

*The role of diffusion of ionic species and of interdiffusion in the solid state in electrolytic deposition processes from molten salts**

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Technical applications of electrocoating from molten salts involve the study of electrochemical reactions which are under the control of diffusion of electroactive species. Chemical reactions and ionic transport in the melt have previously been examined. Now the role of interdiffusion in the solid state is considered in the electrolytic deposition processes for coating metal and alloy substrates. The rate of diffusion into the substrate is the rate-controlling process. The study of the kinetics of incorporation by pulse electrochemical techniques is described.

It is shown that the classical treatment used to describe the diffusion-controlled phenomena has to be modified to take account of the volume change of the electrode due to the metal incorporation. A mathematical analysis is presented to include the perturbation resulting from the boundary motion which occurs during electrolysis at constant potential or at constant current (galvanodiffusion). Examples of application of this treatment in recent studies of metalliding reactions are given and discussed in relation to the experimental case of aluminiding iron.

1. Introduction

The technical applications of electrocoating from molten salts involve the study of electrochemical reactions which are often under the control of diffusion of the electroactive species [1]. There are two electrolytic deposition processes for coating metal or alloy substrates: electroplating [2, 3] which produces a constant composition layer of metal coating on the substrate, and metalliding which involves simultaneous deposition and solid-state intermetallic diffusion [4]. In the former process the rate of deposition is generally limited by the diffusion of ions in the liquid electrolyte [5]; the latter is under the control of the diffusion of metallided element into the solid substrate [6]. These two kinds of diffusion in the electrolyte and in the solid intervene when the coating is built up by codeposition of several elements; the composition of the coating depends on the diffusion fluxes in the electrolyte and on the interdiffusion in the coating.

In the present paper the kinetics of diffusion coating is examined in all its stages. Electrochemical pulse techniques are used to study the behaviour of alloy electrodes [7] in fused salts. Special attention is paid to the influence of the metallic interdiffusion coefficient on the electrochemical generation of the coating.

2. Basic principles of the method

The method involves the use of polarization cells which have the general configuration [8]:

Alloy electrode A-B / Liquid or solid electrolyte containing A^{n+} / Pure A

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The reference electrode is a rod of pure A in contact with the electrolyte. At equilibrium the e.m.f., E^* , of the cell depends on the activity, a_A^* , of the element A at the surface of the alloy electrode:

$$E^* = -\frac{RT}{nF} \log a_A^* \quad (1)$$

where the superscript * refers to the equilibrium situation. The activity, a_A , is related to the concentration, C_A , by

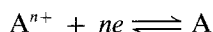
$$a_A = f_A C_A \quad (2)$$

The term f_A is a coefficient which depends on the activity coefficient, γ_A , and on the atomic fraction X_A ($\gamma_A = a_A/X_A$):

$$f_A = \gamma_A \frac{X_A M_A + (1 - X_A) M_B}{\rho_{AB}} \quad (3)$$

ρ_{AB} being the alloy specific mass, and M_A and M_B the atomic masses of A and B. Then when the activity coefficients are known the concentration of A at the surface of the working electrode can be deduced from the measurement of the e.m.f. E .

The mechanism of the coating formation can be studied when a perturbation of the surface concentration occurs. The simple electrochemical reaction



is considered. For a fast charge transfer reaction it is assumed that the potential, E , is given by the Nernst equation:

$$E = \frac{RT}{nF} \log \frac{a_{n+}}{a_{n+}^* a_A} \quad (4)$$

A sufficiently long time scale is chosen to avoid the influence of the capacity of the double layer, of the adsorbed species and of the chemical reactions. The problem is limited to the relation between the surface activities and the transport of matter. When diffusion is the rate-determining step, the concentration changes in the bulk of the two phases (electrolyte and metal) obey the equation

$$\frac{dC_j(x, t)}{dt} = \frac{d}{dx} \left(D_j \frac{dC_j(x, t)}{dx} \right) \quad (5)$$

where j represents the electroactive species (A^{n+} or A) and x is the distance normal to the electrode surface. The initial boundary condition is

$$C_j(x, 0) = C_j^* \quad (6)$$

The thickness of the diffusing medium is considered to be large compared with the diffusion penetration depth; the condition of semi-infinite diffusion is fulfilled:

$$C_j(\infty, t) = C_j^* \quad (7)$$

The flow of metal away from the cathode surface into the interior of the cathode by diffusion is limited by the flow of metal, J_A , by electrodeposition, and is equal to it. Therefore, the current density, i , associated with the perturbation is (i being positive for an oxidation process):

$$i = -J_A nF = -v nF D_j \left(\frac{dC_j(x, t)}{dx} \right)_{\text{interface}} \quad (8)$$

with $v = +1$ for $j = A^{n+}$ and $v = -1$ for $j = A$.

