IONIC MELT PROPERTIES AND THEIR USE IN THE ELECTROWINNING OF REFRACTORY METALS

Frédéric Lantelme & Henri Groult
Université Pierre et Marie Curie, France

ABSTRACT

In the context of the preparation of refractory metals, thermodynamic and kinetics properties of salts of refractory metals (mainly titanium and niobium) dissolved in alkali chloride melts were determined by transient electro¬chemical techniques. Two kinds of reactions occur in the melts: i) homogeneous reactions such as: $Me^{(n+z)+} + ne^- \leftrightarrow Me^{z+}$ where $Me^{(n+z)}+$ and Me^{z+} are two oxidation states of metal ions, ii) heterogeneous reactions corresponding to the metal deposition: $Me^{n+} + ne^- \leftrightarrow Me$.

The potential corresponding to the reactions are linked to the Gibbs free energy of formation of salt solutions. The standard potentials of the various "redox" reactions were measured by transient electrochemical techniques. These techniques were also used to determine the reaction kinetics and to measure the diffusion coefficients of the active ions which control the deposition process.

The stability of the oxidation states depends on the composition of the melt and especially on the nature of the anions. In pure chloride melts, the metal is obtained from the reduction of lower oxidation states, Ti^{2+} and Nb^{3+}. But, disproportionation reactions and the formation of insoluble subhalides perturb the reduction reaction. When a small amount of NaF was added to the bath, the direct reduction of Ti^{3+} or Nb^{4+} to metal was obtained, which greatly improved the quality of the deposit.

INTRODUCTION

One of the main feature of many melts is to be made of charged particles; consequently, most of them can be considered as pure ionic liquids. Due to this nature they are convenient media for electrochemical preparations. A wide potential span between decomposition limits allows the electro-winning of highly electropositive metals or very electronegative elements [5]. In our laboratory, a great deal of research has been devoted to the industrial preparation of aluminium and fluorine. More recently, this interest has been extended to the preparation of refractory metals. Indeed, the electrochemical route produces very pure metals directly; also, it is less polluting than the chemical processes. Moreover, the electrochemical reduction is well adapted for surface treatments. At high temperature, the deposited metal diffuses into the substrate metal and results in a compact, protecting and refractory layer. For example, chromium deposition by fused salt electrochemistry leads to chromium coatings which resist thermal shock (rockets); this is not the case for coatings produced by the classical electrochemical deposition in aqueous solution.

The success of the preparation requires a careful examination of the experimental conditions. Indeed, in contrast with the preparation of alkali metals or aluminium, refractory metals in fused baths exist in several oxidation states [3]. This induces parasitic effects such as reoxidation and disproportionation reactions. According to the pioneer work of Mellors and Sanderoff [7], most of the preparations described in the literature were carried out in alkali fluorides. However, there is now some interest in alkali chlorides; they are cheaper, less toxic and corrosive than fluorides. In addition, the salts adhering on the metal pieces can be easily washed. However, the presence of low oxidation states in chloride melts perturbs the deposition process. To counteract this, it has been proposed to add a small amount of fluoride ions, as they form strong complexes with metal ions. This can lead to an efficient electrochemical preparation. The present paper's aim is to show how to proceed in order to optimise the concentration of fluorides without loosing the advantages of chloride baths.

METHODOLOGY

Equipment

Linear sweep voltammetry was used as the main experimental technique. In addition, chronopotentiometry was applied for determi¬ning the diffusion coefficients of the active species. Electrochemical investigations were conducted with a potentiostat (Tacussel PRT20-10), a programmer (Tacussel GSTP4) and recorded on an oscilloscope (Nicolet 210) with a Hewlett Packard X-Y recorder. The three-electrode electrochemical cell applied in the experiments as well as the other experimental procedures have been described previously [6]. The glassy carbon crucible used to contain the melt also served as counter electrode.

