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Diffusional kinetics of metalliding zinc into solid copper

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The process of incorporation of zinc into a copper cathode has been experimentally studied in a molten salt system at 381 ± 2° C and at various current densities. The process is shown to be kinetically controlled by the diffusion of Zn into the solid matrix. A galvanostatic pulse titration technique has been used to determine the chemical diffusion coefficient at various alloy compositions, and an exponential relationship has been found between the diffusivity and the third power of the zinc concentration in the alloy. This relationship was then used in the diffusion equation within the solid matrix and a numerical integration was performed. Very good agreement was found between the calculated and experimental data for Zn interfacial concentration versus time. The same calculation procedure was used to determine zinc concentration profiles in the alloys.

Nomenclature

c_A	concentration of the diffusing metal (mol cm^{-3})
D_{AB}	chemical diffusion coefficient of A into B (cm^2 s^{-1})
E	cell e.m.f. (mV)
F	Faraday number
i	current density (A cm^{-2})
t	time (s)
V_M	alloy molar volume (cm^3 mol^{-1})
x	linear dimension in the diffusion direction (cm)
X	zinc mass fraction in the alloy
z	ionic valence of Zn
δ	stoichiometric ratio Zn/Cu

1. Introduction

The incorporation of a metal into a cathode can occur both in molten salts and in various electrolytes and has been the subject of many recent studies [1–7]. Amongst the electrolytes used, of particular interest are molten halides. The high temperatures used in these electrolytes increase the kinetics of incorporation and the molten salt system allows the deposition of metals less noble than zinc and even these which cannot be deposited from aqueous solution, e.g., Ti, Ta, Nb, Zr, W, etc. [1, 8, 9].

These peculiar features of the molten salt systems and the possibility of obtaining microcrystalline and homogeneous superficial structures [1], make incorporation in a molten salt system an attractive alternative for obtaining superficial alloys with a desired thickness and specific mechanical and anticorrosion properties. In a previous paper [10] the incorporation of zinc into copper has been studied at various temperatures. The electrolyte was molten $ZnCl_2$, the two electrodes were solid Zn and Cu and brass in the α phase was the superficial alloy formed. Pure $ZnCl_2$ was used so that concentration polarizations were not present during the passage of the current. It has been shown [10] that this system has kinetics where the rate-determining step is the diffusion of the metalliding metal into the solid cathode. Examples of a similar behaviour are reported by Weppner and Higgins [4] and Tedmon and Hagel [11].

In order to define the operating conditions for obtaining the desired composition and thickness of the superficial alloy, a knowledge of the parameters which govern the rate of diffusion is necessary. To this purpose an experimental study of the previously reported system [10] has been

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carried out at various current densities and at the constant temperature of 381 ± 2° C. During the incorporation processes the diffusivity varies with the concentration profile of the superficial alloy so that the experimental results have been interpreted by integration of Fick's second equation in which the diffusivity is a function of the alloy composition.

2. Experimental

The electrochemical system studied in this work was the following galvanic cell: W/Zn/$ZnCl_2$/Cu/W. The two plane electrodes, of rectangular shape (1.5 cm x 2.3 cm), were spectroscopically pure Zn and Cu, and were positioned exactly parallel to one another. The cathode was embedded in a BN shield so that only one surface was active and so that uniformity of the current distribution was assured. The electrolyte was directly prepared in a Pyrex glass cell in the following way. Pure $ZnCl_2$ was dried by an anhydrous HCl flow for several hours and then washed with an argon flow. Before each experimental run a pre-electrolysis with Zn electrodes was performed for several hours.

The electrode surfaces were prepared by abrading with 600-grit fine metallurgical paper. A final polish was performed on the Cu cathodes by 0–2 μm Mecaprex diamond paste. The electrodes were introduced into the cell under an argon atmosphere. The cell was thermostated at 381 ± 2° C in a Mazzali furnace (Ionos 541 model). The cathodic potential was measured with respect to a Zn/$ZnCl_2$ reference electrode by a Keithley electrometer (610C model).

