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Electrochemical behaviour of manganese in the aluminium electrorefining bath

J. CHRYSSOULAKIS, J. BOUTEILLON

Laboratoire d'Energétique Electrochimique Associé au CNRS (LA 265) E.N.S.d'Electrochimie et d'Electrométallurgie B.P. 44, Domaine Universitaire, 38401 St-Martin D'Heres, France

D. INMAN

Department of Metallurgy and Materials Science, Imperial College, London SW7, UK

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The study of the mechanism of the electrode reaction Mn(II)/Mn in the aluminium electrorefining bath free of aluminium fluoride (1·48 NaF–1·05 $BaCl_2$) has been carried out by chronopotentiometry with an inert graphite electrode, a manganese electrode and a platinum electrode; this study was supplemented by utilizing anodic chronopotentiometry with current reversal from a stationary state. The tests carried out at 800° C show that the exchange mechanism of Mn(II)/Mn is reversible, involves the exchange of two electrons and that the diffusion coefficient $D_{\mathrm{Mn(II)}} = (1{\cdot}9 \pm 0{\cdot}5) \times 10^{-5}\ \mathrm{cm^2\,s^{-1}}$.

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1. Introduction

We have studied previously the electrochemical behaviour of copper in the aluminium electrorefining bath. We have also studied iron [1] which is the other main impurity of electrolytic aluminium [2]. Here we are interested in the anodic and cathodic behaviour of manganese, another important impurity [3] of electrolytic aluminium.

The literature about the electrochemical behaviour of manganese in the molten fluoride mixtures or the molten mixtures of chlorides and fluorides is rather restricted [4–7]. Grjotheim [5] gives the value $E_{i=0} = -1{\cdot}04$ V versus the Ni(II)/Ni reference electrode while Delimarskii [6] indicates that it is the oxidation number 2+ for manganese which is stable in different mixtures of molten fluorides between 700° C and 1000° C. The measurements of Boronenkov [7] also concern aluminates. He studies the reduction of Mn(II) ions on a molybdenum electrode in an aluminate molten bath between 1370° C and 1470° C; he determines the diffusion coefficients of these ions ($D = 2 \times 10^{-5}$–$6 \times 10^{-5}\ \mathrm{cm^2\,s^{-1}}$) in the same temperature range.

2. Experimental technique

2.1. *Solvent and solute*

The voltammetric curves obtained with a graphite electrode in the molten refining bath 1·48 NaF–AlF_3–1·05 $BaCl_2$ containing MnF_2 (Fig. 1) show that the reduction of the manganese ions takes place at a potential only slightly more anodic than that of aluminium. The study of the system Mn(II)/Mn is thus best carried out in a bath free of aluminium fluoride. The region of electro-inactivity of the solvent [between the potentials for the oxidation of the Cl^- ions and the reduction of the Al(III) ions] is shown in Fig. 1.

The preparation and purification of the solvent (1·48 NaF–1·05 $BaCl_2$) was described before [1, 2].

Manganese fluoride MnF_2 (Koch-Light > 95%) has been utilized as the solute; it is added to the solvent melt without pre-treatment.

2.2. *Electrodes*

The working electrodes, graphite, manganese or platinum, were rectangular plates of surface area between 2·2 $\mathrm{cm^2}$ and 3·3 $\mathrm{cm^2}$.

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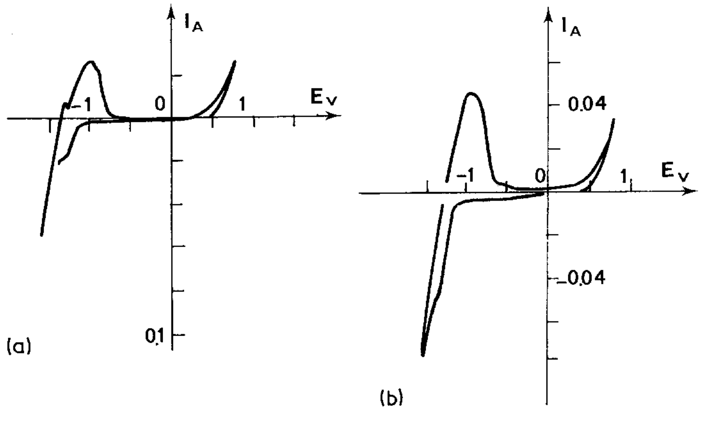

Fig. 1. Voltammetric traces at a graphite electrode, in the aluminium electrorefining bath (1·48 NaF, 1 AlF$_3$, 1·05 BaCl$_2$). $E_{i=0} = -0{\cdot}31$ V versus the reference electrode; $C_{\mathrm{Mn(II)}} = 11 \times 10^{-5}$ mol cm^{-3}; sweep rates: (a) 1 V s^{-1}, (b) 10 V s^{-1}.