Chemicals

Commercially available chemicals ('pro analysis' and 'pure' grade) were used to prepare the electrolyte. Before use, the components were dried in vacuum at 130ºC. The experiments were carried out in the eutectic mixture LiCl (59 mole%)–KCl (41 mole%) or in the equimolar mixture NaCl-KCl. When introduced in the cell, the salt mixture was again maintained under vacuum while the temperature was increased. An argon atmosphere was provided as soon as the temperature reached 350ºC. The fused salt was maintained under a chlorine stream during a few minutes; the purity of the melt was checked by cyclic

voltammetry on a glassy carbon electrode. This treatment was very useful to eliminate traces of oxides. Indeed, the residual peak current density, at a sweep rate of 1 V s^{-1}, in the region -1.0 to $^{-2}$. V vs Pt^{2+}/Pt, changed from 1-2 mA cm^{-2} to around 0.2 mA cm^{-2}, before and after the treatment.

The niobium or titanium ions were generated by addition of K_2TiF_6 or K_2NbF_7 salts (Alpha, Johnson-Matthey) twice crystallized from an aqueous hydrogen fluoride solution. In the case of experiments in fluoride-free solutions, the solutions of refractory metal salts were prepared in situ by anodic oxidation of rods of metal. A chlorine electrode was used as cathode during the process.

Working Electrode

The nature of the working electrode depends on the potential range of the experiment. A vitreous carbon or a platinum electrode was used for reactions concerning the higher oxidation states. However, some problems occur at lower potentials. Indeed, titanium and niobium form alloys with many metals. Alloy formation normally occurs at potentials more negative than about 1.6 V. Noble metals such as platinum can be used as working electrodes in a potential range from -1.5 V up to the oxidation potential of the platinum without interference due to alloy formation. Previous studies have shown that titanium and niobium react rapidly with graphite or vitreous carbon and form carbides. Titanium and niobium form alloys with most of the metals usually employed as working electrodes, such as nickel, silver, platinum, gold, copper, iron. The only way to proceed was to use extremely refractory metals such as tungsten or molyb¬denum, where the kinetics of alloy formation was very slow and did not perturb the electrochemical response.

Reference Electrodes

The obvious primary reference for molten alkali halides is the corresponding halogen/halide electrode. In alkali chloride melts, the chlorine electrode utilises the equilibrium between chlorine molecules and chloride. Unfortunately, the presence of even minor amounts of fluoride ions leads to a change in the electrode function due to freon evolution on graphite; this occurs with a marked depolarisation preceding the oxidation of chloride ions. In view of the difficulties encountered for obtaining a reliable reference electrode, many authors have used so called quasi-reference electrodes which consist in a metallic wire (generally platinum) immersed in the electrolyte.

However, the use of quasi-reference electrodes, with all their simplicity and convenience in operation, may be regarded only as a temporary solution because they provide a random potential that is very sensitive to impurities and also depends on the melt composition. To obtain a more stable reference electrode it has been proposed to use an internal reference system. The principle is based on the theoretical analysis of cyclic voltam¬mograms on a metal electrode. During the forward sweep a small amount of metal is dissolved; the ions generated are reduced during the reverse sweep. The analysis of current response provides an accurate determination of the standard potential of the metallic couple. More details concerning this procedure are given in the literature [2]. In the present work, the Pt^{2+}(1M)/Pt system was used as the reference system for melts containing fluoride ions.

RESULTS AND DISCUSSION

Transient Curves

Physicochemical properties of the melt were examined in order to determine the best conditions for refractory metal electrowinning. Special attention was devoted to the stability domain of the various oxidation states of the solute ions. Transient electrochemical techniques were used to determine the physicochemical properties of the melts and to obtain a better understanding of the deposition mechanism. As an example some transient records are given in Figures 1-4.

