a much higher residual current was observed in all the curves obtained in the melts containing MgCl$_2$. A new peak, A, associated to A prior to the Mg electrodeposition (B/B') appears. The A/A' system could be related to the UPD formation of Mg or the formation of Mg-W or Mg-Na alloys.

The main characteristic of the electrodeposition of Mg in the equimolar NaCl-KCl melt containing 5 mol$\%$ MgCl$_2$ is that the process is controlled by nucleation phenomena, specially on tungsten materials.

Chronoamperometry is the method most frequently used to study nucleation phenomena in aqueous media (28-34). The curves shown in Figure 8 are characteristics of the phenomena described in the literature according to the nucleus formation and growth. After a certain induction time, the current increases, which is attributed to an increase in the active area of the electrode, due to the growth of the nuclei that were formed. When the current reaches a maximum value, $I_m$, at a maximum time, $t_m$, it starts to decrease again slowly which is typical of the limitation of the reaction process by the semi-infinite diffusion of the magnesium ions to the nuclei. It has been proved that for values of the time higher than 5 s, the curve follows the linear relationship $I=f(t^{1/2})$ expressed by Cottrell’s law.

![Figure 8](image_url)

*Figure 8.* Current transients obtained in the equimolar NaCl-KCl + 5 mol$\%$ MgCl$_2$ on a tungsten rod electrode. The applied potentials are shown in figure.

In order to analyze and elucidate the type of nucleation the entire dimensionless experimental current-time transients were compared to the appropriate theoretical transients that are reported in the literature (35) for instantaneous (equation [3]) and progressive (equation [4]) nucleation, respectively:

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The experimental curves (Figure 8) fit better to the theoretical ones in the case of instantaneous nucleation at potential values positive of \(-1680\) mV (i.e. Figure 9). However at potentials values negative of \(-1680\) mV (i.e. Figure 10), a very good fit is obtained for progressive nucleation. In both cases the growth of the Mg nuclei is three-dimensional with diffusion controlled hemispherical growth.

\[
\left( \frac{I}{I_{\text{max}}} \right)^2 = 1.9542 \left[ 1 - \exp \left( -1.2564 \left( \frac{t}{t_{\text{max}}} \right) \right) \right]^2
\]  \hspace{1cm} [3]

\[
\left( \frac{I}{I_{\text{max}}} \right)^2 = 1.2254 \left[ 1 - \exp \left( -2.3367 \left( \frac{t}{t_{\text{max}}} \right)^2 \right) \right]
\]  \hspace{1cm} [4]

**Figure 9.** Comparison of the dimensionless experimental transient \((E=-1.63\) V) with the theoretical models for three-dimensional nucleation with diffusion-controlled growth of the nuclei.

**Figure 10.** Dimensionless plots in the case of \(E=-1.72\) V.
In the case of glassy carbon substrates, it was very difficult to obtain curves showing clearly the presence of nucleation. In some experiments just some irreproducible curves were obtained.

The results indicate that the electrodeposition of Mg in the equimolar NaCl-KCl with 5 mol% MgCl₂ at 727°C, is a complex process and highly dependent on the state of the electrode surface, intercalation of sodium and presence of oxide and other impurities. This is still not understood in detail, thus needing further investigations.

ACKNOWLEDGEMENTS

The authors are grateful to the Norwegian Research Council, Norsk Hydro ASA and DGES PB96-0364 (Spain) for financial support, which enabled this study. One of the authors (A.M.M.) wishes to thank D.G.I.C.Y.T. (Spain) for a doctoral grant. Special thanks are also given to Prof. B. Scharifker for valuable discussions about nucleation phenomena.

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