Chronoamperometric Determination of Solid State Diffusion Coefficients in Copper-Gold Alloys Using a Molten Salt Electrolyte

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Dedicated to Professor Alfred Klemm on the occasion of his 70th birthday

The intermetallic diffusion coefficient in Cu-Au alloy between 400 °C and 550 °C is measured by chronoamperometry using a Cu-Au electrode in a molten LiCl-KCl electrolyte containing small amounts of Cu^+ ions. The current response to a defined constant potential step is controlled by the rate of diffusion in the alloy electrode. The mathematical treatment developed by introducing the Boltzman transformation shows that the current density is a linear function of the reciprocal square root of time whatever the dependence of D versus concentration is.

The method is applied to cathodic as well as anodic potential pulses which correspond to surface alloying or dissolution i.e. diffusion "in" or "out" the sample. The shift of the interface due to the copper deposition or dissolution is considered according to the Oldham and Raleigh's method.

By studying the electrochemical response at very short times the diffusion can be examined in the first atomic layers of the electrode interface.

Introduction

The electrodeposition of metals in fused salts [1] is used both for metal production [2, 3] and electroplating [4, 6]. To this latter case belongs the technique of metalliding [7] which involves simultaneous electrodeposition and solid state intermetallic diffusion in molten salt systems at elevated temperatures [8–14]. The subject has recently been reviewed by R. S. Sethi [15]. For reversible electrochemical reactions the activity of the electroactive material is obtained by e.m.f. measurements and the rate of the metal deposition (or dissolution) is given by the current density. The determination of the diffusion coefficient by measurements of diffusion controlled currents in solid electrolyte cells has been previously carried out by Raleigh and Crowe [16] who examined the Ag-Au alloys; more recently Goldman and Wagner [8] have studied the diffusion in the Cu-Au system. These authors have used a polarization cell with a solid electrolyte constituted by a single-crystal of AgBr or CuCl.

We present here the measurements of diffusion controlled currents in the liquid-electrolyte cell:

$$\text{Cu-Au/LiCl-KCl} + Cu^+/\text{Cu}.$$

By use of transient electrochemical techniques, the motion of electroactive atoms in the first atomic layers at the interface is studied. It is shown that the electrochemical response depends on the time scale under consideration. At very short times the response is mainly a characteristic of double-layer charging, electron transfer, etc. ..., whereas at longer times ($\geqq 5$ ms) it is known to be under the control of mass transport processes.

Experimental

The eutectic LiCl-KCl was prepared from Merck Reagent Grade salts; it is pre-melted in an HCl atmosphere. The experiment is carried out in a vacuum-tight Pyrex cell [11] filled with an argon atmosphere containing less than 5 ppm of O_2 and H_2O. The Cu^+ ions are introduced by anodic dissolution of a copper rod (specpure Johnson-Matthey) up to a Cu^+ concentration of about $5 \cdot 10^{-2}$ M. It was verified that a ten fold change of

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C_{Cu^+} in the electrolyte has no influence upon the measured e.m.f. which depends only on the alloy composition. The working electrodes are prepared by fusion of pure copper and gold in a quartz tube under vaccum [17].

The counter electrode and the reference electrode are a sheet and a wire of pure copper respectively. The equilibrium potential of the working electrode is measured with a high-impedance ($10^{12}\,\Omega$) digital voltmeter. The values obtained with different Au-Cu alloys are in good agreement with our previous determinations [17]. As already observed a show shift towards more positive values (a few millivolts per 24 h) appears as a result of a slight oxidation of copper by the atmosphere (traces of oxygen).

A potential step is then applied to the working electrode by means of a potentiostatic device built in the laboratory, the signal being delivered with a rise time less than 5 µs. The corresponding current intensity is determined by a differential measurement in the counter-electrode circuit and recorded on a Tektronix storage oscilloscope or on a Digital Recorder Biomation Model 805.

At the end of the potentiostatic pulse the initial potential is restored. We consider that the equilibrium situation is restored when the current becomes less than 20 $\mu A\,cm^{-2}$. The equilibrium potential of the electrode at rest is then equal to the initial value within ± 1 mV.

Basic Principles of the Method

If we use the cell:

$$\begin{array}{lll} \oplus\ \text{Au-Cu} & \text{molten} & \text{pure Cu}^{\ominus} \\ \quad\text{Alloy} & \text{LiCl-KCl} & \\ & \text{with Cu}^{+} & \end{array} \tag{1}$$

the e.m.f. E of this cell depends on the activity a_{Cu} of the copper at the surface of the alloy electrode:

$$E = \frac{RT}{F} \ln a_{Cu} \,. \tag{2}$$

The activity a_{Cu} is related to the copper concentrations C_{Cu} or the atomic fraction X_{Cu} by

$$a_{Cu} = \gamma_{Cu} X_{Cu} \text{ or } f_{Cu} C_{Cu} \,, \tag{3}$$

γ_{Cu} and f_{Cu} being the activity coefficients; X_{Cu} and C_{Cu} are connected by:

$$C_{Cu} = X_{Cu} \frac{\varrho_{AuCu}}{X_{Cu} M_{Cu} + (1 - X_{Cu})\, M_{Au}} \,, \tag{4}$$

$\varrho_{Au\text{-}Cu}$ being the alloy specific mass, and M_{Cu} and M_{Au} the atomic masses of copper and gold. Since the activity coefficients are known from previous studies [17], the value of the e.m.f. of the cell (1) leads to the copper surface concentration of the alloy.