3. Results

The experimental runs have been carried out at various constant cathodic current densities by monitoring the variation with time of the cathode potential. The ohmic voltage drop was evaluated by opening the circuit very rapidly. Fig. 1 reports the values of the $E_{ZnCu} - E_{Zn}$ versus time curves monitored for the various zinc fluxes, each corresponding to a particular current density.

Fig. 2 reports the experimental relationship between the cell e.m.f. and the zinc mass fraction X in the alloy. This diagram was obtained in a previous study [10] of the same system using an X-ray diffractometric technique for the quantitative analysis of the alloy.

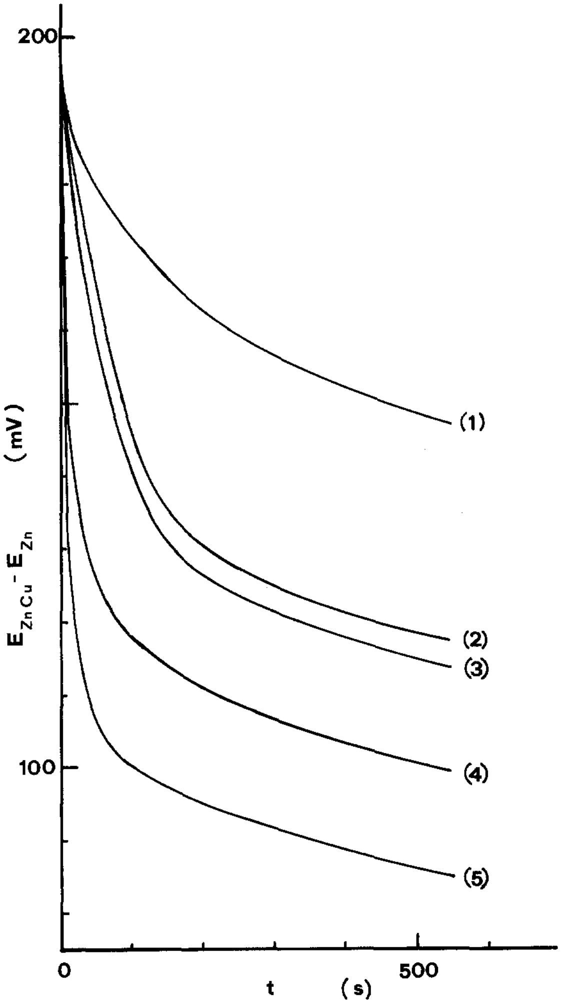

Fig. 1. Experimental curves for cathodic potential versus time for various current densities corresponding to the following zinc fluxes (10^{-9} mol cm^{-2} s^{-1}): (1) 1.66, (2) 3.91, (3) 4.66, (4) 9.31, (5) 13.60.

From the curves in Fig. 1 and using the linear relationship of Fig. 2, the interfacial alloy compositions versus time were obtained. These are reported in Figs. 3 and 4. In order to determine the chemical diffusion coefficient, the galvanostatic pulse titration technique, GPTT [4] was used. A series of constant current pulses was imposed on the cell. Each pulse was sent when the open-circuit cell voltage had achieved an almost constant value corresponding to an 'almost' steady state. The time interval of the pulses was about 10 s. A typical diagram of a single pulse for the GPTT technique is reported in Fig. 5.

