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Solving the Stefan problem for a solid phase growth on plane plate and spherical surfaces and testing of theoretical equations

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Abstract

Solutions of the Stefan problem in the 2D space considering a moving boundary of a solid deposit growing under mass transfer control on either plane plate or spherical solid substrates are reported. In the former case, the displacement of the growth front at the plane plate occurs perpendicularly to the substrate, whereas for the latter it shifts radially. For both substrates, in the absence of convection and surface roughness effects, the phase growth kinetics is determined by diffusion and advection, the latter being due to the linear displacement of the growth front with time. For both geometric arrangements the theory predicts two limiting kinetic situations, namely a diffusion control when the time and/or the radius of the substrate approach zero, and an advection control for the reverse conditions. For the spherical substrate, when its radius tends to infinity, the kinetics of the process approaches that found at the plane plate substrate. Theoretical potentiostatic current density transients are tested utilising growth pattern data for the formation of 2D silver dense branching electrodeposits on a plane plate cathode in a quasi-2D cell, and silver electrodeposits on spherical cathodes employing a high viscosity plating solutions.

Keywords: Stefan problem; Diffusion–advection; Plane plate and spherical electrode; Silver electrodeposition

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1. Introduction

Most rate equations that have been derived solving the convective-diffusion differential equations for the growth of a solid phase at a solid substrate have considered that the interface remains at rest [1]. This implies a limitation to the extension of those rate equations to processes in which the solid phase growth front moves inward (forward) into the bulk of the reactant supplier environment [2]. In this case, the solution of the corresponding differential equations depends on the moving boundary conditions [3].

Since about a century ago, solutions of moving boundary problems have been proposed for heat transfer in iceberg displacement [4–6], although their extension to mass transfer processes, such as those involved in solid phase growth, has received much less attention. These mass transfer problems are generically denoted as Stefan problems, irrespective of the driving force. They are often found in a number of processes occurring in different areas of natural sciences and technologies.

In principle, both Fick's and Fourier's equations can be solved in each phase for different situations. (i) For a fixed boundary the transfer equations are solved for the immobile interface assuming constant spatial domains for each phase. (ii) For a moving boundary the spatial domain of each phase changes as the interface front moves according to a certain law that is known a priori. (iii) For an implicit free boundary the spatial domain changes and the moving boundary equations are unknown. They usually depend on the physics of each problem and have to be found in order to solve them [7].

This paper compares two solutions of the Stefan problem in the 2D space considering the moving boundary of solid phase growth [case (ii)] on either a plane plate or a spherical solid under mass transfer control. In the former case, the displacement of the growth front occurs perpendicularly to the substrate surface, whereas for the latter it shifts radially. For this case, when the radius tends to infinity, the limiting solution of the mass transfer differential equation approaches the solution for the plane plate

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substrate. Neither changes in the macroscopic roughness of the moving boundary nor convective effects from density gradients are considered in solving the transfer equations.

On the other hand, theoretical potentiostatic current density transients are tested with experimental data related to the electrochemical formation of silver dense branching patterns under mass transfer control on plane plate and spherical cathodes. For this purpose, to make the contribution of free convection negligible, in the former case a quasi-2D cell and conventional plating solutions are utilised, whereas for the latter high viscosity plating solutions are employed. After correction for the roughness of the electrodeposits, the agreement of theoretical and experimental data in the time range where the contribution of advection is dominant is fairly good.

2. The solution of Fick's equation with the Stefan boundary condition

2.1. Plane plate substrate

Let us consider the deposition of species *i* on a plane plate substrate of infinite dimensions by a diffusion process from a fluid phase (plating solution) that occurs normally (*y*-direction) to the plane plate. This process is expressed by Fick's equation in Cartesian coordinates

$$D_i \frac{\partial^2 c_i}{\partial y^2} = \frac{\partial c_i}{\partial t} \tag{1}$$

D_i and c_i being the diffusion coefficient and the concentration of species *i* (reactant) in the fluid phase and *t* is the deposition time. The advance of the growth front occurs in the *y*-direction. Eq. (1) is solved with the following boundary conditions:

$$c_i(y, 0) = c_i^0; \qquad y \geq 0; \qquad s(t) = s(0) \tag{2a}$$

$$c_i[s(t), t] = 0; \qquad t > 0 \tag{2b}$$

$$s(t) = \beta \cdot t \tag{2c}$$

$$c_i(y, t) = c_i^0; \qquad y \to \infty \tag{2d}$$

Condition (2a) corresponds to the initially uniform reactant concentration in the plating solution, and *s*(*t*) is the front coordinate at time *t*. The surface area of the growth front is equal to that of the inert substrate upon which the growth of the solid phase commences ($t = 0$); β denotes the advance velocity of the moving boundary. Condition (2b) indicates that the concentration of *i* just at the growing front is null for $t > 0$, as expected from mass transfer-controlled kinetics. Condition (2c), usually called the Stefan condition, indicates the instantaneous location of the growing front.