The concentration profile $C_j(x, t)$ can be calculated by integrating the rate equation 5 for different boundary conditions, taking into account the electrochemical constraints. It is proposed to examine these solutions when the electrolysis is performed under potentiostatic or galvanostatic conditions.

3. Potentiostatic transients

A potential step is applied to the working electrode by means of a potentiostatic device and the corresponding current intensity is determined by differential measurement in the counter electrode circuit and recorded. The concentrations at the interface are now fixed,

$$C_j(0, t) = C_j^s \quad (9)$$

and obey the equation

$$\frac{f_A^s C_A^s}{f_{n+}^s C_{n+}^s} = \frac{f_A^* C_A^*}{f_{n+}^* C_{n+}^*} \exp\left(-\frac{nF\eta}{RT}\right) \quad (10)$$

where η is the potential step, $E - E^*$. For a constant value of D_j and the initial condition of Equation 6, Equation 5 has the solution

$$C_j(x, t) = C_j^* + (C_j^s - C_j^*) \operatorname{erfc} [x/2(D_j t)^{1/2}] \quad (11)$$

where erfc is the complement error function. Insertion in Equation 8 leads to

$$i = nF(C_j^s - C_j^*) \left(\frac{D_j}{\pi t}\right)^{1/2} \quad (12)$$

Depending on the values of the ratios $(C_j^s - C_j^*)/C_j^*$, two different situations can be considered. The greater ratio indicates the rate-determining process (diffusion in the electrolyte or in the electrode). In fact, Equation 12 shows that the concentration changes in the electrode and in the electrolyte are inter-related at any time by

$$\frac{C_A^s - C_A^*}{C_{n+}^* - C_{n+}^s} = \left(\frac{D_{n+}}{D_A}\right)^{1/2} \quad (13)$$

Then, when $C_A^* D_A^{1/2} \gg C_{n+}^* D_{n+}^{1/2}$, the electrode response is controlled by the ion diffusion in the electrolyte. An extreme situation is reached when the working electrode is made of pure A. In this case the concentration $C_A(x, t)$ remains constant during the whole experiment; The electrode potential depends only on the value of C_{n+}^s , and D_{n+} can be measured from the slope of the straight line, $i = f(t^{-1/2})$ (see Equation 12). This procedure has often been used to determine the ionic diffusion coefficients in fused electrolytes [9, 10] provided that no dendrite formation occurs and modifies the electrode surface.

When $C_A^* D_A^{1/2} \ll C_{n+}^* D_{n+}^{1/2}$, the ratio C_{n+}^s/C_{n+}^* is near to unity and the e.m.f measurement gives the value of C_A^s (Equation 10). Now the diffusion coefficient, D_A , in the metallic electrode can be determined from the slope of the straight line, $i = f(t^{-1/2})$.

The previous calculations concern a semi-infinite diffusion process. When a liquid electrolyte is used this condition requires that the mean diffusion path $(2D_{n+}t)^{1/2}$ remains smaller than the thickness, δ , of the diffusion layer. When

$$(2D_{n+}t)^{1/2} \gg \delta \quad (14)$$

Equation 12 should be replaced by

$$i = nFD_{n+} \frac{C_{n+}^s - C_{n+}^*}{\delta} \quad (15)$$

where i is taken to be positive for an oxidation process ($\eta > 0$). Taking account of Equation 12 for $j = A$ and for

$$t \gg \frac{D_A}{\pi} \left(\frac{\delta C_A^*}{D_{n+} C_{n+}^*}\right)^2 \quad (16)$$

the concentration change of A^{n+} at the electrode surface can be neglected, and the electrode response

depends only on the solid-state diffusion provided that the inequality 14 is also verified and that the concentration of pure A is not reached.

To illustrate these calculations the case of diffusion of aluminide iron coatings is briefly considered. In this case A = aluminium and B = iron, and the electrolyte is a solution of AlF_3 in NaF at 1020°C . The reference electrode and the counter electrode comprise a pool of liquid aluminium. Preliminary experiments are carried out on a liquid aluminium electrode made of a rod of titanium boride covered by a thin layer of liquid aluminium. The concentration, $C_{\text{Al}}(x, t)$, remains constant and according to the previous procedure the diffusion coefficient, $D_{\text{Al}^{3+}}$ of aluminium ions is measured.