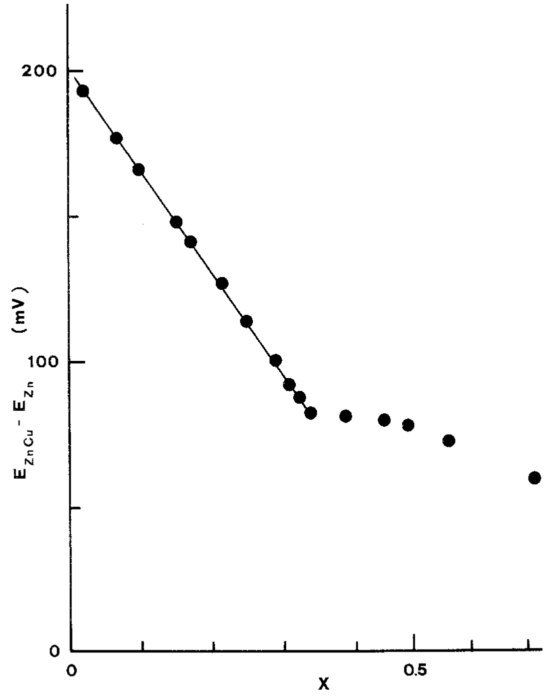

Fig. 2. Experimental values of the cell e.m.f. versus X, the zinc mass fraction in the alloy.

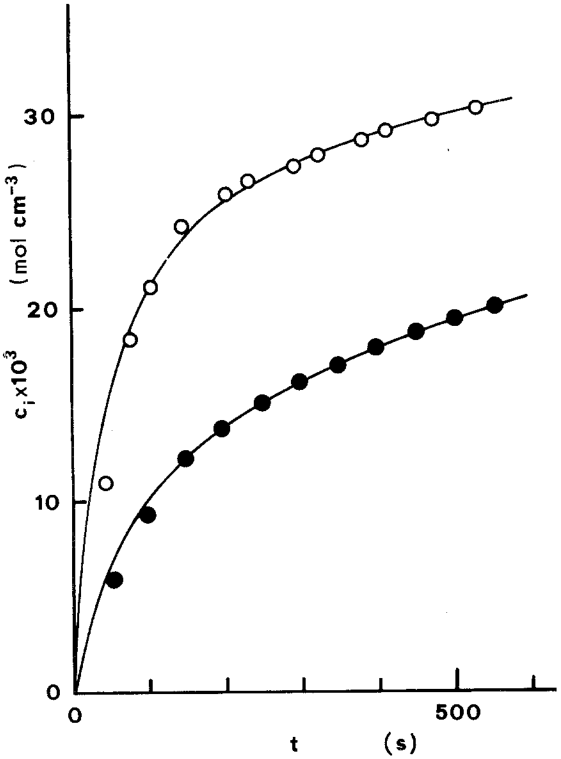

Fig. 3. Interfacial alloy composition versus time. ●, Data for curve (1); ○, data for curve (2) of Fig. 1.

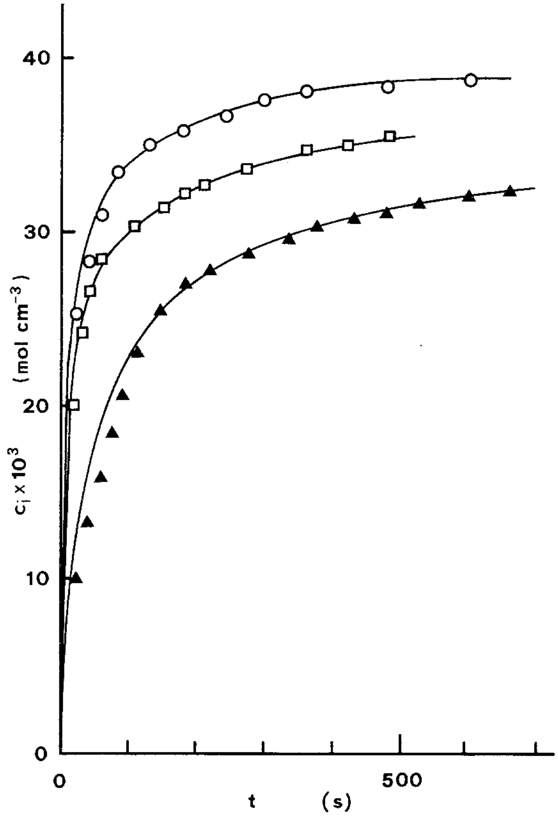

Fig. 4. Interfacial alloy composition versus time. ▲, Data for curve (3); □, curve (4) and ○, curve (5) of Fig. 1.

