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Dieter Landolt, Rolf H. Muller and Charles W. Tobias
(January 1969)

HIGH RATE ANODIC DISSOLUTION OF COPPER

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ABSTRACT

The anodic dissolution of copper at current densities of 10 to 150 A/cm² has been studied in neutral KNO₃ and K₂SO₄ solutions. An experimental flow system has been built which allows to perform electrochemical measurements of the dissolution process under defined hydrodynamic conditions typical for the technical electrochemical machining operation. Design criteria for such a system have been analyzed. Copper dissolution proceeds in an "active" or a "passive" mode which differ in overvoltage by 10-20 volts. The onset of passivation seems to be due to the limiting mass transfer of dissolved metal from the electrode surface. The still higher dissolution rates in the passive state appear to be made possible by the removal of solid dissolution products. Etched, dull surfaces have resulted from active dissolution; pitted, bright surfaces from passive dissolution.

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INTRODUCTION

Electrochemical machining (ECM) has found widespread use in recent years for the shaping of metals. In this process, the workpiece is dissolved anodically at current densities in the order of 100 A/cm^2 , characteristically with electrolyte flow rates of 0.5 to 70 m/sec and electrode spacings of 0.1 to 0.5 mm. As an electrochemical process, ECM is of particular interest because the current densities employed are about three orders of magnitude higher than those applied in conventional electrolysis. Most of the published literature on ECM deals with the correlation of practical process variables such as cathode feed rate, applied voltage, and electrolyte pressure, but little is known about the electrochemical factors involved.

A more detailed understanding of ECM may not only lead to further development and wider practical adoption of this highly interesting process, but it may also yield information relevant to the operation of other electrochemical processes at much higher rates, than employed in current industrial practice. With this purpose in mind, the anodic dissolution of a metal with reasonably well understood electrochemical and metallurgical properties was subjected to study under conditions similar to those employed in ECM. The principal goal of the study was to develop an experimental method for estimating the anode potential values prevailing at high current density and for investigating the role of hydrodynamics in the anodic dissolution process. In addition, optical observations of the interelectrode gap were to be carried out in order to determine the influence of flow rate and current density on cathodic hydrogen evolution. The design of the experimental system, and results obtained on the dissolution of copper in neutral KNO_3 and K_2SO_4 solutions

in the current density range of 10-150 A/cm², are reported here.

DESIGN CONSIDERATIONS

Cell Voltage: In order to keep the cell voltage in manageable limits electrodes have to be spaced closely. For example, assuming a current density of 100 A/cm², a specific electrolyte resistance of $\rho = 10 \Omega \text{ cm}$ and an inter-electrode gap of 0.5 mm the ohmic drop is as large as 50 volts. Geometrical arrangements like rotating disks or cylinders are not well suited since the cell resistance is dependent on the diameter which determines the surface area, and is therefore not independent.¹

Temperature Increase in Solution: The temperature rise per unit volume of solution due to power dissipation may be estimated from

$$\frac{\Delta T}{\Delta t} \approx \frac{i^2 \rho}{d c_p} \quad (^\circ/\text{sec}) \quad [1]$$

As an example, setting $i = 100 \text{ A/cm}^2$, $\rho = 10 \Omega \text{ cm}$, $d = 1 \text{ g/cm}^3$, $c_p = 4.18 \text{ joule/}^\circ\text{g}$, one obtains

$$\frac{\Delta T}{\Delta t} \approx 2.4 \times 10^4 (^\circ/\text{sec})$$

In order to control the temperatures short experimental times are therefore required, or the solution has to be replaced at a high rate.

¹ Using the values above, one obtains for a rotating disk electrode of $R = 2 \text{ mm}$ radius (primary current distribution (1)) $U \approx \pi/4 i \rho R \approx 160$ volts. For two concentric cylinder electrodes of 2 and 10 mm radius $U \approx i \rho R \ln R_2/R_1 \approx 320$ volts.

In the latter case, the use of parallel plate electrodes is more suitable than e.g. rotating disk or cylinder electrodes but high linear velocities of the electrolyte are to be employed, and the length of the electrode in flow direction is to be kept short. A rough estimate of the temperature increase in the flow direction is obtained from [1] by setting $\Delta t = L/u$ with L = electrode length and u = linear velocity. For example, using the current density and electrolyte properties given above, one obtains for $u = 1000$ cm/sec, and $L = 1$ cm, $\Delta T = 25^\circ$.