In the concentration range $10^{-6} < C_{\text{Al}^{3+}} < 10^{-4} \text{ mol cm}^{-3}$, a value $D_{\text{Al}^{3+}} = 8.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ has been found which can be compared to the value $D_{\text{Al}^{3+}} = 6.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ obtained [11] in cryolite ($C_{\text{Al}^{3+}}^* = 0.0087 \text{ mol Al}^{3+} \text{ cm}^{-3}$) at the same temperature. On the recorded chronoamperograms for $t = 1 \text{ s}$ and $C_{\text{Al}^{3+}}^* = 2 \times 10^{-6} \text{ mol cm}^{-3}$, a current density $i = -1.25 \text{ mA cm}^{-2}$ is observed for a potential jump $\eta = -20 \text{ mV}$ ($C_{\text{Al}^{3+}}^s = 1.17 \times 10^{-6} \text{ mol cm}^{-3}$). An iron working electrode is then used and equilibrated at $E^* = 400 \text{ mV}$ versus $\text{Al}-\text{Al}^{3+}$ electrode. At that potential a small positive current of a few μA is detected, which probably corresponds to the oxidation of iron. The activity coefficients of aluminium dissolved in iron are deduced from vapour pressure measurements [12]:

$$\log \gamma_{\text{Al}} = 16.336 - 68.441(1 - X_{\text{Al}}) + 75.477(1 - X_{\text{Al}})^2 - 29.543(1 - X_{\text{Al}})^3 \quad (17)$$

for $0 < X_{\text{Al}} < 0.5$.

The equilibrium concentration, C_{Al}^* , at $E^* = 400 \text{ mV}$ is $1.28 \times 10^{-3} \text{ mol cm}^{-3}$. A potential step is applied to the electrode and the corresponding current is measured. For $t = 1 \text{ s}$ and $\eta = -20 \text{ mV}$, a current density of $-0.055 \text{ mA cm}^{-2}$ is observed. As the diffusion coefficient, $D_{\text{Al}^{3+}}$, is known, the value of $C_{\text{Al}^{3+}}^s$ is deduced from Equation 12: $C_{\text{Al}^{3+}}^s = 1.635 \times 10^{-6} \text{ mol cm}^{-3}$. By introducing this value in Equation 10 it is found that $C_{\text{Al}}^s = 1.77 \times 10^{-3} \text{ mol cm}^{-3}$. Finally, from Equation 12 the interdiffusion coefficient [13] is found: $D_{\text{Al}-\text{Fe}} = 4.8 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$.

The concentration profiles, $C_j(x, t)$, corresponding to these numerical values are presented in Fig. 1. The ionic concentration overvoltage is

$$\eta_{\text{Al}^{3+}} = \frac{RT}{nF} \log \frac{C_{\text{Al}^{3+}}^s}{C_{\text{Al}^{3+}}^*} = -7.5 \text{ mV}$$

For this experiment $\eta_{\text{Al}^{3+}}$ constitutes a large part of the total overvoltage (-20 mV) and cannot be neglected. However, as pointed out above, the concentration change of ionic species becomes negligible at long times. For example, at $t = 50 \text{ s}$ Equation 15 can be used to calculate the surface concentration $C_{\text{Al}^{3+}}^s = 1.95 \times 10^{-6} \text{ mol cm}^{-3}$. The thickness of the diffusion layer has been taken to be equal to 0.01 cm ; in this situation the ionic concentration overvoltage is smaller than 1 mV .