4. Discussion

As previously mentioned, the kinetics of this system is controlled by the diffusion of the zinc into the solid copper. Thus, in order to perform a quantitative study of the whole metalliding process, a diffusion problem must be solved. It is well known that the basic relationship by which this type of problem can be treated is Fick's second law. By assuming that the alloy partial volumes can be considered almost constant during compositional changes [12] and for monodirectional binary diffusion, Fick's law can be written as

$$\frac{\partial c_A}{\partial t} = \frac{\partial}{\partial x}\left(D_{AB}(c_A)\,\frac{\partial c_A}{\partial x}\right) \qquad (1)$$

where D_{AB} is generally a function of the alloy composition.

In order to determine the relationship between D_{AB} and c_A, the experimental results have been treated using the two following hypotheses.

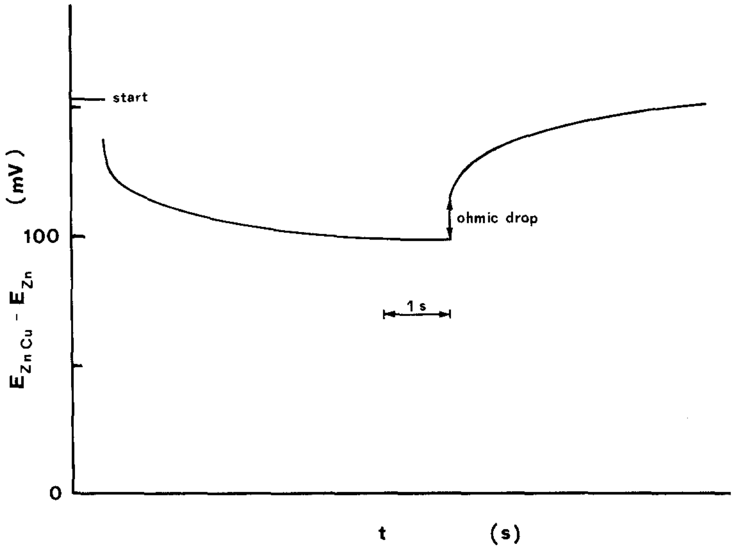

Fig. 5. Single pulse diagram of the GPTT experiment.

Firstly, in the very initial stages, the diffusional phenomenon regards only the superficial layers of the cathode. Secondly, the diffusion coefficient can be considered almost constant during the current pulse of the GPTT.

Taking into account that the diffusion coefficient of a metal into a solid matrix generally has a low value and that the time interval of the current pulse in the GPTT is very small, the previous hypotheses are realistic. Under these conditions the chemical diffusion coefficient can be written as [13]:

$$D_{\mathrm{AB}} = \frac{4}{\pi}\left(\frac{iV_{\mathrm{M}}}{Fz}\right)^2 \left(\frac{\mathrm{d}E}{\mathrm{d}\delta}\bigg/\frac{\mathrm{d}E}{\mathrm{d}\sqrt{t}}\right)^2 . \qquad (2)$$

Equation 2 has been used to determine the value of the chemical diffusion coefficient of Zn into various alloy compositions, by determining the ratio $\mathrm{d}E/\mathrm{d}\sqrt{t}$ from the GPTT experimental results and $\mathrm{d}E/\mathrm{d}\delta$ from the following mass balance:

$$\mathrm{d}\delta = \frac{\mathrm{d}X}{(1-X)^2} \qquad (3)$$

applied to the experimental data reported in Fig. 2.

A fitting procedure using these values was applied in the relationship

$$D_{\mathrm{AB}}(c_{\mathrm{A}}) = D_{\mathrm{AB}}(0)\exp\left(Kc_{\mathrm{A}}^{3}\right) \qquad (4)$$

where $D_{\mathrm{AB}}(0)$ is the chemical diffusion coefficient of Zn into solid Cu. The best fit is reported in Fig. 6, and Equation 4 becomes

$$D_{\mathrm{AB}}(c_{\mathrm{A}}) = 3.2 \times 10^{-12}\exp\left(10^5 c_{\mathrm{A}}^3\right). \qquad (5)$$

The values of $D_{\mathrm{AB}}(0)$, calculated from the initial portion of the experimental results shown in Fig. 1, are practically coincident with that of Equation 5. It is worth noting that, in the range of alloy composition obtained in this work, the value of the diffusivity coefficient increases by two orders of magnitude.