Let us consider the simple electrochemical reaction:

$$Cu^+ + e \rightleftarrows Cu \,.$$

As a first approximation, we shall assume that, during a potentiostatic transient, the potential of the polarised electrode changes instantaneously; η represents the overvoltage $\eta = E - E^*$, where E is the potential of the working electrode versus a pure copper reference electrode, E^* is the equilibrium potential of this alloy electrode. For a fast charge transfer where diffusion is rate-determining, η is given by the Nernst equation:

$$\eta = \frac{RT}{F} \ln \left\{ \left(\frac{a_{Cu^+}}{a^*_{Cu^+}} \right)_{\text{liq}} \left(\frac{a^*_{Cu}}{a_{Cu}} \right)_{\text{sol}} \right\} , \tag{5}$$

where $a^*_{Cu^+}$ and a^*_{Cu} are the equilibrium activities of Cu^+ in the electrolyte and of Cu in the solid alloy, respectively; a_{Cu^+} and a_{Cu} are the corresponding activities during the transient signal.

The current density is then

$$i = -\, F D_{Cu^+} \frac{dC_{Cu^+}}{dx} = F D_{Cu} \frac{dC_{Cu}}{dx} \,. \tag{6}$$

The time change of the concentration gradient is deduced from the integration of Fick's second law which gives

$$\begin{aligned} i &= F(C^*_{Cu} - C_{Cu}) \sqrt{\frac{D_{Cu}}{\pi t}} \\ &= F(C_{Cu^+} - C^*_{Cu^+}) \sqrt{\frac{D_{Cu^+}}{\pi t}} \,. \end{aligned} \tag{7}$$

The current density i is taken positive for an oxidation process ($\eta > 0$).

In our experimental conditions, the ionic concentration C_{Cu^+} does not change very much during the potentiostatic pulse. In fact, Eq. (7) shows that the concentration changes in the electrode and the electrolyte are interrelated at any time by

$$\frac{C^*_{Cu} - C_{Cu}}{C_{Cu^+} - C^*_{Cu^+}} = \sqrt{\frac{D_{Cu^+}}{D_{Cu}}} \,. \tag{8}$$

The diffusion coefficient in the solid metal D_{Cu} being smaller by a factor 10^5 than D_{Cu^+} in the ionic melt, most of the perturbation concerns the surface concentration of copper in the alloy.

Depending on the amplitude of the potential pulse η, several cases are considered:

a) For high positive values of η, $C_{\mathrm{Cu}} \rightarrow \mathrm{O}$ and the limiting expression is obtained (Cottrell's law):

$$i = F C^*_{\mathrm{Cu}} \sqrt{\frac{D_{\mathrm{Cu}}}{\pi t}} \, . \tag{9}$$

In this case the upper values of η are limited by side electrochemical reactions such as oxidation of Cu^+ or of Au; the standard potential of these reactions are respectively 1.018 V and 1.162 V versus the normal $\mathrm{Cu}^+/\mathrm{Cu}$ electrode [18].

A similar approximation could be used for a large cathodic overvoltage $\eta \ll -RT/F$; however, in this situation the pure-copper concentration is rapidly reached, and the current is only under the control of the diffusion of Cu^+ ions in the melt, which is not of interest for the present study.

b) More interesting is the case where $|\eta| \ll 10\,\mathrm{mV}$, the activity coefficient of Cu^+ in the melt being a constant as a result of large excess of supporting electrolyte, the value of the current is then given by the following expression:

$$i = \frac{F}{\sqrt{\pi t}} \left(\frac{F\eta}{RT} + \ln \frac{f_{\mathrm{Cu}}}{f^*_{\mathrm{Cu}}} \right) \left(\frac{1}{C^*_{\mathrm{Cu}^+} \sqrt{D_{\mathrm{Cu}^+}}} + \frac{1}{C^*_{\mathrm{Cu}} \sqrt{D_{\mathrm{Cu}}}} \right) \tag{10}$$

which corresponds to small perturbations of the surface concentration and the value of the diffusion coefficients D_{Cu} may be considered as the intrinsic diffusion coefficient corresponding to this alloy composition.

In this derivation, it has been supposed that the diffusion coefficient D_{Cu} remains constant during the pulse.

c) For intermediate values of potentials, $|\eta| \simeq RT/F$, a concentration profile is set up near the surface of the electrode. In this case, it is known that D_{Cu} is concentration-dependent.

Thus, for large potential jumps, the previous assumption is a rough approximation. However, even in this case, we have observed a good linear variation of i vs. $1/\sqrt{t}$ (cf. Figure 1).