Cyclic Voltammetry

A cyclic voltammogram in fused LiCl-KCl containing Ti^{3+} ions is reported in Figure 1. The peak on the right hand side of the curve corresponds to the oxidation of chlorine ions; it can be used to check the validity of the reference electrode. In this potential range two peaks, O_1 and R_1, were obtained. It was shown that the current density was proportional to the square root of the sweep rate. The peak potentials did not depend on the sweep rate. They correspond to the reversible *redox* reaction
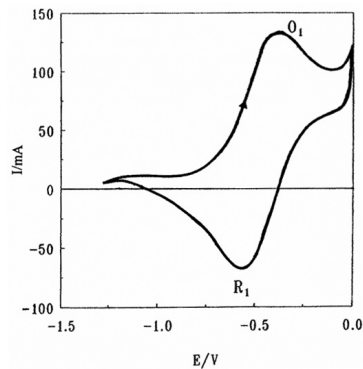
$$Ti^{4+} + e^- \leftrightarrow Ti^{3+} \tag{1}$$

Figure 1: Cyclic voltammogram for the reaction $Ti^{4+} + e^- \leftrightarrow Ti^{3+}$ at a vitreous carbon electrode, area: 0.34 cm^2; solution of $TiCl_3$ at a concentration of 0.18 mol dm^{-3} in LiCl-KCl; reference electrode: Cl_2/Cl^-. Sweep rate, 5 V s^{-1}. Temperature: 620°C
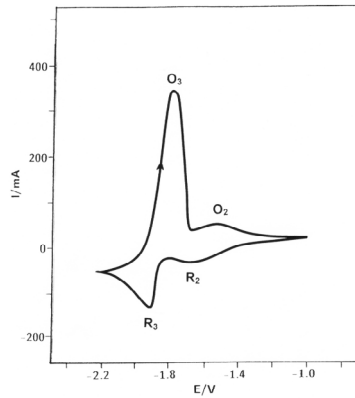
Figure 2: Cyclic voltammogram for the reactions $Ti^{3+} + e^- \leftrightarrow Ti^{2+} + 2e^- \leftrightarrow Ti$ at a tungsten electrode, area: 0.39 cm^2; solution of $TiCl_2$ at a concentration of 0.2 mol dm^{-3} in NaCl-KCl; reference electrode: Cl_2/Cl^-. Sweep rate, 0.5 V s^{-1}. Temperature: 690°C

In fused NaCl-KCl containing $TiCl_2$, on a tungsten electrode in the potential range -1.5, -2.5 V, three current waves, O_2, O_3 and R_2, and a current peak, R_3, were obtained (Figure 2). The waves, O_2, R_2, are associated with the reaction

$$Ti^{3+} + e^- \leftrightarrow Ti^{2+} \tag{2}$$
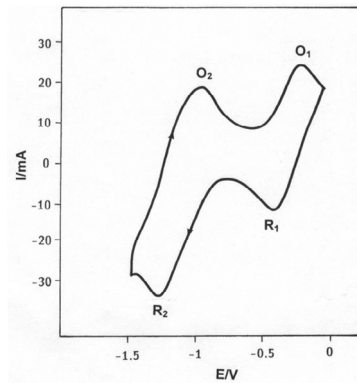

Figure 3: Cyclic voltammogram for the reactions $Nb^{5+} + e^- \leftrightarrow Nb^{4+} + e^- \leftrightarrow Nb^{3+}$ at a vitreous carbon electrode (area: 0.5 cm^2) in LiCl-KCl containing niobium ions at the concentration 0.07 mol dm^{-3}; reference electrode: Cl_2/Cl^-. Sweep rate, 1 V s^{-1}. Temperature: 465°C
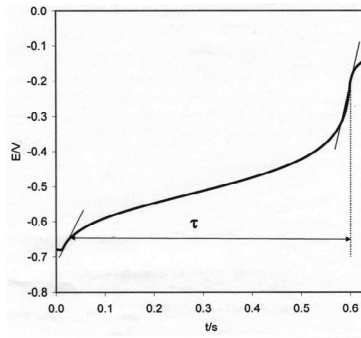
Figure 4: Chronopotentiogram of LiCl-KCl containing 0.2 mol dm^{-3} TiCl$_3$, at a vitreous carbon electrode; area: 0.54 cm^2; reference electrode: Cl$_2$/Cl$^-$. Current: 32 mA. Tempe¬rature: 450 °C

The wave R$_3$, corresponds to the reduction of Ti^{2+} and the peak current, O$_3$, comes from the oxidation of deposited titanium (stripping peak).

