ELECTROPLATING AT HIGH TEMPERATURE.
METAL INTERDIFFUSION AT THE SOLID STATE.
FAST TRANSPORT IN THE FIRST LAYERS.

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ABSTRACT

The interdiffusion of metals in the solid state was studied by transient electrochemical techniques at high temperature using molten salts. The method was applied to several binary metal systems and proved to be efficient to determine the diffusion coefficient $D$ as a function of temperature and composition of the generated alloys. The electrochemical response at short time showed a net departure from usual diffusion laws and could be interpreted as revealing a very fast transport in the first layer of the metal interface.

INTRODUCTION

Electrodeposition from fused electrolytes has been used to form protective metallic coatings with good anti-corrosion properties. Three electrolytic deposition processes were developed:-(i) electroplating which produces a constant composition layer of metal coating on the substrate,-(ii) metalliding which involves deposition and solid state intermetallic diffusion,-(iii) alloy deposition by simultaneous electroreduction of two or more cations. When deposition is carried out at high temperature the kinetics of formation of a diffusion layer is fast and it results in the growing of an intermediate alloy and in a good adhesion of the deposited coating to the substrate metal [1].

These technical applications of electrocoating from molten salts involve the study of electrochemical reactions which are under the control of diffusion of electroactive species: diffusion of ions in the liquid electrolyte and of metallided atoms into the solid substrate. These two kinds of diffusion in the electrolyte and in the solid state intervene also when coating is built up by

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codeposition of several elements; the composition of the coating depends on the diffusion fluxes in the electrolyte and on the interdiffusion in the coating [2].

These mechanisms can be studied quantitatively by use of transient electrochemical techniques. The response is dependent on the time scale under consideration. Most generally, as a consequence of the elementary electrochemical reaction and the high temperature, the electron transfer is fast enough to give a reversible response, and then the surface activity of deposited metal is controlled by the electrode potential.

On the other hand, at very short time the response contains additional terms such as double layer capacity charging or electroreduction of adsorbed species. Moreover, we could find, in most cases, that the current density shows an excess with respect to the computed values at very short time. This result could be assigned to a rapid motion of the deposited atoms in the very first layers of the interface.

EXPERIMENTAL

The method involves the use of polarization cell which have the general configuration

Alloy electrode / Liquid or solid electrolyte / Pure M
M-M' containing M^{n+}  (1)

The electrochemical cell for molten salt study was built to be sufficiently tight to sustain a residual pressure of 0.1 torr at 500 °C. In most of our experiments the electrolyte was a eutectic LiCl-KCl mixture whose component salts were of analytical reagent grade Merck. Before each experiment, the mixture was heated in the cell at 130°C under vacuum for 4h, and then heated at the experiment temperature (400 - 540°C) under HCl atmosphere for 6h. Finally, argon gas was kept flowing for a few hours to eliminate HCl.

A special electronic device built in the laboratory was used to deliver potentiostatic or galvanostatic pulses. The pulse and the electrode responses were recorded on double-trace digital oscilloscope Nicolet 310.

The purity of the bath is examined by cyclic voltammetry. The residual current density measured on a platinum electrode was less than 0.1 mA cm^{-2}. In these experiments
the metal ions $M^{n+}$ are generated by anodic dissolution of a rod of pure $M$, the counter electrode being a chlorine electrode [3] set in a separated compartment adapted with a porous connecting tube. The chlorine electrode is also used as reference electrode. For the measurements using cell (1) secondary reference electrode and counter electrode were made of a rod of pure $M$.

**BASIC PRINCIPLE OF THE METHOD**

When diffusion is the rate determining step, the concentration changes of electroactive species $j$ ($M^{n+}$ ions or metal atoms $M$) in the bulk of the two phases (electrolyte and metal) obey the equation

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

(2)

where $D_j$ and $C_j$ are the diffusion coefficient and the concentration of electroactive species; $x$ is the distance normal to the electrode. The initial boundary condition is

$$
C_j(x,0) = C^*_j
$$

(3)

$C^*_j$ is the concentration of electroactive species at equilibrium. 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

$$
C_j(\infty,t) = C^*_j
$$

(4)