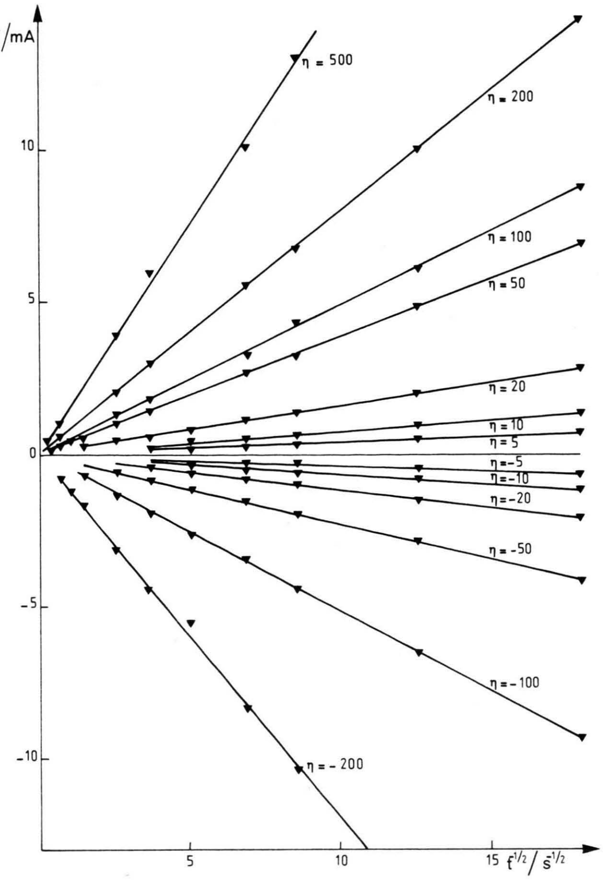

Fig. 1. I vs. $t^{-1/2}$ plot for a gold-copper electrode (copper concentration: $C^*_{\mathrm{Cu}} = 13.7 \cdot 10^{-3}\,\mathrm{mol\,cm^{-3}}$ or copper atomic fraction $X^*_{\mathrm{Cu}} = 13.91\%$) in LiCl-KCl eutectic containing $9.1 \cdot 10^{-5}\,\mathrm{Cu}^+$ ion cm^{-3}. Electrode surface = 1.11 cm^2. Ohmic resistance = 0.280 Ω. Temperature 402 °C. The applied overvoltages η are indicated on the figure (mV).

In fact, it is easy to demonstrate that a linear relationship of i versus $1/\sqrt{t}$ must be obeyed even if D is c-dependent and whatever the variation of D as a function of c is. This result can be obtained using the Boltzmann [19] transformation; i.e., $\lambda = x/\sqrt{t}$ which changes the partial differential equation

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(D(c) \frac{\partial c}{\partial x} \right) \tag{11}$$

to a differential equation:

$$-\frac{\lambda}{2} \frac{\partial c}{\partial \lambda} = \frac{\partial}{\partial \lambda} \left(D(c) \frac{\partial c}{\partial \lambda} \right) . \tag{12}$$

This transformation is very efficient in the case of chronoamperometry, since we are interested in the knowledge of the gradient of concentration at the interface $x = 0$.

Extending to our case the technique introduced by Matano [20], integration of (12) between $x = 0$ to $x = \infty$, leads to:

$$\left(D\frac{\partial c}{\partial \lambda}\right)_{x=0} = -\frac{1}{2}\int_0^\infty c\,\mathrm{d}\lambda \tag{13}$$

which can be written as:

$$\left(D\frac{\partial c}{\partial x}\right)_{x=0} = -\frac{1}{2t}\int_0^\infty c\,\mathrm{d}x = -\frac{1}{2t}Q\,. \tag{14}$$

In this equation Q is the integrated quantity of diffusing species in the whole matrix, which is related to the flux $D\,\partial c/\partial x$ at the plane $x = 0$, this means that the value of D corresponds to the concentration at the boundary of the electrode as it is defined by the potentiostatic signal.

Now, $(D\,\partial c/\partial x)_{x=0}$ is written as i/nF and $i = nF\,\partial Q/\partial t$ which leads to

$$\frac{\partial Q}{\partial t} = \frac{Q}{2t} \tag{15}$$

and

$$Q = A t^{1/2} \quad \text{and} \quad i = \frac{nFA}{2}t^{-1/2}\,, \tag{16}$$

where A is an arbitrary constant of integration.

As a result, plotting i versus $1/\sqrt{t}$ will lead to a straight line whose slope describes the variation of flux $(D\,\partial c/\partial x)_{x=0}$. The precise calculation of i as a function of time needs numerical computation since it needs the resolution of the diffusion equation involving variable D. These computations lead to a useful empirical formulae [21] which can be employed. Nevertheless, in the special case of chronoamperometry, we are only interested in the concentration profile in the vicinity of electrode boundary i.e. $x \approx 0$. As a first order approximation, we can consider that the partial differential equation involves a few layers near the interface, where variations of c (respectively D) are small. Consequently, Eq. (7) is a good approximation for variations of current density, provided that D_{Cu} is supposed constant and equal to the value corresponding to the concentration C_{Cu} fixed at the interface by the potentiostatic signal. This qualitative conclusion is in agreement with computation results obtained by Vallet and Braunstein [22].

The technique of chronoamperometry allows the investigation of diffusion in a layer the thickness of which can be varied over a large range. Indeed, at the time t after the onset of the pulse, the mean path δ of the electroactive species is $\sqrt{2D_{\mathrm{Cu}}t}$; for a diffusion coefficient $D_{\mathrm{Cu}} \simeq 10^{-10}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$ at $t = 50$ s, the diffusion is observed in a thickness $\delta = 1$ µm. At $t = 0.4$ ms the thickness is 28 Å, but in such short time measurements, perturbations may occur such as electrolysis of adsorbed species, charging of a capacitive double-layer and response of the potentiostat (5 µs). One advantage of the fused salts is that, since they have a low electrical resistance ($R \simeq 0.3\,\Omega$), the time constant of the charging process is very short; for a capacity of 100 µF, the RC constant is 30 µs. The details of the study at very short times will be examined after the study at longer times ($t > 2$ ms).