The vitreous carbon counter electrode is a rectangular plate with much larger surface area arranged parallel to the working electrode.

The half cell Ag/AgCl(M)–NaCl–KCl//NaCl–KCl//NaF–BaCl$_2$ is the reference electrode.

2.3. *Electrolytic cell and electrical equipment*

The measurements were carried out under an atmosphere of purified argon in the cell described previously [2]. We have utilized the same chronopotentiometric equipment [1, 8].

3. Chronopotentiometric study of the cathodic behaviour of Mn(II)

The chronopotentiometric curves were recorded for manganese (II) fluoride concentrations between 10^{-5} and 10^{-4} mol cm^{-3}. With the graphite electrode we observed (Fig. 2a) that the Sand's relationship was not verified because of reactions taking place before the formation of the manganese deposit. Also on the manganese electrode (Fig. 2b) the transition is badly defined and not reproducible (this anomaly can be explained by a modification of the surface) but with the platinum electrode the transition is well defined (Fig. 3). We have verified that the Sand's law is satisfied when the transition time is between 0·1 and 0·5 s.

Examination of the curves representing the variation of potential with $\ln(\tau^{1/2} - t^{1/2})/\tau^{1/2}$ or $\ln(\tau^{1/2} - t^{1/2})/t^{1/2}$ does not permit a conclusion on the form (whether insoluble or soluble) of the deposit formed on the platinum electrode. We therefore propose a diagnostic criterion for making this distinction.

Let $A(t)$ be a function defined by

$$A(t) = E(t) - \frac{2{\cdot}3\,RT}{nF} \ln \frac{\tau^{1/2} - t^{1/2}}{t^{1/2}}$$

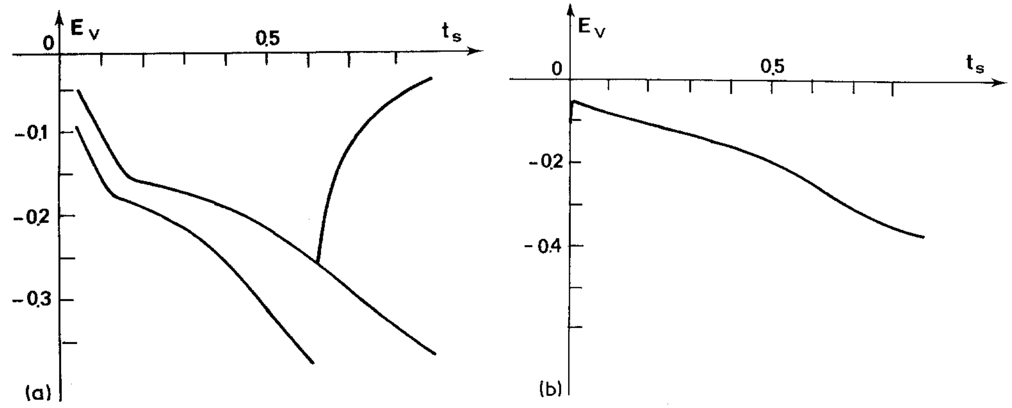

Fig. 2. Chronopotentiograms obtained in the solvent 1·48 NaF, 1·05 BaCl$_2$ using: (a) a graphite electrode, $C_{\mathrm{Mn(II)}} = 11 \times 10^{-5}$ mol cm^{-3}; $|i| = 0{\cdot}156$, $0{\cdot}187$ A cm^{-2}; (b) a manganese electrode, $C_{\mathrm{Mn(II)}} = 5 \times 10^{-5}$ mol cm^{-3}; $|i| = 0{\cdot}134$ A cm^{-2}.

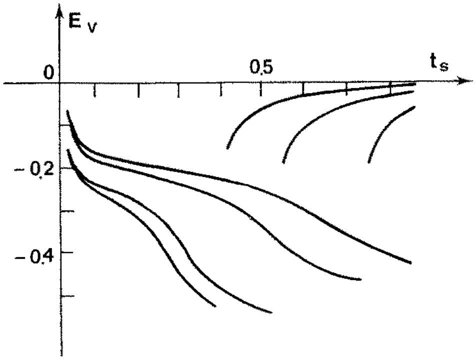

Fig. 3. Chronopotentiograms obtained at a platinum electrode in the solvent 1·48 NaF, 1·05 BaCl$_2$. $C_{\mathrm{Mn(II)}} = 2{\cdot}8 \times 10^{-5}$ mol cm^{-3}; $|i| = 33{\cdot}5$, 38·2, 47·8, 52·6 mA cm^{-2}.