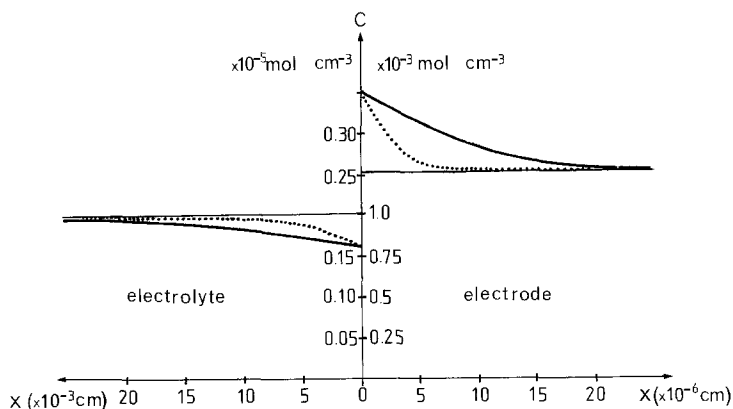


Fig. 1. Concentration profiles during potentiostatic deposition of aluminium from fused NaF containing AlF_3 ($C_{\text{Al}^{3+}}^* = 0.2 \times 10^{-5} \text{ mol cm}^{-3}$) on an iron working electrode at 1020°C . $E^* = 0.4 \text{ V}$ versus $\text{Al}-\text{Al}^{3+}$ reference electrode; $C_{\text{Al}}^* = 1.28 \times 10^{-3} \text{ mol cm}^{-3}$; potential step, $\eta = -0.02 \text{ V}$; $C_{\text{Al}}^s = 1.77 \times 10^{-3} \text{ mol cm}^{-3}$; $C_{\text{Al}^{3+}}^s = 0.164 \times 10^{-3} \text{ mol cm}^{-3}$. \cdots Profile at $t = 0.1 \text{ s}$; — profile at $t = 1 \text{ s}$.

However, at that time the current density is very small (about $-130 \mu\text{A cm}^{-2}$) and the current fluctuations ($\pm 10 \mu\text{A cm}^{-2}$) become relatively important.

To avoid these perturbations, higher aluminium concentrations can be used. For $t = 1 \text{ s}$ and $\eta = -20 \text{ mV}$, a current density of -0.80 mA cm^{-2} is observed when $C_{\text{Al}^{3+}}^* = 10^{-5} \text{ mol cm}^{-3}$. The surface concentrations are $C_{\text{Al}^{3+}}^s = 9.5 \times 10^{-6} \text{ mol cm}^{-3}$ and $C_{\text{Al}}^s = 2.02 \times 10^{-3} \text{ mol cm}^{-3}$. The calculated diffusion coefficient is $D_{\text{Al-Fe}} = 4.3 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$. If the ion concentration changes were neglected, an error of -25% would result on the $D_{\text{Al-Fe}}$ value. For higher values of $C_{\text{Al}^{3+}}^*$ this influence becomes negligible; for $C_{\text{Al}^{3+}}^* = 10^{-4} \text{ mol cm}^{-3}$, neglecting ion concentration change causes an error smaller than 1% .

In these examples a small overvoltage has been used ($\eta = -20 \text{ mV}$), and therefore the aluminium concentration in the working electrode does not change very much. The calculated interdiffusion coefficient, $D_{\text{Al-Fe}}$, is assigned to the mean composition $\frac{1}{2}(C_{\text{Al}}^s + C_{\text{Al}}^*)$. Indeed the exact solution of the differential Equation 5, represented by Equation 11, implies that D_{A} is concentration independent. For larger values of η it would be necessary to consider that D_{A} is not constant. The integration of Fick's equation shows that even in this situation there is always a linear dependence of i on $t^{-1/2}$ as for Cottrell's law [14]. By analogy a diffusion coefficient, D_{Cot} , can be defined from the experimental result:

$$D_{\text{Cot}} = \pi \left[\frac{p}{nF(C_{\text{Al}}^s - C_{\text{Al}}^*)} \right]^2 \quad (18)$$

where p is the slope of the straight line $i = pt^{-1/2}$, and D_{Cot} is associated with the diffusion of aluminium into an iron substrate at diffusion concentration, C_{Al}^* , from a surface concentration C_{Al}^s . The concentration for which $D_{\text{Al-Fe}} = D_{\text{Cot}}$ depends on the function $D_{\text{Al-Fe}} = f(C_{\text{Al}})$, but this problem is not yet solved except by numerical integration methods.