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

$$
i = -nFJ_{M} = -\beta nFD_j \left( \frac{dC_j(x,t)}{dx} \right)_{x=0}
$$

(5)

with $\beta=+1$ for $j=M^{n+}$ and $\beta=-1$ for $j=M$. The concentration profile $C_j(x,t)$ is calculated by integrating the rate equation (2) for boundary conditions expressing the electrochemical constraints arising from the experimental conditions.
For example, using the potentiostatic method, the variation of current versus time should obey the Cottrell law following the expression:

\[ i = nF \left( C_j - C_j^* \right) \left( D_j / \pi t \right)^{1/2} \]  

(6)

This expression is available as well for the determination of \( D \) in the liquid phase as in the solid metal. However, the concentration changes in the metal and the electrolyte are interrelated at any time by:

\[ \frac{C_j^* - C_j}{C_j^* / n + C_j^* / n^+} = \left( \frac{D_j / n}{D_j / n^+} \right)^{1/2} \]  

(7)

The diffusion coefficient in the solid metal being smaller by a factor \( 10^5 \) than in the melt, the potential step is easily adjusted to values such as the current is only dependent on the solid state interdiffusion.

The values of \( C_j^* \) and \( C_j \) are determined by the values of imposed potentials provided that the activity coefficients of the components are known. In most cases, thermodynamic data are obtained in the literature and then expressed in a polynomial expansion such as:

\[ \log \gamma = a + b(1-x) + c(1-x)^2 + \ldots \]  

(8)

\( x \) being the molar fraction of the species \( j \).

The linear relationship of \( i \) versus \( t^{-1/2} \) remains available even if \( D \) is \( c \)-dependent and whatever the variation of \( D \) as a function of \( c \) is (Figure 1). This property of the potentiostatic method could be demonstrated by using the Boltzmann transformation, since the limiting conditions of the method can be expressed with the adimensional variable \( x/t^{1/2} \). The calculation shows that the slope of the linear variation of \( i \) versus the reciprocal of square root of \( t \) leads to the value of \( D \) nearly equal to that corresponding to the concentration near the metal surface [4].

The potential step can be chosen either positive or negative with respect to the equilibrium value, in order to measure \( D \) when diffusion phenomenon takes place "in" or "out" the sample material. Most generally for a given composition, the experimental \( D \) value does not depend on whether the diffusion takes place "in" or "out" the substrate. Moreover, the variation of the amplitude of the
potential perturbation permits to generate superficial alloys with different compositions. The method then provides an efficient tool for the determination of D values as a function of concentration.

Other electrochemical pulse techniques are used in this investigation. Chronopotentiometry and cyclic voltammetry are useful for obtention of the same informations in the form of signals which are often more readily interpreted [5].

Three mathematical difficulties appear in the resolution of the diffusion equation corresponding to a given technique. 1) The diffusion constant of deposited metal may be quite different from that of the substrate. This property induces a Kirkendall effect and leads to a movement of the internal reference frame. Then only an interdiffusion coefficient D is observed. 2) The interdiffusion coefficient of metal is strongly dependent on the composition of alloy, thus a variable D should be introduced along the concentration gradient. 3) The deposition of metal by itself makes the volume of the substrate to grow. It results in a shift of the interface which must be accounted for as a translation of the abscissae origin.

For these results the equations of chronoamperometry and chronopotentiometry often used by electrochemists are not available in these conditions. We have to develop new mathematical expressions to account mainly for condition 3). Moreover experimental results were checked by numerical simulation of the elementary transport processes using a computer. Figure 2 shows the adjustment of computed values of the potential against time in a typical chronopotentiogram showing the best values of the parameters for adjustment of experimental data.

RESULTS

Several systems forming a solid solution were investigated: copper-gold, lithium-aluminium, lithium-magnesium, aluminium-iron, aluminium-nickel, aluminium-silver and iron-nickel. The first metal is the deposited metal, the second one forms the substrate. Experimental values show that for most of these solid solutions the interdiffusion coefficient D depends on the alloy concentration according to the expansion:

\[ \log D = \log D^* + Ax + Bx^2. \] (9)
It is also pointed out that the transient electrochemical techniques are convenient and probably a unique means to investigate the transport processes at very short time. Experimental results exhibit a large departure from classical laws and indicate that the rate of the electrochemical reaction becomes faster at short time, i.e. at very short distances from the metal surface (Figure 3). For example, the predicted value of concentration near the interface, as computed from diffusion equations, often leads to molar fraction x larger than unity. In fact, this erroneous conclusion can be excluded by considering the real concentration profile near the interface which is a direct consequence of the Relevant Rapid Diffusion Thickness [2] (Figure 4). Various mechanisms can be invoked to account for this observation: double-layer charging, adsorption of electroactive species, surface roughness.