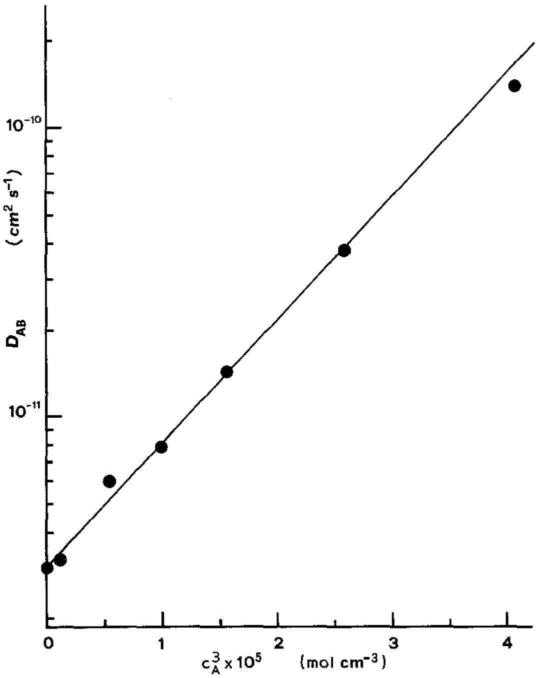

Fig. 6. Best fit of diffusivity data.

Substitution of Equation 5 in Equation 1 gives the general equation that completely describes the macroscopic diffusion phenomenon in this case:

$$\frac{\partial c_A}{\partial t} = 3.2 \times 10^{-12} \times \exp(10^5 c_A^3)\left[\frac{\partial^2 c_A}{\partial x^2} + 3c_A^2\left(\frac{\partial c_A}{\partial x}\right)^2\right]. \qquad (6)$$

Initial and boundary conditions must be defined in order to integrate Equation 6. In our case a constant zinc flux at the cathode interface can be assumed because of the constant current density and the absence of electroplated coating. Moreover, the relatively high thickness of the cathode with respect to the alloy layers allows the assumption of diffusion into a semi-infinite medium, so that the boundary conditions are:

$$\begin{array}{lll} c_A = 0, & t = 0, & 0 \leqslant x \leqslant \infty \\ D_{AB}\dfrac{\partial c_A}{\partial x} = \dfrac{i}{zF}, & t \neq 0, & x = 0 \\ c_A = 0, & t \neq 0, & x = \infty. \end{array}$$

An analytical solution of Fick's second equation, in which the diffusion coefficient is a function of the independent variables, has not been developed so far and a numerical method of integration must be used to solve Equation 6. The Crank and Nicolson implicit method of integration [14] has been applied in this case.

One may note that Equation 6 is a nonlinear partial differential equation which needs a linearization in each time-step in order to apply the finite difference procedure. In our case the terms $3.2 \times 10^{-12} \exp(10^5 c_A^3) = D_{AB}(c_A)$ and $D_{AB}(c_A) \times 3c_A^2(\partial c_A/\partial x)$ of Equation 6 has an assigned value at the beginning of each time-step. The computation was repeated, if necessary, using a mean value, once an estimate had been obtained for the two terms at the end of the time-step.

On this basis a Fortran IV program was developed and used in an IBM 3033 computer. For the five values of the zinc flux used in the experiments, the curves of the interfacial Zn concentration versus time, obtained by the calculations, are reported in Figs. 3 and 4. A very good fit with the experimental data can be noted, confirming that the relationship between D_{AB} and c_A, reported in Equation 5, is satisfactory and that Fick's second law can be applied to describe the metalliding processes.