Results

Determination of D_{Cu}

The value of D_{Cu} is deduced from the slope of the plot $I = f(1/\sqrt{t})$ according to (7). The required value of the copper surface concentration C_{Cu} is deduced from η and i as follows: first we take advantage of the accurate knowledge [23] of the diffusion coefficient $D_{\mathrm{Cu^+}}$ in the melt to determine the concentration of $\mathrm{Cu^+}$ ion at the interface (even if according to (8) the variations of $C_{\mathrm{Cu^+}}$ are small).

$$C_{\mathrm{Cu^+}} = C^*_{\mathrm{Cu^+}} + \frac{i}{F}\sqrt{\frac{\pi t}{D_{\mathrm{Cu^+}}}}\,. \tag{17}$$

Then the activity a_{Cu} is calculated from (5), taking into account the ohmic drop

$$\ln\frac{a^*_{\mathrm{Cu}}}{a_{\mathrm{Cu}}} = F\frac{\eta_p - RI}{RT} + \ln\frac{C^*_{\mathrm{Cu^+}}}{C_{\mathrm{Cu^+}}}\,, \tag{18}$$

where η_p is the potential jump delivered by the potentiostat and $\ln(C^*_{\mathrm{Cu^+}}/C_{\mathrm{Cu^+}})$ is only a minor corrective term. Introducing the equilibrium potential E^*, we obtain (cf. (2))

$$\ln a_{\mathrm{Cu}} = \frac{F}{RT}(E^* - \eta_p + RI) - \ln\frac{C^*_{\mathrm{Cu^+}}}{C_{\mathrm{Cu^+}}}\,. \tag{19}$$

The composition X_{Cu} is calculated, using the activity coefficients γ_{Cu} determined formerly [17]:

$$X_{\mathrm{Cu}} = a_{\mathrm{Cu}}/\gamma_{\mathrm{Cu}}$$

and the concentration C_{Cu} is thus known (see (4)). The value of D_{Cu} is then derived from (7):

$$D_{\mathrm{Cu}} = \frac{\pi\, i^2 t}{F^2 (C^*_{\mathrm{Cu}} - C_{\mathrm{Cu}})^2}\,. \tag{20}$$

An example of the results of this calculation is given in Table I for the I vs. $t^{-1/2}$ plot of Figure 1. From the reproducibility of the chronoamperograms for a given η_p it is observed that the current density may vary by about ± 5%, which induces an error of ± 10% on D. Moreover the sensitivity of the equipment introduces an absolute error of ± 0.05 mA which gives the limit of the useful part of the chronoamperogram at long time.

The Cottrell equation (see (7) and (9)) is not strictly valid for discharge or dissolution of a component of a metal alloy electrode; a correction is required to account for electrode boundary movement. This was first pointed out by Wagner [25a] and is treated by Oldham and Raleigh [25b]. Their reference frame is the bulk of electrode metal; then owing to the electrolysis there is a shift $\mathrm{d}X(t)$ of the electrode/electrolyte interface during a time interval $\mathrm{d}t$:

$$\frac{\mathrm{d}X(t)}{\mathrm{d}t} = i(t)\frac{V_{\mathrm{Cu}}}{nF}\,. \tag{21}$$

With respect to its position at time $t = 0$, the position of the interface at the time t after the beginning of the electrolysis is

$$\int_{-X(t)}^{L} C_{\mathrm{Cu}}(x,t)\,\mathrm{d}x = L C^*_{\mathrm{Cu}} + \int_0^t \frac{i(t)}{nF}\,\mathrm{d}t\,. \tag{22}$$

The * exponent represents the value in the bulk of the alloy for an electrode thickness L. The gold and copper concentrations are related by the expression:

$$C_{\mathrm{Au}} V_{\mathrm{Au}} + C_{\mathrm{Cu}} V_{\mathrm{Cu}} = 1\,. \tag{23}$$

Then (21) is written

$$\int_{-X(t)}^{L} \left(\frac{1}{V_{\mathrm{Au}}} - \frac{V_{\mathrm{Cu}}}{V_{\mathrm{Au}}} C_{\mathrm{Cu}}(x,t)\right)\mathrm{d}x = L\left(\frac{1}{V_{\mathrm{Au}}} - C^*_{\mathrm{Cu}}\frac{V_{\mathrm{Cu}}}{V_{\mathrm{Au}}}\right) \tag{24}$$

which gives under its differential form:

$$\int_{-X(t)}^{L} \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{V_{\mathrm{Cu}}}{V_{\mathrm{Au}}} C_{\mathrm{Cu}}(x,t)\right)\mathrm{d}x = \frac{\mathrm{d}X(t)}{\mathrm{d}t}\left(\frac{1}{V_{\mathrm{Au}}} - C_{\mathrm{Cu}}(-X,t)\frac{V_{\mathrm{Cu}}}{V_{\mathrm{Au}}}\right). \tag{25}$$

The time evolution of the concentration profile obeys Fick's second law:

$$\frac{\mathrm{d}C_{\mathrm{Cu}}}{\mathrm{d}t} = \tilde{D}\frac{\mathrm{d}^2 C_{\mathrm{Cu}}}{\mathrm{d}x^2}\,. \tag{26}$$