The niobium exhibits the same trends, except that now the oxidation state five, Nb^{5+}, is detected as shown in the voltammogram in Figure 3, where the oxidation waves, O$_1$/R$_1$, and, O$_2$/R$_2$, belong, respectively, to the reactions

$$Nb^{5+} + e- \leftrightarrow Nb^{4+} \qquad (3)$$

$$Nb^{4+} + e- \leftrightarrow Nb^{3+} \qquad (4)$$

Analysis of the voltammograms can be carried out from classical theory. For example, for a *reversible and homogenous reaction*, the potential, E$_w$, and the current density, i$_{wO}$, at the maximum of the wave obeys the equations [1]

$$E_w = E° - RT/nF\,[1.109 + 0.5\ln(D_O/D_R)] \qquad (5)$$

and

$$i_{wO}= 0.44*nF\,C_R(nF/RT)\,v^{½}\,DR^{½} \qquad (6)$$

where n is number of electrons involved in the reaction; E° is the *standard potential* of the *redox* reaction; v is the sweep rate; C$_R$ is the concentration of *red* species; D$_O$ and D$_R$ are the diffusion coefficients of *ox* and *red* species, respectively.

Chronopotentiometry

As an example, a chronopotentiogram is reported in Figure 4. The potential change during the constant current pulse is given by

$$E= E_{1/4} - (RT/nF)\ln\,[(\tau^{1/2} -t^{1/2})/t^{1/2}] \qquad (7)$$

τ is the length of the potential plateau, E$_{1/4}$, is the potential at the time, t = τ/4; it is linked to the standard potential through the equation

$$E_{1/4} = E° - (RT/2nF)\ln(D_O/D_R) \qquad (8)$$

The diffusion coefficient obeys the Sand's equation

$$2i\tau^{1/2}/C_R = nF\pi^{1/2}\,DR^{1/2} \tag{9}$$

Analysis

The above equations are related to ideal systems and are useful to obtain qualitative interpretation of the experimental results. Indeed, additional phenomena must be considered: influence of the ohmic resistance, charge transfer, covering factor of the deposited metal. To take into account these perturbing phenomena a program has been developed to solve, by the finite difference technique, the various motion equations involved in the electrochemical process [4].

The standard potentials, $E°_{ij}$ (molar scale, vs Cl_2/Cl^-), determined at various temperatures obey the following equations, where i and j are the charge numbers of the ions involved in the redox couple:

In LiCl-KCl (temperature range: 650-1000 K)
Niobium
$E°_{54}= -0.80 + 6.5 \times 10^{-4}\,T$ (V)
$E°_{43}= -1.53 + 6 \times 10^{-4}\,T$ (V)
$E°_{30}= -1.92 + 6.5 \times 10^{-4}\,T$ (V)

Titanium
$E°_{43}= -0.675 + 1.5 \times 10^{-4}\,T$ (V)
$E°_{32}= -2.765 + 10 \times 10^{-4}\,T$ (V)
$E°_{20}= -2.230 + 3.3 \times 10^{-4}\,T$ (V)

In NaCl-KCl (temperature range: 950-1100 K)
Niobium
$E°_{54}= -0.55 + 5 \times 10^{-4}\,T$ (V)
$E°_{43}= -1.49 + 5 \times 10^{-4}\,T$ (V)
$E°_{30}= -1.69 + 3.5 \times 10^{-4}\,T$ (V)

Titanium
$E°_{43}= -0.565 + 2.2 \times 10^{-4}\,T$ (V)
$E°_{32}= -2.845 + 8.8 \times 10^{-4}\,T$ (V)
$E°_{20}= -2.330 + 3.7 \times 10^{-4}\,T$ (V)

A temperature increase induces a large positive shift of the standard potentials. $NbCl_5$ is a very oxidizing compound which, at a temperature higher than around 1000 K, oxidizes the chloride ions. The value of the standard Gibbs energy of formation (kJ/mol) of the compounds dissolved in the electrolyte can be calculated form the previous results.

