On unsteady electrochemical coating of a cylinder at moderately large Reynolds number

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Electrodeposition on a circular cylinder under forced convection was simulated for Reynolds numbers 10 and 200 by numerical solutions of the incompressible Navier–Stokes and mass transport equations. Current density distribution and concentration fields were computed with changing mass transfer and flux rates. Comparisons with earlier numerical and theoretical results are presented for Reynolds number 10. It is shown that the unsteady wake that appears for Reynolds numbers greater than 50 affects the mass transfer from the surface of the cylinder only in an average sense. This result is compared with a heat transfer case, where unsteadiness is much more manifest.

Keywords: electrodeposition, electrochemical coating, forced convection, cylinder, mass transport, numerical solutions

1. Introduction

The technique of electrolytic deposition of thin metal coatings to other metals evolved during the middle of the last century. This technology has been successfully used for development of new products with unique functional properties. Today it is one of the highest volume chemical technologies; and most metalworking plants have in-house plating shops. More recently, the demands on quality and properties of metal coatings have increased significantly.

Electroplating processes are mainly used in the surface finishing industries for items such as printed circuit boards, magnetic alloys for computer memories, coatings for hard disk drives, wear resistant coatings, corrosion resistant alloys, electroreformed laser mirrors, contacts/connectors and decorative coatings [1,2]. Many factors can affect the rate of an electrodeposition reaction. The imposed electric potential, electrode parameters (material composition, surface state, geometry etc.) and electrolyte parameters (composition, concentrations, conductivity, velocity, temperature etc.) are examples of such factors [3]. Parametric adjustment of an electroplating line is, therefore, a formidable task, which so far has been dealt with on empirical basis [4]. But with the increasing requirements on quantity, quality and productivity, the purely empirical approach to the optimization problem needs to be supplemented with theoretical estimations and computations based on first principles.

Forced convection is commonly used in electroplating processes. For example, the electrolyte may be pumped through a cell. Other examples are stirring by air bubbles or by mechanical agitation. In many electroplating processes a continuous strip or wire or an array of workpieces moves through an electroplating bath. The motion of the material to be plated generates a flow pattern that enhances mass transfer which, in turn, leads to more efficient plating. In such cases, high reaction rates are imposed [5]. The hydrodynamics is then of particular importance as the current distribution is determined by the forced convective mass transport of reactant. Convection–diffusion theory in its classical form is well known and available for the reader in standard textbooks [6,7]. However, at the present time, there are no practical tools that are useful for prediction of electroplating.

Levich [6] remarked that the convective-diffusion transport of ions in electrolytes is characterized by large Schmidt numbers (≈10^3) and is thus akin to heat transport at large Prandtl numbers. Lighthill [8] developed an approximative analytic solution for steady heat transfer from bodies at high Prandtl numbers in the case of forced convection. Acrivos [9]

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applied the method devised by Lighthill to a wide range of problems. The key element of Lighthill’s method is that the concentration distribution, and thus the rate of mass transfer, can be computed approximately in analytic form if the velocity field near the electrode is known. The one-to-one correspondence between mass transfer and velocity gradient is the basis for electrochemical methods for wall shear stress measurements [10, 11].

In the present work electrochemical mass transfer to a circular cylinder oriented perpendicular to a moving electrolyte is studied. At large distances from the cylinder, the velocity of the electrolyte is constant. This case is of canonical type because of the simplicity of the boundary conditions, the complexity of the physico-chemical processes, the fundamental mechanisms exhibited and numerous industrial applications. One example of practical applications is the production of gold plated electrical connectors.

The nature of the flow pattern around a cylinder depends on the Reynolds number $Re$, for example [12, 13]. In most investigations of the unsteady regime attention is focused on the unsteady behaviour of the vortices downstream the cylinder rather than the properties of the flow close to the surface of the cylinder.

For theoretical predictions, since the governing equations are nonlinear and exact solutions are not available, numerical methods have been used in a number of investigations to deal with heat transfer from a circular cylinder. Zukauskas [14] has given an extensive review of published data and proposed several empirical correlations between heat transfer rates and flow variables.

For electrochemical mass transfer to a circular cylinder, comparatively few investigations are reported. Most of these focus on the overall mass transfer [15, 16]. In several studies, the microelectrode technique, which relies on the fact that unsteady mass diffusion at high Schmidt number close to a solid surface depends only on the locally linear tangential velocity component, has been made use of to measure the local shear stress on the cylinder [11, 17, 18].

For rough estimates, the classical Nernst diffusion layer model is often adopted for the complex velocity and concentration profiles near the cathode surface, see [19, 20, 21]. In this model, it is assumed that the motion of the electrolyte near the surface of the electrode can be divided into two zones. Close to the surface it is assumed that there is a thin layer which is totally stagnant such that diffusion is the only mode of mass transport. At steady state, the concentration profile is then linear. Outside this layer, only convection is assumed to be of importance and the concentration is, on an ad hoc basis, taken to be equal to that of far field. In a real flow, however, a sharp limit cannot be observed due to diffusion of momentum [21]. Nevertheless, the Nernst model has been found useful for coarse approximations.

Numerical analysis has so far not been in widespread use for investigation of convection–diffusion problems at high Schmidt numbers. Josserand [18] studied the mass transfer to a circular cylinder at $Re = 10$ and $Re = 5 \times 10^4$. He used a simplified model for the velocity field close to the cylinder. At $Re = 10$ the wall vorticity distribution was taken from the numerical study by Dennis et al. [22], and at $Re = 5 \times 10^4$ from the experimental data reported by Son and Hanratty [23]. In both cases a linear velocity profile was then imposed close to the surface of the cylinder. The concentration field was then computed numerically. Although limited, the investigation of Josserand was pioneering regarding the use of numerical methods for simulation of electroplating processes. The aim of this work is to make a detailed numerical investigation of electroplating of male electrical contacts.

2. Problem statement

The specific case to be studied in this work, gold plating of male electric contacts, is chosen due to its industrial importance. Usually, in the industrial process, an array of cylinders is moving through a series of baths [11, 24]. In this study, however, as a first step, the plating process of a single cylinder is considered.

Gold plating solutions usually include a supporting electrolyte. The ions of the supporting electrolyte have a larger mobility than the reactant and are responsible for the transport of charge outside the mass transfer boundary layer. Consequently, the electric field is reduced in the electrolyte and the fraction of the net charge transport carried by the reacting ions is negligible. The electrical potential can be considered as constant in the bath. The concentration will be the only factor producing nonuniformity in the current distribution around the surface of the cylinder [6, 19, 21].

The mathematical problem for plating of a cylinder is reduced to the computation of forced convective transport of reactant to the surface of the cylinder. The system of equations to be solved for the velocity field $u$ and the pressure field $p$, are the Navier–Stokes equations

$$\frac{\partial u}{\partial t} + u \cdot \nabla u = -\frac{1}{\rho} \nabla p + v \nabla^2 u \quad (1)$$

and the continuity equation for incompressible flow

$$\nabla \cdot u = 0 \quad (2)$$

As forced convection is considered, when $u$ has been computed from Equations 1 and 2, the concentration $c$ of the solute can be computed from the conservation equation

$$\frac{\partial c}{\partial t} + u \cdot \nabla c = D \nabla^2 c \quad (3)$$

The boundary conditions on the cathodic cylinder wall are

$$u = \vec{0} \quad \text{and} \quad \vec{n} \cdot \nabla c = k c \quad (4)$$

In these expressions $\vec{n}$ is the unit vector normal to the cylinder and the rate of reaction $k$ taken as a constant on the cylinder wall. In Equations 1 and 3, $\nu$ is the