In our experimental conditions the boundary conditions are:

$$\begin{aligned} C_{\mathrm{Cu}}(x,0) &= C^*_{\mathrm{Cu}}\,,\\ C_{\mathrm{Cu}}(\infty,t) &= C^*_{\mathrm{Cu}}\,,\\ C_{\mathrm{Cu}}(X,t) &= C^{\mathrm{s}}_{\mathrm{Cu}}\,. \end{aligned} \tag{27}$$

$X(t)$ is the solution of (25). The integration of the Fick's equation (26) according to the previous conditions has been given by Oldham and Raleigh [25b] when V_{Au} and V_{Cu} are supposed to be constant.

$$C_{\mathrm{Cu}}(x,t) = C^*_{\mathrm{Cu}} + \frac{(C^{\mathrm{s}}_{\mathrm{Cu}} + C^*_{\mathrm{Cu}})\,\mathrm{erfc}(x/2\sqrt{Dt})}{\mathrm{erfc}(-\sigma)} \tag{28}$$

with

$$\sqrt{\pi}\;\sigma\exp(\sigma^2)\,\mathrm{erfc}(-\sigma) = \frac{V_{\mathrm{Cu}} C^{\mathrm{s}}_{\mathrm{Cu}} - V_{\mathrm{Cu}} C^*_{\mathrm{Cu}}}{1 - V_{\mathrm{Cu}} C^{\mathrm{s}}_{\mathrm{Cu}}}\,. \tag{29}$$

Then according to (21) the electrical current is given by the equation

$$i(t) = \frac{nF\sigma}{V_{\mathrm{Cu}}}\sqrt{\frac{\tilde{D}}{t}}\,. \tag{30}$$

Then the interdiffusion coefficient $\tilde{D}_{\mathrm{Cu}}$ can be obtained from the Cottrell diffusion coefficient D_{Cu} (given by (7)) by the relation:

$$\frac{\tilde{D}_{\mathrm{Cu}}}{D_{\mathrm{Cu}}} = \frac{(C^{\mathrm{s}}_{\mathrm{Cu}} - C^*_{\mathrm{Cu}})^2 V^2_{\mathrm{Cu}}}{\sigma^2 \pi}\,. \tag{31}$$

An example of the results of these calculations is given in Table I. They are deduced from the slope of the plots of Figure 1. From the reproducibility of the chronoamperograms we recall that the current density may vary by about ± 5% which induces an error of ± 10% on $\tilde{D}_{\mathrm{Cu}}$.

The results of Table I correspond to different potential jumps carried out on the same electrode (alloy containing 13.91 mol Cu %). It is observed that the $\tilde{D}_{\mathrm{Cu}}$'s are strongly dependent on the η values. The change in $\tilde{D}_{\mathrm{Cu}}$ is far outside the range of accuracy indicated above.

For instance the values of $\tilde{D}_{\mathrm{Cu}}$ obtained with anodic pulses are always greater than the values given by the cathodic pulses. In general, decreasing values of $\tilde{D}_{\mathrm{Cu}}$ are observed when η is more negative. This effect is attributed to the change in the alloy

Table I. Mean values of the diffusion coefficients deduced from the chronoamperograms of Fig. 1 at different overvoltages η_P.

η_p mV	X_{Cu} %	Cottrell values Eq. (20) D_{Cu} 10^{-12} cm^2 s^{-1}	Eq. (31) $\tilde{D}_{Cu}$ 10^{-12} cm^2 s^{-1}
−200	72.03	0.077	0.035
−100	38.33	0.11	0.075
− 50	24.72	0.12	0.091
− 20	17.78	0.24	0.19
− 10	15.76	0.34	0.27
− 5	14.81	0.38	0.31
+ 5	13.06	0.51	0.42
+ 10	12.22	0.49	0.40
+ 20	10.69	0.64	0.53
+ 50	6.95	0.84	0.71
+100	3.16	0.56	0.48
+200	0.60	0.97	0.85
+500	0.01	3.5	3.06

composition near the interface. Indeed it has already been observed that the diffusion coefficients decrease when the copper concentration increases.

In order to minimize this dependence, we have measured $\tilde{D}_{Cu}$ for small η; in this case the diffusion coefficient tends towards the diffusion coefficient corresponding to the bulk alloy concentration. In Table II the mean values of $\tilde{D}_{Cu}$ deduced from chronoamperograms are reported for $\eta = \pm 5$ mV and $\eta = \pm 10 \mu$V; the variation of the surface concentration in this case is about ± 7% for $\eta = \pm 5$ mV.

Discussion

Our measurements give a set of the diffusion coefficients in the Au-Cu alloys. The $\tilde{D}_{Cu}$ values are calculated according to the classical treatment of a

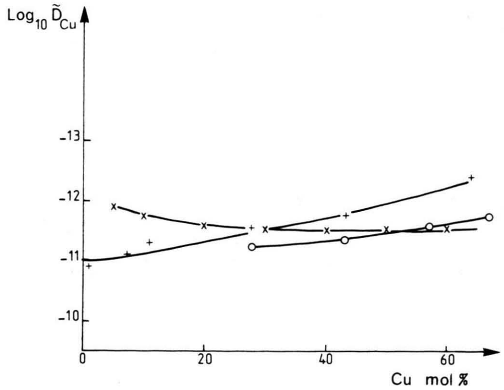

Fig. 2. Values of the interdiffusion coefficient in the copper-gold alloy system as a function of copper concentration. ○ [27]; × [30]; + our results.