4. Galvanostatic transients

Electrolysis at constant current density has often been used for metallurgical preparation and for the study of electrochemical reactions. This regime may lead to a complete depletion of an electroactive species at the electrode interface. The time interval required to reach this situation is referred to as the transition time, τ , and is a function of the concentration of the substance, j , to be electrolysed. When diffusion is the main mass transport mechanism in the electrolysis there is a linear proportionality between τ and D_j :

$$\tau = \pi D_j \left(\frac{nFC_j^*}{2i} \right)^2 \quad (19)$$

This equation has often been used to determine the diffusion coefficient of electroactive species [15, 16]. However, the analysis of the potential changes during the whole experiment is also useful for the determination of electrode processes. For a constant value of i the solution of the boundary value problem is of the form

$$C_j(x, t) = C_j^* + 2J_j \left(\frac{t}{\pi D_j} \right)^{1/2} \exp(-x^2/4D_j t) - \frac{J_j x}{D_j} \operatorname{erfc} \left[\frac{x}{2(D_j t)^{1/2}} \right] \quad (20)$$

where the flux of species j is equal to i/vnF . The flux, J_j , is positive when it corresponds to an enrichment of species j at the electrode interface. For a fast electrochemical reaction the potential is given by Equation 4. The activities at the interface are deduced from the activity coefficients and from the concentrations given by Equation 20 where $x = 0$:

$$C_j(0, t) = C_j^* + \frac{2it^{1/2}}{vnF(\pi D_j)^{1/2}} \quad (21)$$

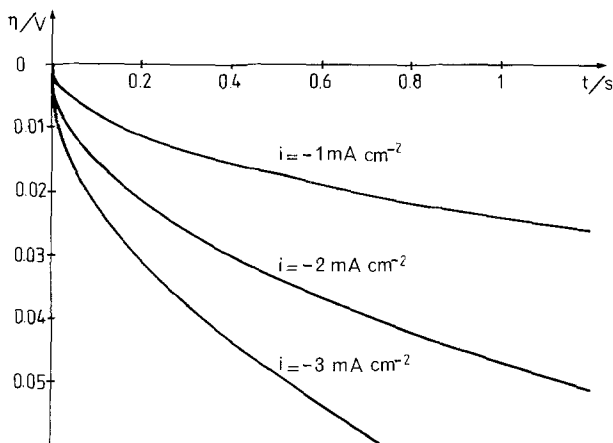


Fig. 2. Chronopotentiograms for aluminium deposition on an iron working electrode in a fused NaF electrolyte containing AlF_3 ($C_{\text{Al}^{3+}}^* = 0.2 \times 10^{-5} \text{ mol cm}^{-3}$) at 1020°C . $E^* = 0.4 \text{ V}$ versus $\text{Al}-\text{Al}^{3+}$ reference electrode; $C_{\text{Al}}^* = 1.28 \times 10^{-3} \text{ mol cm}^{-3}$.

As previously, the controlling process (diffusion in the electrolyte or in the electrode) is determined by the relative values of the products $C_j^* D_j^{1/2}$. At long times ($t > \delta^2/2D_{n+}$) the concentration, $C_{n+}(0, t)$, is given by the equation

$$C_{n+}(0, t) = C_{n+}^* + \frac{\delta i}{nFD_{n+}} \quad (22)$$

According to Equation 19 no transition time will be observed when

$$|i| < \left(\frac{nF\pi^{1/2} D_{n+} C_{n+}^*}{2^{1/2} \delta} \right) \quad (23)$$

Moreover, when the concentration changes are not too large ($C_j(0, t)/C_j^* \simeq 1$) the concentration change of ionic species can be neglected in Equation 4 at sufficiently long times:

$$t \gg \left[\pi D_A \left(\frac{\delta C_A^*}{2D_{n+} C_{n+}^*} \right)^2 \right] \quad (24)$$

By chronopotentiometry the diffusion coefficient of Al^{3+} in NaF has been determined at 1020°C using an aluminium working electrode; when a transition time is obtained, the quantity $i\tau^{1/2}/C_{\text{Al}^{3+}}^*$ is constant and equal to $2350 \text{ mol}^{-1} \text{ A cm s}^{1/2}$. The diffusion coefficient deduced from Equation 19 is $D_{\text{Al}^{3+}} = 8.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. The greatest transition time, τ_c , experimentally obtained is 1.1 s. From Equation 14 it can be deduced that the thickness of the diffusion layer, δ , is $(2D_{\text{Al}^{3+}} \tau_c)^{1/2} = 135 \times 10^{-4} \text{ cm}$. According to Equation 19 the smallest current density giving rise to a transition time is $-i_c = 2280 C_{\text{Al}^{3+}}^*$. For $C_{\text{Al}^{3+}}^* = 2 \times 10^{-6} \text{ mol cm}^{-3}$ this critical current density is -4.5 mA cm^{-2} .

