SHORT COMMUNICATION

A mass transfer study of the electropolishing of vertical discs under free convection

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Nomenclature

A anode area

C_s saturation solubility of copper phosphate (as Cu^{2+}) in H_3PO_4

d disc diameter

D diffusivity of copper ions

F Faraday's constant

g acceleration due to gravity

I_L limiting current

K mass transfer coefficient

z number of electrons involved in the reaction

Gr Grashof number, $gd^3(\rho_i - \rho_b)/v_{av}^2\rho_i$

Sc Schmidt number v_{av}/D

Sh Sherwood number, Kd/D

ρ_i density at the interface between the anode and the solution

ρ_b bulk solution density

v_{av} average kinematic viscosity

1. Introduction

Mechanistic studies [1–3] of electropolishing have revealed the fact that it is a diffusion controlled process which takes place at the limiting current. The magnitude of the limiting current is determined by the rate of removal of the anodic dissolution products away from the anode surface. In unstirred solutions removal of the anodic dissolution products takes place mainly by diffusion and by natural convection arising from the density difference between the interfacial solution which is saturated with the dissolution products and the solution bulk which contains the polishing agent. Under such conditions the geometry and orientation of the workpiece, among other factors, affect the rate of electropolishing. In an earlier study [4] the rate of electropolishing of horizontal downward facing discs was investigated and the limiting current was correlated to other variables with the equation

$$Sh = 0.19(Sc \cdot Gr)^{0.33} \qquad (1)$$

The present work is concerned with studying the rate of polishing of vertical discs. Vertical discs are of frequent occurrence in practice either alone or as a part of a more complex geometry such as a horizontal cylinder. Recently it has been shown that for bodies of complex geometry the overall rate of a diffusion controlled process under natural convection can be predicted in terms of the separate rates at the different surfaces of the complex object [5, 6]. Accordingly, the present study would assist in predicting rates of polishing of objects consisting of vertical discs such as horizontal cylinders with active ends and horizontal cones with active bases. Rates of polishing were deter-

mined by measuring the limiting current of the anodic dissolution of vertical copper discs in phosphoric acid.

2. Experimental technique

The cell consisted of a one litre rectangular plexiglass container divided into two compartments by a porous PVC diaphragm to prevent the cathodic hydrogen bubbles from reaching the anode surface. The cathode consisted of a rectangular sheet of copper measuring 10 cm × 10 cm. The anodes were made of vertical circular copper discs ranging in diameters from 1.5 to 10 cm. The back of the anode was isolated with epoxy resin. Each run was repeated twice using a fresh solution. Solution temperature was maintained at $22 \pm 0.5°C$. Electrical circuit and procedure for limiting current determination were similar to that reported elsewhere [7].

3. Results and discussion

Figure 1 shows typical polarization curves with a well defined limiting current plateau obtained at different phosphoric acid concentrations. From these curves the limiting current was obtained and plotted against disc diameter as shown in Fig. 2. It is seen that the limiting current decreases with disc diameter in accordance with the prediction of the boundary layer theory [8] according to which the thickness of the downward moving hydrodynamic boundary layer at the anode surface increases with disc diameter with a consequent increase in the anode diffusion layer thickness. An overall mass transfer correlation of the polishing data was envisaged in terms of the dimensionless groups Sh, Sc and Gr usually used in correlat-

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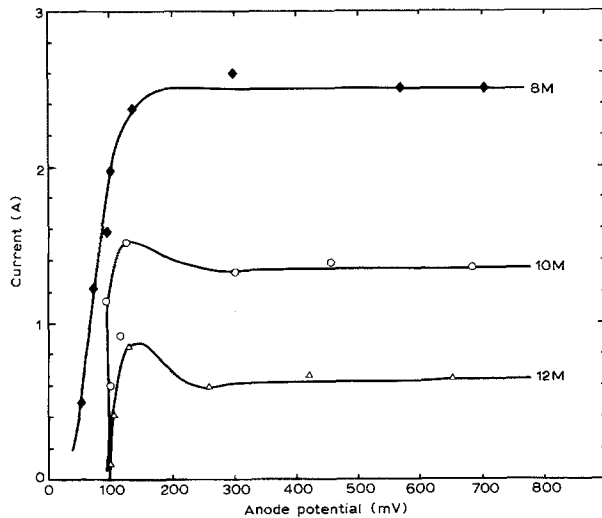
Fig. 1. Typical polarization curves obtained for the electropolishing of 10 cm diameter copper disc in different phosphoric acid concentrations.