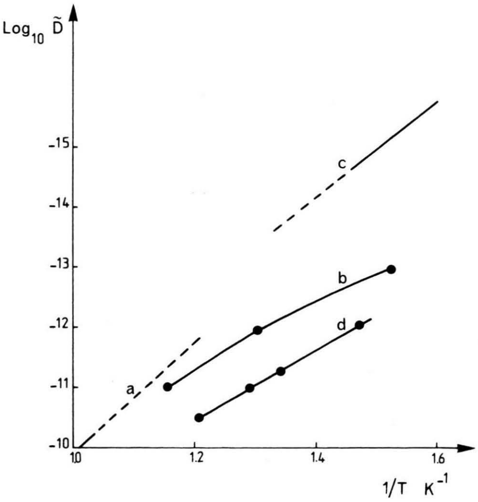

Fig. 3. Impurity diffusion coefficients of copper in pure gold as a function of reciprocal absolute temperature. a) [29]; b) [30]; c) [8]; d) our measurements.

Table II. Values of the diffusion coefficients derived from potentiostatic measurements at low overvoltages $|\eta| \leq 10$ mV for different copper atomic fractions of gold-copper alloys at different temperatures; Cottrell values (20), and $\tilde{D}_{Cu}$ values by taking into account of the electrode boundary movement (31) (values in $-\log_{10} D$).

0 °C	X_{mol}%	0.8	7.1	10.8	13.9	28.2	43.2	64.2
402 °C	Cottrell	11.95	12.42	12.68	12.36	12.67	13.21	13.41
	Eq. (31)	11.96	12.46	12.75	12.46	12.87	13.55	14.04
473 °C	Cottrell	11.06	11.28	11.31	11.32	11.68	11.76	12.27
	Eq. (31)	11.07	11.32	11.37	11.41	11.89	12.10	12.91
502 °C	Cottrell	10.89	11.02	11.24	11.02	11.38	11.40	11.86
	Eq. (31)	10.90	11.06	11.31	11.11	11.58	11.75	12.49
554 °C	Cottrell	10.42	10.56	10.89	10.46	10.85	10.89	11.72
	Eq. (31)	10.43	10.60	10.95	10.55	11.05	11.23	12.36

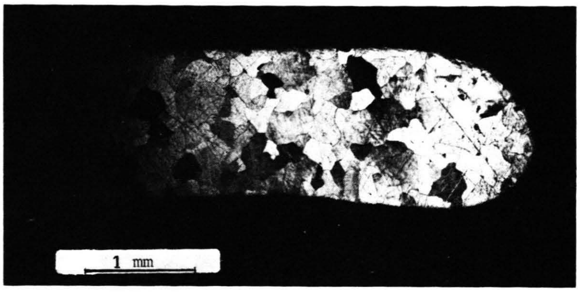

Fig. 4. Micrography of a gold-copper alloy: $C_{\mathrm{Cu}} = 13.7 \cdot 10^{-3}$ mol cm^{-3}.

diffusion-controlled chronoamperometry response taking into account the boundary movement. For small overvoltages it is assumed that $\tilde{D}_{\mathrm{Cu}}$ gives the interdiffusion coefficient. These values are in good agreement with previous determinations carried out by other techniques [26]. Pinnel and Bennett [27] have carried out interdiffusion experiments with polycrystalline copper/electroplated gold specimens; the concentration profiles were obtained from electron probe analysis and the interdiffusion coefficients were calculated with the aid of Matano analysis (Figures 2 and 3).

The large difference observed between the determination carried out in monocrystals [8, 28] and polycrystals [27, 29, 30] indicates that in this latter case the main copper flux occurs in the grain boundary region. A micrography of the alloy surface is given on Figure 4. To compare the tracer diffusion coefficient and the diffusion in a chemical concentration gradient, it is necessary to introduce a thermodynamic factor [31] $\mathrm{d}\ln\gamma/\mathrm{d}\ln X$; these values were given in a previous paper [24].

Our values can also be compared with the results deduced from the galvanostatic techniques, using the same alloy electrode [24]. A fair agreement is observed; generally, the potentiostatic technique leads to higher values; these latter data seem more reliable, since the surface concentration is defined, whereas the galvanostatic method results in a continuous change of surface composition.

However, the influence of the boundary movement is in general more important for the potentiostatic conditions than for the galvanostatic conditions. Indeed, in potentiostatic conditions, the boundary displacement $\delta_{\mathrm{B}} = \int_0^t \frac{V_{\mathrm{Cu}}\, i\, \mathrm{d}t'}{nF}$ is equal to $2\sigma\sqrt{\tilde{D}t}$ and is thus proportional to the mean path of the diffusing species $\delta_M = \sqrt{2\tilde{D}t}$; the ratio δ_B/δ_M does not depend on the time t; for small value of the potential step the correction introduced by Raleigh depends essentially on the partial molar volume of gold $V_{\mathrm{Au}} C_{\mathrm{Au}}$. In galvanostatic conditions the ratio δ_B/δ_M is equal to $V_{\mathrm{Cu}}\, i\sqrt{t}/(nF\sqrt{2\tilde{D}})$, and at short times, the correction due to the boundary motion (24) remains negligible. This is the case for our previous determinations by the flash deposit method [24].