$\Delta G°_{(NbCl5)s} = F(E°_{54} + E°_{43} + 3E°_{30})$
$\Delta G°_{(NbCl4)s} = F(E°_{43} + 3E°_{30})$
$\Delta G°_{(NbCl3)s} = 3FE°_{30}$

$\Delta G°_{(TiCl4)s} = F(E°_{43} + E°_{32} + 2E°_{20})$
$\Delta G°_{(TiCl3)s} = F(E°_{32} + 2E°_{20})$
$\Delta G°_{(TiCl2)s} = 2FE°_{20}$

LiCl-KCl	NaCl-KCl

$\Delta G^\circ_{(NbCl5)s} = -781 + 3.1 \times 10\text{-}3\ T$ $\Delta G^\circ_{(NbCl5)s} = -696 + 2.0 \times 10^{-3}\ T$
$\Delta G^\circ_{(NbCl4)s} = -703 + 2.5 \times 10\text{-}3\ T$ $\Delta G^\circ_{(NbCl4)s} = -643 + 1.5 \times 10^{-3}\ T$
$\Delta G^\circ_{(NbCl3)s} = -556 + 1.9 \times 10\text{-}3\ T$ $\Delta G^\circ_{(NbCl3)s} = -489 + 1.0 \times 10^{-3}\ T$

LiCl-KCl	NaCl-KCl

$\Delta G^\circ_{(TiCl4)s} = -762 + 1.7 \times 10\text{-}3\ T$ $\Delta G^\circ_{(TiCl4)s} = -779 + 1.8 \times 10^{-3}\ T$
$\Delta G^\circ_{(TiCl3)s} = -697 + 1.6 \times 10\text{-}3\ T$ $\Delta G^\circ_{(TiCl3)s} = -724 + 1.6 \times 10^{-3}\ T$
$\Delta G^\circ_{(TiCl3)s} = -430 + 0.6 \times 10\text{-}3\ T$ $\Delta G^\circ_{(TiCl3)s} = -450 + 0.7 \times 10^{-3}\ T$

The diffusion coefficients of the electroactive species involved in the metal deposition, mainly Ti^{2+} and Nb^{3+} were determined by chronopotentiometry using the Sand's equation. The temperature dependence obeys the Arrhenius equation, $D = D_0 \exp(-\Delta H/RT)$, with:

Niobium in LiCl-KCl $D_0 = 1.95 \times 10^{-2}\ cm^2\ s^{-1}$ $\Delta H = 50\ kJ$
NaCl-KCl $D_0 = 1.15 \times 10^{-2}\ cm^2\ s^{-1}$ $\Delta H = 48\ kJ$

Titanium in LiCl-KCl $D_0 = 0.83 \times 10^{-2}\ cm^2\ s^{-1}$ $\Delta H = 43\ kJ$
NaCl-KCl $D_0 = 0.49 \times 10^{-2}\ cm^2\ s^{-1}$ $\Delta H = 41\ kJ$

Fluoride Ions

Taking into account the properties of the electrolytic solutions, the refractory metals can be obtained by electro-reduction in molten alkali halides. However, in pure alkali chlorides melts, it is difficult to obtain deposits of good quality. Most of them are porous, powdery and the coatings adhere poorly to the substrate surface. This results from the influence of disproportionation reactions such as:
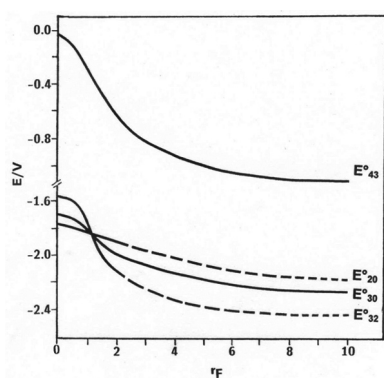
$$3Ti^{2+} \leftrightarrow 2Ti^{3+} + Ti \tag{10}$$