However careful examination of the results leads to another interpretation, based on a net increase of the diffusion coefficient in the region close to the surface, which takes into consideration the mechanism of diffusion itself. The theories of solid state physics indicate that the atom diffusion is controlled by the concentration \( N_d \) of lattice defects. According to the Schottky theory,

\[
N_d = A \exp(-\frac{\Delta G_d}{RT})
\]  

where \( A \) is the frequency factor depending on the crystal structure. In the theory developed by Schottky the energy of defect formation \( \Delta G_d \) is the sum of several terms containing mainly the coulombic interaction, the repulsion term, Van der Waals and polarization interactions, and the residual energy at zero point. In the classical lattice defect theory, \( \Delta G_d \) is deduced from the summation of the potential terms carried out on the whole space (\( 4\pi \) solid angle). The important consequence of our results is that, in the very first atomic layers, the number of lattice defects should be different of that in the bulk of the solid, since the integration of potential terms is performed on a smaller solid angle. In the extreme case of the first layer, the summation is made on a \( 2\pi \) solid angle and thus \( \Delta G_d(s) = 1/2 \Delta G_d(b) \). Then the molar fraction of defects at the surface could reach the value \( N_d(s) = N_d(b)^{1/2} \), and could be responsible for a steep increase of the diffusion coefficient.
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Figure 1. Analysis of chronoamperograms after potential steps on a copper-gold alloy. Temperature: 402°C. \( C_{\text{Cu}} = 91 \times 10^{-3} \) M in LiCl-KCl. Alloy composition: \( C_{\text{Al}} = 13.7 \) mmol cm\(^{-3}\). Electrode area: 1.11 cm\(^2\). Values of the potential step: a, a' ±200 mV; b, b' ±100 mV; c, c' ±50 mV; d, d' ±20 mV; e, e' ±10 mV.

Figure 2. Analysis of a chronopotentiogram for the reduction of Al\(\text{III}\) in LiCl-KCl at 500°C on a nickel electrode; \( I = 18 \) mA, \( C_{\text{AlIII}} = 10^{-4} \) mol cm\(^{-3}\). S = 0.44 cm\(^2\). 

\[ n = \eta - \eta^* \text{ vs, } U = \log [ (t/t_0)^{1/2} - 1 ]; \] 

\[ n = E - E^* \text{, } E^* \text{ is the equilibrium potential. Influence of the computed value of the transition time } \tau : \text{ Continuous line, } \tau = 6.22 \text{ s. Dashed line, } \tau = 5.91 \text{ s. Dotted line, } \tau = 6.53 \text{ s.} \]
Figure 3. Analysis of a chronoamperogram at short time after potential steps on a copper-gold alloy. Temperature: 554°C, \(C_{\text{Cu}}^* = 64 \times 10^{-3}\) M in LiCl-KCl. Alloy composition: \(C_{\text{Cu}}^* = 10.5\) mmol cm\(^{-3}\). Electrode area: 0.372 cm\(^2\). Values of the potential step: a, 500 mV; b, 200 mV; c, 80 mV; d, 40 mV; e, 20 mV; f, -80 mV.

Figure 4. Computed relative concentrations at the surface of a nickel electrode during the reduction of Ni\(^{2+}\) and Fe\(^{2+}\) in LiCl-KCl at 503°C. Relevant Rapid Diffusion Thickness: \(7.2 \times 10^{-8}\) cm \([2]\). \(r_1 = 0.93\) s. Constant current \(I = 3.4\) mA, \(C_{\text{Ni}}^{2+} = C_{\text{Fe}}^{2+} = 7.5 \times 10^{-3}\) M, S = 0.78 cm\(^2\). At the end of the pulse (when \(C_{\text{Fe}}^{2+} = 0\)) the current was switched off. a = Ni\(^{2+}\); b = Fe\(^{2+}\); c = Fe.