A general feature of all these data is the large variation of $\tilde{D}_{\mathrm{Cu}}$ observed when the alloy composition varies. In pure gold, the diffusion coefficient $\tilde{D}_{\mathrm{Cu}}$ is about 30 times greater than the self-diffusion coefficient of copper-50 gold-50 mol %. A similar trend has been observed by Oldham and Raleigh for the Ag-Au system [25 b].

This dependence of $\tilde{D}_{\mathrm{Cu}}$ on X_{Cu} explains the influence of the overpotential η on the results as shown in Table I. During a potentiostatic pulse, the surface concentration C_{Cu} is under the control of η according to the Nernst law; the resulting concentration gradient creates a copper flux following Fick's law. But, all along this concentration profile, $\tilde{D}_{\mathrm{Cu}}$ is no longer constant, since the diffusion occurs in a medium where the copper concentration varies between the surface value C^{s}_{Cu} and the bulk composition C^{*}_{Cu}. However, as pointed out above, the current response is always proportional to $1/\sqrt{t}$, and Cottrell's law remains valid considering that $\tilde{D}_{\mathrm{Cu}}$ is constant. Within the range of accuracy of the measurements, it may be considered that $\tilde{D}_{\mathrm{Cu}}$ corresponds to the inter-diffusion coefficient for the superficial atomic fraction X_{Cu}.

However for large values of $|\eta|$ some discrepancies appear. The oxidation of other species such as Cu^+ or Au may occur and, on the reduction side, when the pure copper concentration is reached, the process is under the control of the diffusion of Cu^+ ions, which leads to much higher electrical currents. Then, for not too large η, the results reported on Table I show that the rate of both anodic and cathodic electrochemical reactions is correctly represented by the classical treatment corresponding to the diffusion in the solid phase.

Moreover, for a given potentiostatic pulse, the homogeneity of the $\tilde{D}_{\mathrm{Cu}}$ values in a very large time interval indicates that the active surface of the alloy remains constant [11, 23]. The electron scanning micrograph (cf. Figure 5) indicates the presence of small grooves, but their influence on the electrode area seems to be negligible at the accuracy of our measurements.

We can also add the diffusion in the solid metal is so slow that it remains the rate-determining process, even in transient techniques at very short time; for instance, there is no chance to observe the kinetics of electron transfer, since the exchange current density of the reaction $Cu^+ + e \rightleftarrows Cu$ has been proved very high [32].

At short times, some systematic deviation occurs: the linear dependence of I vs. $1/\sqrt{t}$ is no longer obeyed, as shown in Figure 6. The experimental values of I are well above the straight line in the short time region. This behaviour may have several causes:

i) Electrochemical reactions involving superficial or adsorbed redox compounds.

ii) Short effective diffusion length at the times involved.

The observed deviations occur generally at times less than 2 ms which correspond to a mean path of the copper atom of about $\delta = \sqrt{2\tilde{D}t} \simeq 10^{-7}$ cm. Thus, this diffusion occurs only in the first few atomic layers, where diffusion may be easier than in the bulk of the alloy; some calculated values of $\tilde{D}$ are reported on Table III. As these values are used to calculate $\sqrt{2\tilde{D}t}$, it is worth remarking that this quantity remains constant or even decreases during the first instants of the potentiostatic pulse; this mean distance might be considered as the thickness of the skin of the metallic phase in which the concentration of lattice defects is much higher than in the bulk and then the diffusion is no longer described by the classical treatment: in fact, when the mean path involved in the experiment reaches the atomic dimensions, the concept of diffusion itself becomes questionable.

Table III. Analysis at short times of some chronoamperograms of Fig. 6; η_P applied overvoltage, η overvoltage on the electrode (corrected from the ohmic drop); C_{Cu} copper concentration at the interface. Surface of the electrodes: 0.372 cm^2; Resistance: 0.330 Ω; Temperature: 554 °C. Copper concentration of the electrodes: first two chronoamperograms $C^*_{Cu} = 28.3 \cdot 10^{-3}$ mol cm^{-3}; three last ones: $C^*_{Cu} = 10.6 \cdot 10^{-3}$ mol cm^{-3}.

η_P	time ms	I mA	η mV	C_{Cu} 10^{-3} mol cm^{-3}	$\tilde{D}_{Cu}$ 10^{-12} cm^2 s^{-1}	$\sqrt{2\tilde{D}t}$ 10^{-8} cm
40	0.40	45.7	24.9	23.9	65	23
	1.05	23.8	32.2	22.0	24	22
	1.93	15.8	34.8	21.3	15	24
	2.77	12.7	35.8	21.0	13	27
	4.33	9.8	36.8	20.7	11	31
−40	0.27	−59.7	−20.3	31.4	148	28
	1.07	−24.4	−31.9	35.3	19	20
	1.92	−16.2	−34.7	36.3	11	21
	2.76	−12.9	−35.8	36.8	10	23
	4.70	− 9.6	−36.8	37.2	8	27
80	0.35	75.9	54.9	6.0	210	38
	0.73	34.2	68.7	4.8	55	28
	1.92	15.1	75.0	4.3	24	30
	4.18	9.1	77.0	4.1	19	40
	8.19	6.4	77.9	4.1	17	52
−80	0.39	−79.0	−53.9	16.7	123	31
	0.73	−45.7	−64.9	19.5	37	23
	1.92	−21.8	−72.8	21.9	13	22
	4.19	−13.3	−75.6	22.7	10	29
	7.47	−10.2	−76.6	22.9	10	39
200	0.60	91.9	170	1.39	134	40
	1.75	31.7	190	0.95	42	38
	3.21	21.3	193	0.91	34	47
	8.41	12.9	196	0.87	32	73
	16.8	9.6	197	0.85	36	110