ing natural convection mass transfer data. The mass transfer coefficient (K) was obtained from the limiting current using the equation

$$K = I_L/AzFc_s \qquad (2)$$

The saturation solubility of copper phosphate in phosphoric acid, C_s, and the physical properties of the solutions (ρ, μ, D) in correlating the data are reported elsewhere [4]. Figure 3 shows that the data can be correlated with the equation

$$Sh = 1.44(Sc \cdot Gr)^{0.25} \qquad (3)$$

The exponent 0.25 in the above equation agrees with the prediction of the boundary layer theory and agrees also with the exponent of the experimentally obtained equation representing laminar flow natural convection mass transfer at a vertical plate [9]
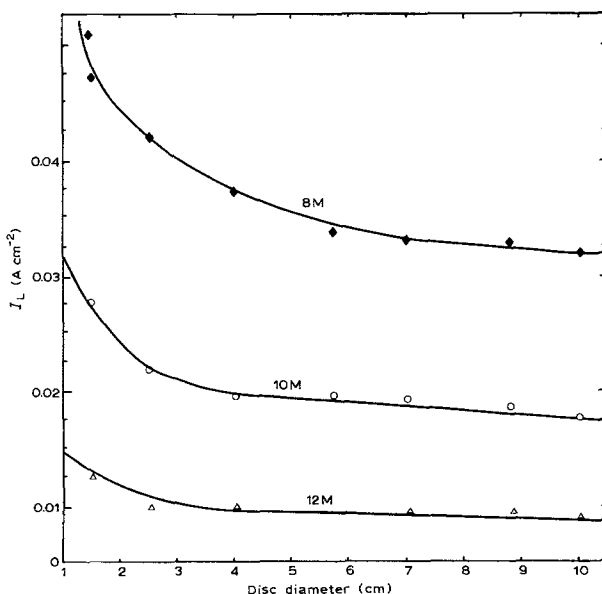
$$Sh = 0.67(Sc \cdot Gr)^{0.25} \qquad (4)$$

Fig. 2. The effect of disc diameter on the limiting current density at different H_3PO_4 concentrations.
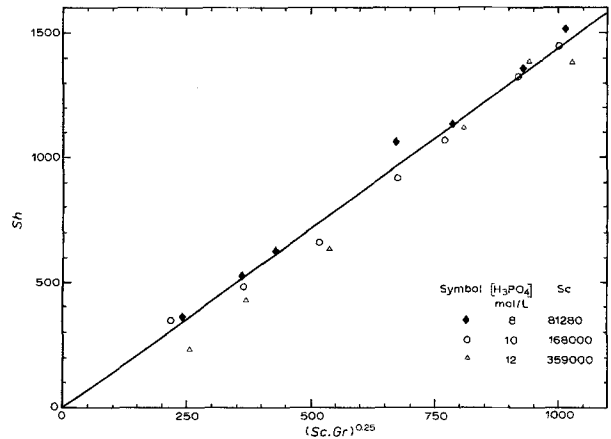

Fig. 3. Overall mass transfer correlation for electropolishing.

Equation 4 represents mass transfer by convection and diffusion. The discrepancy between the coefficient 1.44 in Equation 3 and the value of 0.67 in Equation 4 may be attributed in part to the possibility of copper ion transfer from the anode surface to the solution bulk by electrical migration in addition to natural convection and diffusion. It is probable that the concentration of H_3PO_4 supporting electrolyte in the diffusion layer becomes insufficient to eliminate the transfer of Cu^{2+} by migration at the limiting current where some H_3PO_4 is converted to copper phosphate. The remaining H_3PO_4 is not completely ionized especially under the present conditions where relatively high concentrations of H_3PO_4 are used [10].

According to Alkire and Reiser [11] the effect of electrical migration can increase the rate of mass transfer of a divalent ion by a factor of up to two depending on the ratio between the concentrations of the supporting electrolyte and that of the electroactive ion. It is noteworthy that in the case of turbulent flow natural convection mass transfer, the correlations [4, 10] obtained from electropolishing data using the anodic dissolution of copper in phosphoric acid agree well with the established equations representing convective-diffusion mass transfer, i.e., without transfer by electrical migration. This agreement suggests that in the case of turbulent flow free convection the amount of copper ions transferred by electrical migration is negligible compared to the amount transferred by the combined diffusion and turbulent flow natural convection. Further work is needed to clarify the role of electrical migration in the transfer of the dissolution products away from the anode surface during electropolishing under laminar flow natural convection.

The high value of the coefficient of Equation 3 compared to the value of the vertical plate equation may also be ascribed in part to the nature of the disc geometry. For a vertical flat plate, the height across which the hydrodynamic boundary layer is formed is uniform all over the width of the plate whereas for a disc, the path of the hydrodynamic boundary layer ranges in height from zero at the periphery to 'd' at the center of the disc. Accordingly at the disc surface

there is a parallel array of downward flowing natural convection streams, each stream having a different velocity profile and a different concentration profile. It seems that the interaction between these streams results in a higher average mass transfer coefficient at the disc compared to the flat plate. Recently, Sedahmed and Nirdosh [6] measured rates of natural convection mass transfer from the electrodeposition of Cu from acidified $CuSO_4$ at vertical discs in the context of their study of natural convection mass transfer at horizontal cylinders with active ends. The authors found that the average mass transfer coefficient is about 8.8% higher than the value at a vertical plate of a height equal to the disc diameter.

In conclusion, established natural convection mass transfer equations should be used with caution in predicting the rate of electropolishing of vertical discs as they may seriously underestimate the limiting current, especially under laminar flow conditions.

Acknowledgement

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