where $E(t)$ is the experimental value of the electrode potential as a function of time, and n is the number of electrons exchanged in the electrode reaction. One sees that if one postulates a number n corresponding to the true number of electrons exchanged then the function $A(t)$ will be independent of t if the product is insoluble [9]

$$E = E_i - \frac{0{\cdot}203}{n}\log\frac{\tau^{1/2}-t^{1/2}}{\tau^{1/2}}$$

but will vary linearly as a function of log (t/τ) if the product is soluble [9]

$$E = E_{1/2} + \frac{0{\cdot}203}{n}\log\frac{\tau^{1/2}-t^{1/2}}{t^{1/2}}.$$

If one postulates an incorrect value for n then the variation of $A(t)$ will be complex.

In the acceptable range of concentration ($< 6 \times 10^{-5}$ mol cm^{-3}) and assuming $n = 2$ one establishes (Fig. 4, curves 1–4) for short transition times that $A(t)$ is constant. Hence the reduction of the Mn(II) ions to Mn takes place with the exchange of two electrons and the formation of an insoluble product on the electrode.

On the other hand when the transition time increases (Fig. 4, curves 5 and 6) $A(t)$ varies linearly with ln t/τ; this can be attributed to the dissolution of manganese in platinum as we have confirmed by identifying the compound Mn·Pt$_3$ by electron microprobe analysis of a deposit of manganese on a platinum electrode. Nevertheless one cannot eliminate the possibility of a modification of the surface of the platinum electrode as the result of the formation of dendrites.

In order to confirm these results and to study

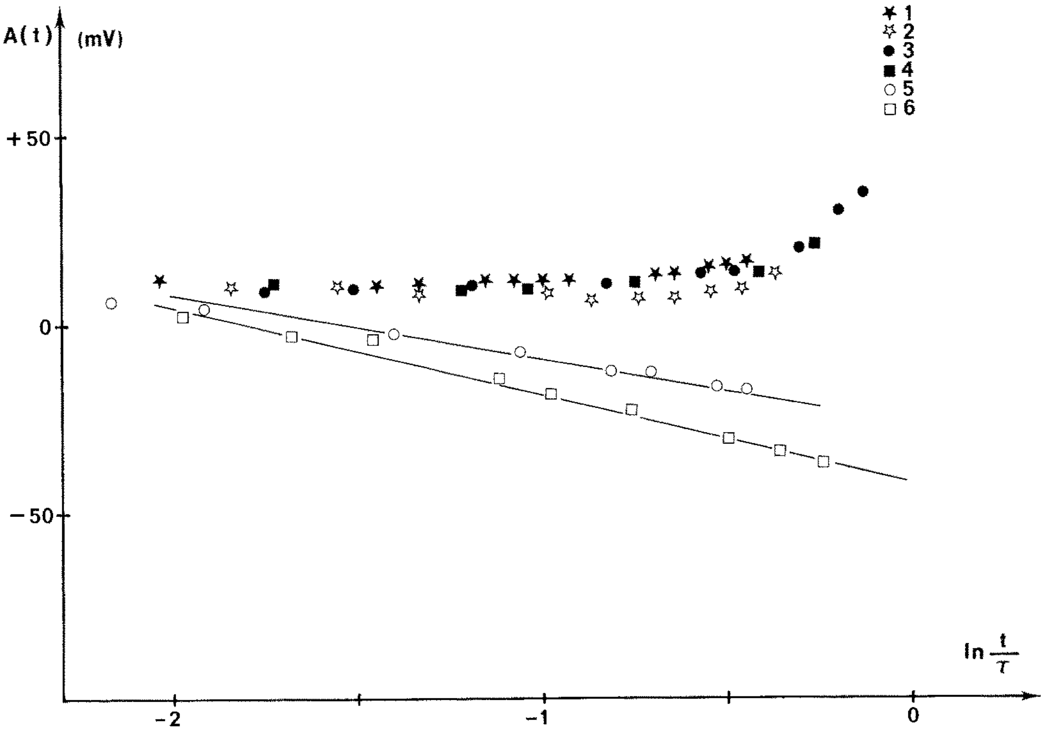

Fig. 4. Curves $A(t) = f \ln(t/\tau)$ drawn at a platinum electrode for various transition times: (1) $\tau = 0{\cdot}19$ s; (2) $\tau = 0{\cdot}23$ s; (3) $\tau = 0{\cdot}34$ s; (4) $\tau = 0{\cdot}38$ s; (5) $\tau = 1{\cdot}75$ s; (6) $\tau = 2{\cdot}03$ s.

the anodic behaviour of manganese we have studied the system Mn(II)/Mn by anodic chronopotentiometry with current reversal from a stationary state; this method permits us to study the exchange Mn(II)/Mn with a manganese electrode.