$$4Nb^{3+} \leftrightarrow 3Nb^{4+} + Nb \tag{11}$$

Figure 5: Influence of the fluoride ions on the standard potential of the *redox* couples Ti^{4+}/Ti^{3+}, Ti^{3+}/Ti^{2+}, Ti^{3+}/Ti and Ti^{2+}/Ti in NaCl-KCl containing increasing amounts of fluoride ions. Concentration of titanium ions: 0.1 mol dm^{-3}; molar ratio r_F = F/Ti. Reference electrode: Pt^{2+}/Pt. Temperature: 720°C.
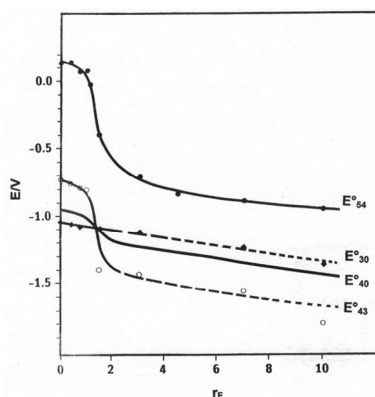
Figure 6: Influence of the fluoride ions on the standard potential of the *redox* couples Nb^{5+}/Nb^{4+}, Nb^{4+}/Nb^{3+}, Nb^{4+}/Nb and Nb^{3+}/Nb in NaCl-KCl containing increasing amounts of fluoride ions. Concentration of niobium ions: 0.196 mol dm^{-3}; molar ratio r_F = F/Nb. Reference electrode: Pt^{2+}/Pt. Temperature: 670°C.

Moreover, in the case of niobium, insoluble subhalides, such as Nb_3Cl_8, were generated at the electrode surface and perturb the deposition process. To avoid these inconveniences it is useful to introduce fluorides ions which give strong complexes with the refractory ions. The effect of increasing amount of fluoride ions on the various standard potentials of redox couples is shown in Figures 5 and 6. A strong decrease of potentials involving the higher oxidation states was obtained. This effect is due certainly to the introduction of small fluoride ions in place of large chloride ions in the metal complexes, $NbCl_6^-$, $NbCl_6^{2-}$ or $TiCl_6^{2-}$ and $TiCl_6^{3-}$. The fluoride complexes being more stable than chloride complexes result in a large negative shift of the corresponding potentials. At the lower oxidation states, the complex formation is very weak, and no complex has been identified; so the influence of fluoride ions in this case remains very weak. The standard potential concerning the reduction reaction of these low valency ions did not change very much when fluoride ions were introduced.

The shift of the standard potential was attributed to the energy of formation of the fluorides complexes. The introduction of 6 fluorine atoms for one metal ion in solution induces a change in the Gibbs energy of formation of around -250 kJ/mol for Ti^{4+} complexes and of -150 kJ/mol for Ti^{3+} complexes. For niobium, the changes are -190 kJ/mol for Nb^{5+} and -100 kJ/mol for Nb^{4+}. Consequently, the higher oxidations were stabilized and the direct reduction of Nb^{4+} to Nb and Ti^{3+} to Ti was obtained. The reduction to metal was not perturbed any more by disproportionation reaction or by the presence of subhalides. Compact and coherent deposits were obtained as soon as the ratio F/Me reached a value of around three.

CONCLUSIONS

Transient electrochemical techniques indicate that, in fused alkali halides, the refractory metal ions exist in several oxidations states. The values of the standard potentials of the corresponding redox couples were determined. It is shown that, in pure chloride baths, the metal is obtained from the reduction of the stables species Ti^{2+} or Nb^{3+}, however these ions are involved in disproportionation reactions which give rise to deposits of low quality, porous or powdery. Introducing fluoride ions strongly improve the quality and adherence of the deposits. This beneficial effect comes from the strong complexing power of fluoride ions which increases significantly the formation energy of complexes

involving the higher oxidation states of refractory metal ions. From an industrial point of view, the present study shows that a small amount of fluorides is required to obtain convenient good quality deposits without loosing the advantage of chlorides which remain less corrosive and expensive than fluoride baths.

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