Solving Eq. (1) with boundary conditions ((2a)–(2d)), the explicit expression for $c_i(y, t)$ results in

$$c_i = c_i^0 - \frac{c_i^0}{2}\left\{\exp\left[\left(\frac{\beta}{D_i}\right)\cdot(\beta t - y)\right] \times \left[1 - \operatorname{erf}\left(\frac{y - 2\beta t}{2\sqrt{D_i t}}\right)\right] + 1 - \operatorname{erf}\left[\frac{y}{2\sqrt{D_i t}}\right]\right\} \tag{3}$$

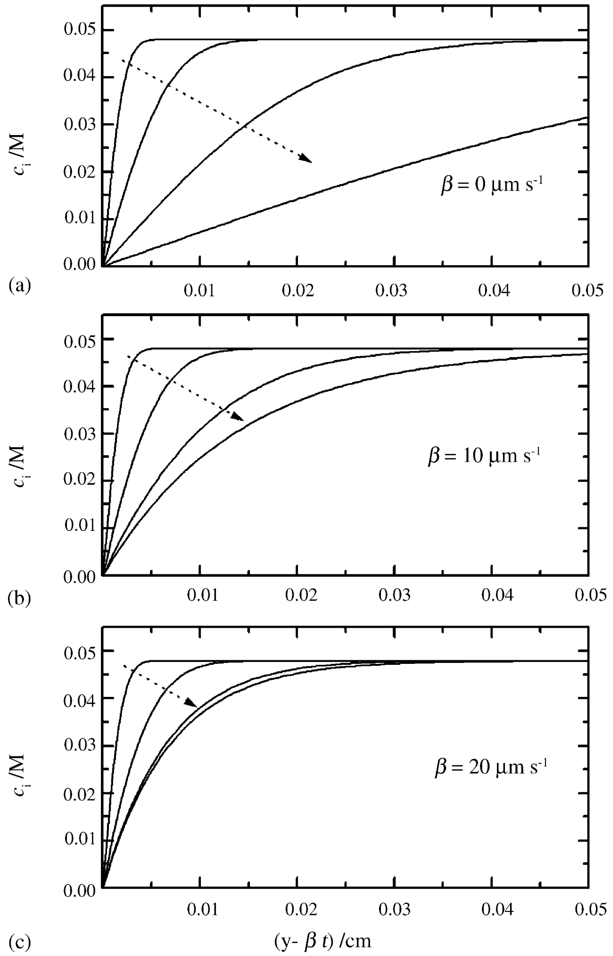

Fig. 1. (a–c) Concentration profiles calculated for the plate plane with Eq. (3) plotted as c_i vs. $y - \beta t$ at different values of β for $t = 0.1$, 1, 10 and 100 s. The value of *t* increases as indicated by the arrows. The following values were used in the calculations: $z_i = 1$; $D_i = 1.39 \times 10^{-5}\ \mathrm{cm^2\ s^{-1}}$; $c_i^0 = 4.8 \times 10^{-5}\ \mathrm{mol\ cm^{-3}}$. These figures were taken from the electrodeposition of silver from aqueous solution [9].

Eq. (3) fulfills boundary conditions (2a) and (2b). Plots of c_i versus $y - \beta t$ for various values of β and different values of *t* are shown in Fig. 1. At constant $y - \beta t$ the gradient of c_i perpendicular to the substrate increases with β. This effect is more remarkable at longer *t*.

Let us apply Eq. (3) to evaluate the potentiostatic current density transients, which represent the instantaneous rate of metal electrodeposition from the plating solution on the plane plate. The rate of this process under diffusion control is given in terms of the cathodic current density $j_c(t)$

$$j_c(t) = z_i F D_i \left[\frac{\partial c_i(y, t)}{\partial y}\right]_{y=\beta t} \tag{4}$$

z_i, c_i and *F* being the electric charge per reactant species, the reactant concentration in the plating solution and the Faraday constant, respectively. Then, considering the differential expres-