4. Study by anodic chronopotentiometry with current reversal from a stationary state

This method was proposed simultaneously by Kisza and Twardoch [10], and Baraboshkin and Vinogradov [11]; it permits the study of a system

$$\mathrm{Me}^{n+} + ne \rightleftarrows \mathrm{Me}$$

with the aid of an electrode of metal Me immersed in the solvent free of the ions Me^{n+}. Warren *et al.* [12] used this method to study the anodic and cathodic behaviour of tantalum in the fused solvents CsCl–KCl and LiCl–KCl.

An anodic current density, i_a, is first applied and kept constant during a time, t_a, necessary to reach a stationary state at the electrode surface. Then the dissolution is reversed by applying a constant current density i_c

$$\mathrm{Me} \underset{i_a}{\overset{i_c}{\leftrightarrows}} \mathrm{Me}^{n+} + ne.$$

During time t_a, the flux of metal ions towards the bulk of the solution is constant and given by

$$D_{\mathrm{Me}^{n+}}\left(\frac{\partial C}{\partial x}\right)_{x=0} = -\frac{i_a}{nF}.$$

During the metal disposition, we have the condition

$$D_{\mathrm{Me}^{n+}}\left(\frac{\partial C}{\partial x}\right)_{x=0} = \frac{i_c}{nF}.$$

The concentration of metal ions follows Fick's second law. If the transition time is defined in an ordinary way

$$C(0, t) = 0 \quad \text{for} \quad t = \tau_c$$

when Fick's laws are solved, the following relation is obtained:

$$\tau_c^{1/2}\frac{i_a + i_c}{i_a} = t_a^{1/2}$$

It is necessary to verify this relation to be sure that the stationary state has been reached during the first pulse, then the cathodic wave can be analysed normally.

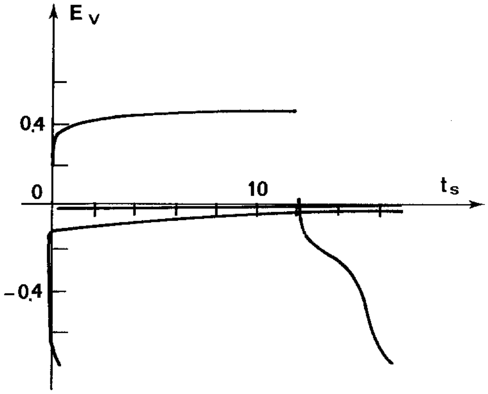

Fig. 5. Anodic chronopotentiogram with current reversal from a stationary state drawn on a manganese electrode in pure 1·48 NaF, 1·05 $BaCl_2$ solvent; $|i| = 0{\cdot}856\ \mathrm{A\,cm^{-2}}$.

In our experiments, the manganese electrode is polarized anodically by a constant current; when the stationary state is reached, the current is reversed and one measures the transition time τ_c corresponding to the reduction of the ions (Fig. 5) then available in the solution.

We have verified that the equations relating τ_c, i_a, i_c and t_a are satisfied for values of current density between 0·4 and 0·85 A cm^{-2}. The electrode potentials $E_{t_a/4}$ and $E_{\tau_c/4}$ are equal and depend on the concentration of the ions dissolved. The overpotential $\Delta E_{\tau_c/4}$ is in neighbourhood of 0·034 V versus the reference electrode, the order of magnitude corresponding to the reversible exchange of two electrons [10].

These results confirm that the process

$$\mathrm{Mn(II)} + 2e \rightleftarrows \mathrm{Mn}$$

is reversible as was indicated earlier by the measurements made on the platinum electrode by cathodic chronopotentiometry.

5. Determination of the diffusion coefficient of the manganese ions Mn(II)

The number of electrons exchanged in the course of the process Mn(II) ⇄ Mn is equal to two. The average value of

$$\frac{i\sqrt{\tau}}{C_0}\ (= 7{\cdot}5 \times 10^2\ \mathrm{A\,s^{1/2}\,mol^{-1}\,cm})$$

obtained by the aid of chronopotentiometric curves enables us to evaluate the diffusion coefficient for the manganese ions Mn(II).

$$D_{\mathrm{Mn(II)}} = (1{\cdot}9 \pm 0{\cdot}5) \times 10^{-5}\ \mathrm{cm^2\ s^{-1}}$$

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