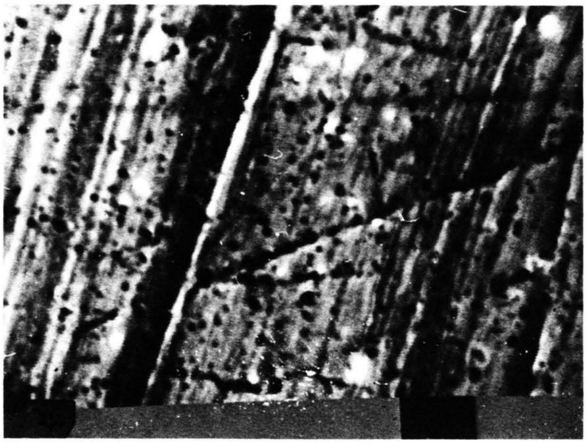

Fig. 5. Scanning electron micrograph of gold-copper alloy $C_{Cu} = 10.5 \cdot 10^{-3}$ mol cm^{-3}. The length of the black spot at the bottom of the picture is indicated on the left.

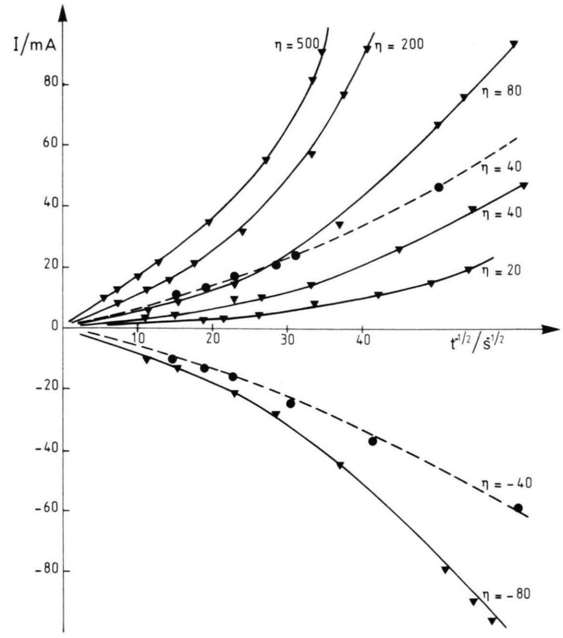

Fig. 6. I vs. $t^{-1/2}$ plots for gold-copper electrodes. (▶ :$C^*_{Cu} = 10.5 \cdot 10^{-3}$ mol cm^{-3}, ●: $C^*_{Cu} = 28.3 \cdot 10^{-3}$ mol cm^{-3}) in LiCl-KCl eutectic containing $6.4 \cdot 10^{-5}$ Cu$^+$ ion cm^{-3}. Electrode surface: 0.372 cm^2; ohmic resistance: 0.330 Ω. Temperature: 554 °C. The applied overvoltages are indicated on the figure (mV). It is pointed out that $t^{-1/2} = 10$ corresponds to 10 msec and $t^{-1/2} = 50$ corresponds to 0.4 msec.

Conclusion

The present research shows that chronoamperometry in molten salts at high temperatures is a suitable means for the determination of diffusion coefficients of the less noble metal in metallic alloy.

Applied to the copper-gold system we could show that both the anodic dissolution rate and the kinetics of surface alloying may be represented by the classical treatment of a process controlled by the diffusion in the solid phase. The method was easily used to determine $\tilde{D}$ as a function of temperature; moreover, it constitutes a very efficient tool for the study of two more important parameters.

a) Dependence of $\tilde{D}$ as a function of the alloy composition: the theory of chronoamperometry shows that a constant potential jump results in a current density obeying the $1/\sqrt{t}$ law, whatever the dependence of $\tilde{D}$ versus C is. Moreover, computation of the diffusion equation indicates that, provided the variation of $\tilde{D}$ is not too large, the application of Cottrell's law will lead to the value of $\tilde{D}$ corresponding approximately to the surface concentration of the sample. Then, the complete set of values of $\tilde{D}$ in the whole range of composition could be obtained in a single experiment using a gold electrode and applying negative potentiostatic pulses of different amplitude. Notwithstanding, better precision is reached with a small overvoltage applied to alloy electrodes of different compositions.

b) Thickness of the zone of concentration gradient: introducing the time as a new parameter in the electrochemical techniques, the pulsed methods introduce also a distance parameter [11, 23]; when the process is under diffusion control this distance corresponds to the mean path of the electroactive species. In our study, this distance varies from a few angströms to a few micrometers. So it is shown that the atomic motion in the very first atomic layers is very easy, the concept of diffusion being itself meaningless for a mean path of the order of magnitude of ten atomic diameters. But our result shows also that, beyond this very thin skin, the atomic motion in the next layers is under the control of a diffusion process, the diffusion coefficient near the interface being the same as in the bulk metallic phase.

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