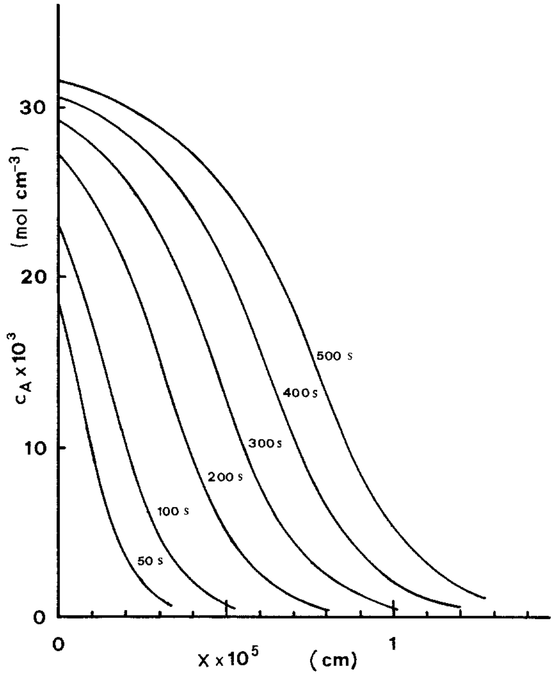

Fig. 7. Calculated alloy composition versus depth of penetration for a zinc flux of 4.66×10^{-9} mol cm^{-2} s^{-1}.

A knowledge of the concentration profiles of the diffusing metal is very important in the metalliding processes and can be exactly calculated by the previously reported procedure. In Fig. 7, for one value of the zinc flux, the alloy composition profiles at various times from the starting of the process are reported. It is also important to know the zinc concentration profile in the cathode for a fixed amount of incorporated zinc. This profile can be calculated by the same procedure and the corresponding diagram is reported in Fig. 8 for three values of the zinc flux.

5. Concluding remarks

The main results of this study can be summarized as follows.

(a) It has been shown that by means of the galvanostatic pulse titration technique a satisfactory relationship can be obtained that correlates the chemical diffusion coefficient and the composition of the alloy. The influence of c_A on

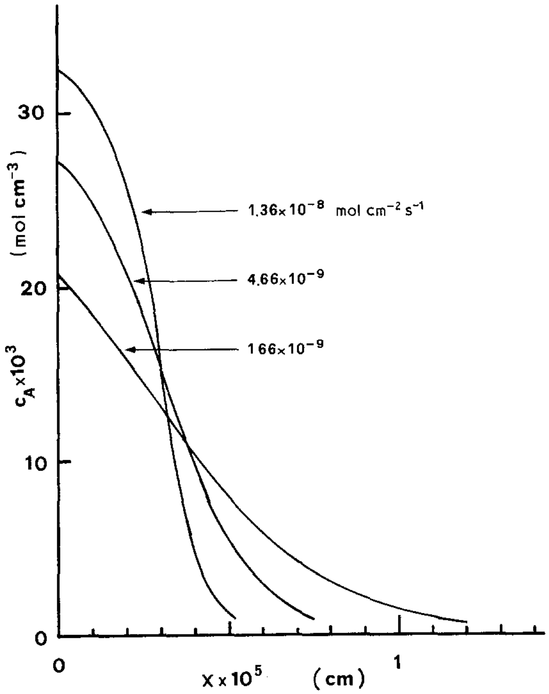

Fig. 8. Calculated zinc concentration profiles in the cathode. The amount of incorporated zinc has the value of 9.52 × 10^{-7} mol cm^{-2}.

D_{AB} appeared to be very strong, as can be seen in Equation 5.

(b) A numerical integration of Fick's second law, by substituting Equation 5, was performed.

(c) The good agreement with the experimental data confirmed that, in the range in which the α-phase of brass exists, from a macroscopical point of view the incorporation of Zn into a solid Cu cathode can be treated as a diffusion phenomenon and completely and quantitatively described by the previous equations.

(d) The integration of Equation 6 also allows the determination of the role played by the current density and the electrodeposition time on the concentration profiles of Zn in the Cu cathode.

(e) The mechanical and anticorrosion properties of the formed superficial alloy depend on specific alloy composition and thickness; a knowledge of these concentration profiles is fundamental.

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