When an iron electrode is used, aluminium diffusion contributes to the electrochemical process. Typical chronopotentiograms are reported in Fig. 2. These experiments correspond to a very low concentration of Al^{3+} ($C_{\text{Al}^{3+}}^* = 2 \times 10^{-6} \text{ mol cm}^{-3}$) and the ion diffusion brings a large contribution to the potential changes. As long as no convection process occurs this contribution increases at long times as indicated in Table 1. These chronopotentiograms have been chosen to illustrate the role of the two diffusion processes. The concentration profiles are given in Fig. 3 for $t = 0.1 \text{ s}$ and $t = 1 \text{ s}$.

The value of the diffusion coefficient $D_{\text{Al}^{3+}}$ is used to calculate the concentration $C_{\text{Al}^{3+}}(0, t)$ at the interface. From the experimental value of the overpotential the surface concentration of aluminium is determined by use of Equations 2, 3, 4 and 17. The slope of the straight line $C_{\text{Al}}(0, t) = f(t^{1/2})$ gives the interdiffusion coefficient $D_{\text{Al-Fe}}$ (Equation 21); the results are reported in Table 2.

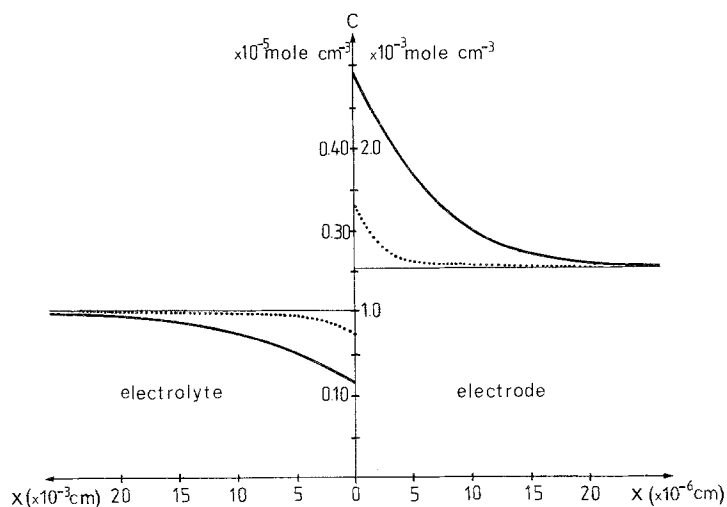


Fig. 3. Concentration profiles during galvanostatic deposition of aluminium corresponding to the chronopotentiogram of Fig. 2; $i = -2 \text{ mA cm}^{-2}$ Profile at $t = 0.1 \text{ s}$; — profile at $t = 1 \text{ s}$.

Neglecting the concentration changes of ionic species minimizes the values of the interdiffusion coefficient; this error is very important at low ion concentration but it becomes negligible at high concentration. The error is -25% for $C_{\text{Al}^{3+}} = 10^{-5} \text{ mol cm}^{-3}$; it is less than -1% for $C_{\text{Al}^{3+}} = 10^{-4} \text{ mol cm}^{-3}$.

5. Influence of the electrode boundary motion

When the concentration of electroactive species A^{n+} and A remains small the transport process can be considered as resulting from the diffusion of A^{n+} in the electrolyte and of A in the metal substrate of the electrode. In liquid electrolytes it has been shown that the diffusion coefficients measured by electrochemical techniques had the same value as the tracer diffusion coefficients [17]. Indeed, at low concentration the activity coefficients remain constant and the tracer diffusion coefficient is equal to the chemical or intrinsic diffusion coefficient.

However, in the electrochemical experiments the measured diffusion coefficient is the interdiffusion coefficient; the composition of the electrode surface depends on the diffusion of metal B into the deposited metal A and of the diffusion of A into the B matrix. The interdiffusion coefficient, D_A , is related to the intrinsic diffusion coefficients, \mathcal{D}_A and \mathcal{D}_B , by the equation

$$D_A = C_B V_B \mathcal{D}_A + C_A V_A \mathcal{D}_B \quad (25)$$

Table 1. Overvoltages deduced from the chronopotentiograms reported in Fig. 2

$i \text{ (mA cm}^{-2}\text{)}$	$t \text{ (s)}$	$-\eta \text{ (mV)}$	$\eta_{\text{Al}^{3+}}/\eta$
-1	0.1	7	0.34
	0.5	18	0.34
	1	25	0.35
-2	0.1	15	0.34
	0.5	33	0.39
	1	47	0.44
-3	0.1	23	0.36
	0.5	50	0.45
	1	72	0.52

Table 2. Results obtained at $t = 1$ s from galvanostatic transients at 1020°C on an iron electrode in fused NaF containing AlF_3 . The starting potential is 400 mV versus $\text{Al}-\text{Al}^{3+}$ electrode ($C_{\text{Al}}^* = 1.28 \times 10^{-3} \text{ mol cm}^{-3}$)

$C_{\text{Al}^{3+}}^*$ ($\times 10^{-5} \text{ mol cm}^{-3}$)	$-i$ (mA cm^{-2})	$-\eta$ (mV)	$C_{\text{Al}^{3+}}$ ($\times 10^{-5} \text{ mol cm}^{-3}$)	C_{Al} ($\times 10^{-3} \text{ mol cm}^{-3}$)	$D_{\text{Al-Fe}}$ ($\times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$)
0.2	1	25	0.16	1.9	3.95
	2	47	0.12	2.5	4.15
	3	72	0.07	3.0	4.5
1.0	1	16	1.0	1.9	4.3
	2	28	0.9	2.4	4.6
	3	38	0.8	2.9	5.0
10.0	1	15	9.95	1.9	4.5
	2	25	9.9	2.4	4.8
	3	33	9.8	2.9	5.2

where V_{A} and V_{B} are the partial molal volumes of the two components of the alloy. When the concentration of the deposited metal becomes important, the diffusion treatment should take account of the electrode boundary movement created by deposition or dissolution of the electroactive metal. The previous calculations are valid when $V_{\text{A}} = 0$ (interstitial incorporation). Generally $V_{\text{A}} \neq 0$, and the boundary shift which results from the incorporation of A has to be introduced into the analysis of the diffusion process. When V_{A} , V_{B} and D_{A} remain constant within the studied concentration range the diffusion problem can be solved by use of a dimensional analysis approach and of Laplace transformation. A detailed paper [18] has been recently devoted to these calculations and the results of this study are briefly recalled here.

When a boundary motion of the interface intervenes during a potentiostatic transient [19], Equation 11 has to be replaced by

$$C_j(x, t) = C_j^* + \frac{(C_j^s - C_j^*) \operatorname{erfc} [x/2(D_j t)^{1/2}]}{\operatorname{erfc}(-\sigma)} \quad (26)$$

The constant, σ , satisfies the functional equation

$$\pi^{1/2} \sigma \exp(\sigma^2) \operatorname{erfc}(-\sigma) = \frac{C_j^s - C_j^*}{1/V_j - C_j^s} \quad (27)$$

The influence of the boundary motion on the analysis of the interdiffusion process depends strongly on the composition of the alloy. The conventional procedure (Equation 11) can be used to calculate an interdiffusion coefficient which is denoted D_{A}^{a} . For the same experiment the true interdiffusion coefficient is deduced from Equation 26 which takes account of the motion of the electrolyte-electrode boundary. These two values are seen to differ by the factor

$$D_{\text{A}}/D_{\text{A}}^{\text{a}} = \frac{V_{\text{A}}^2(C_{\text{A}}^s - C_{\text{A}}^*)^2}{\pi\sigma^2} \quad (28)$$

When the difference $C_{\text{A}}^s - C_{\text{A}}^*$ is small, this equation can be written

$$D_{\text{A}}/D_{\text{A}}^{\text{a}} = (1 - V_{\text{A}}C_{\text{A}}^s)^2 \quad (29)$$

These equations show that the classical result is valid only if both C_{A}^s and C_{A}^* are small, and not simply when their difference is small. Notice that when $V_{\text{A}} = V_{\text{B}}$ the product $C_{\text{A}}V_{\text{A}}$ represents the mole fraction of the component A, and that the preceding analysis is valid for both deposition and dissolution of A.

Table 3. Values of the aluminium concentration and of the ratio D_A^a/D_A (boundary shift correction) for different starting potentials during aluminiding iron at 1020° C

E^* (mV)	C_{Al}^* ($\times 10^{-3}$ mol cm $^{-3}$)	$C_{Al}^*V_{Al}$	X_{Al}^* (mol %)	D_A^a/D_A
400	1.28	0.014	0.95	1.03
350	4.32	0.047	3.20	1.10
300	12.3	0.13	9.2	1.32
250	27.8	0.30	21.2	2.04
200	44.8	0.48	35.3	3.70
150	56.7	0.61	46.0	6.60
120	62.0	0.67	51.0	9.20

In the case of diffusion aluminide iron coating the correction factor due to the electrode boundary shift remains negligible when the working electrode is a low-content iron rod, i.e. when E^* is greater than 350 mV versus the Al–Al $^{3+}$ electrode. With the assumption that the molar volumes are additive, the ratios D_A^a/D_A are given in Table 3.

When the electrolyte–electrode interface moves with a velocity $u = -iV_j/vnF$ during a galvanostatic transient [20], Equation 20 has to be replaced by

$$C_j(x, t) = C_j^* + \left(\frac{i}{vnFu} + C_j^* \right) \left\{ u \exp \left[-\frac{u(x-ut)}{D_j} \right] \left[\left(\frac{t}{\pi D_j} \right)^{1/2} \exp \left(-\frac{(x-2ut)^2}{4D_j t} \right) - \frac{x-2ut}{2D_j} \right. \right. \\ \left. \left. \times \operatorname{erfc} \left(\frac{x-2ut}{2(D_j t)^{1/2}} \right) \right] - \frac{1}{2} \operatorname{erfc} \left[\frac{x}{2(D_j t)^{1/2}} \right] + \frac{1}{2} \exp \left[-\frac{u(x-ut)}{D_j} \right] \operatorname{erfc} \left[\frac{x-2ut}{2(D_j t)^{1/2}} \right] \right\} \quad (30)$$

At the interface ($x = X = ut$) the preceding equation reduces to

$$C_j(X, t) = C_j^* + \left(\frac{i}{vnFu} + C_j^* \right) \left\{ \frac{u^2 t}{2D_j} + \left(\frac{u^2 t}{2D_j} + 1 \right) \operatorname{erf} \left[\frac{u}{2} \left(\frac{t}{D_j} \right)^{1/2} \right] + u \left(\frac{t}{\pi D_j} \right)^{1/2} \exp \left(-\frac{u^2 t}{4D_j} \right) \right\} \quad (31)$$

As previously, the use of a classical procedure (Equation 20) over-estimates the interdiffusion coefficient. When the duration of the experiment is short enough, i.e. $t < D_{A-B}(nF/iV_A)^2$, the ratio D_A^a/D_A is given by Equation 29 so that $C_A^f(X, t) \simeq C_A^*$. For longer times this ratio can be calculated, and some values are reported in Table 4 for a final concentration $C_A^f(X, t) = C_A^*(1 \pm 0.5)$ and for different conditions of electrolysis (deposition or dissolution of the component A).

 Table 4. Values of the ratio D_A^a/D_A (boundary shift correction) for different values of the product $C_A^*V_A$

$C_A^*V_A$	For a final value $C_A^f \simeq C_A^*$	For a final value $C_A^f = C_A^*(1 \pm 0.5)$	
		Deposition	Dissolution
0.02	1.04	1.05	1.03
0.05	1.11	1.13	1.09
0.1	1.23	1.29	1.18
0.2	1.56	1.73	1.42
0.3	2.04	2.46	1.75
0.4	2.78	3.78	2.2
0.5	4.00	6.70	2.9

6. Conclusion

These electrochemical techniques provide rapid means for the determination of interdiffusion coefficients in metallic alloys. By contrast, standard metallurgical techniques involving tracers and sectioning generally require at least a few days of annealing as well as precise sectioning techniques [19]. It is shown that both anodic dissolution rate and kinetics of surface alloying may be represented by processes controlled by the diffusion in solids. The analysis of the interdiffusion process shows that the classical laws normally used have to be modified when a motion of the electrolyte–electrode interface occurs and when the diffusion coefficient is dependent on concentration.

A correct understanding of the process kinetics is required to support the development of electrochemical techniques for coating metal and alloy substrates. For example, it would be desirable to control the simultaneous deposition [21] of different metals in order to obtain better protective coatings. The success of this attempt depends on the use of suitable experimental conditions and on the accurate knowledge of the transport processes; the surface composition is directly deduced from the flows of electroactive species in the electrolyte and thus from their diffusion rate. The rearrangement of the distribution of the components at solid state results from their interdiffusion. Moreover, the electrocrystallization processes [22] and the appearance of new phases [23] have also been proved to be under the control of diffusion [24]. It is hoped that the analysis of diffusion processes studied in the present work will stimulate the development of the electrodeposition techniques.

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