Pressure Drop: The pressure drop in a flow system is proportional to the square of the flow velocity and proportional to the length of the system. In a flow channel cell, it is desirable to have a hydrodynamic entrance length of 70 to 100 hydraulic diameters² upstream of the electrodes. The entrance length serves to establish a fully developed velocity profile (2, 3), which is necessary in order to have well reproducible and analytically amenable mass transfer conditions. The requirement of a hydrodynamic entrance length increases the value of the inlet pressure necessary to maintain a given linear velocity at the electrodes manifold. A decision has therefore to be made as to whether close control of mass transfer conditions justifies a substantial increase in pressure requirements. Data of a channel cell containing a hydrodynamic entrance length are given in the next section.

² The hydraulic diameter is defined as $D_h = \frac{4 \text{ cross section}}{\text{perimeter}}$

Mass Transfer Conditions: Numerical estimations indicate that a rectangular flow channel cell under turbulent flow conditions is the most suitable experimental arrangement for realizing extremely high mass transfer rates. This arrangement has the drawback that the thickness of the diffusion layer increases in the flow direction (4). However, under turbulent flow conditions, if the electrode is sufficiently long the variation of the diffusion layer thickness can be neglected (6) since a constant value is reached at a short distance from the leading edge of the electrode. Mass transfer rates for turbulent flow in pipes have been reported by Van Shaw, Reiss and Hanratty (6). If the pipe diameter is replaced by the hydraulic diameter³ D_h , their results should be applicable to predict mass transfer in rectangular flow channels. In the mass transfer entry region, i.e., at short distances from the leading edge of the electrode, experimental mass transfer rates under conditions corresponding to fully developed velocity profiles were described by Van Shaw, Reiss and Hanratty (6) by the relation

$$Nu = 0.28 Re^{0.58} Sc^{1/3} \left(\frac{D_h}{L} \right)^{1/3} \quad [3]$$

³ For fully developed mass transfer profiles, i.e., if

$$\frac{0.2 L Re^{7/8}}{D_h} >> 10^3 \quad [5]$$

mass transfer rates are described by the Deissler relation

$$Nu = 0.079 \sqrt{f^*} Re Sc^{1/4} \quad [6]$$

where f^* represents the friction coefficient which is often given by the Blasius relation (7)

$$f^* = \frac{0.079}{Re^{1/4}}$$

where Nu represents the average Nusselt number defined by $Nu = \frac{i_{\ell} D_h}{z F c_o D}$ with i_{ℓ} = limiting current density, D_h = hydraulic diameter, z = number of electrons transferred per mole, F = Faraday constant, c_o = bulk concentration of reacting species, D = diffusion coefficient. The Reynolds number Re is defined by $Re = \frac{u D_h}{\nu}$ with u = linear flow velocity, ν = kinematic viscosity. Sc represents the Schmidt number defined by $Sc = \nu/D$. L is the distance from the leading edge of the electrode. Relation [3] applies if the condition

$$\frac{0.2 L Re^{7/8}}{D_h} < 10^3 \quad [4]$$

is satisfied. Such was the case in the metal dissolution experiments described below.

In the region of laminar flow ($Re < 2000$) average mass transfer rates at fully developed velocity profile are given by (5)

$$Nu = 1.85 \left(Re Sc \frac{D_h}{L} \right)^{1/3} \quad [7]$$

The hydrodynamic entrance length here is $S = 0.035 D_h Re$ (3).

Current Distribution: Uniform current distribution can be realized with cylindrical or spherical electrodes. Non-uniform current distribution on the rotating disk electrode has been treated by Newman (1, 8).

Wagner (9) gave an analytic solution of the Laplace equation for two parallel plate electrodes for linear current-voltage relationships. Uniform current distribution is approximated if the parameter $\frac{1}{\kappa} \frac{d\epsilon}{di}$ (conductivity of solution times slope of current voltage curve) is large compared to a characteristic dimension, either the distance between two plane electrodes or the length of a small electrode, positioned far from the counter electrode. In high-rate electrolysis studies, both a small length of the electrode and a small distance from the counter electrode (see above) are desirable. This is in conflict with the requirement of uniform current distribution.⁴

Potential Measurement: Under the assumptions of the present study, potential gradients in the solution are in the order of 1000 volt/cm. Consequently a separation of electrode surface and reference electrode junction (capillary tip) of only 0.1 mm leads to an error of 10 volts. If a backside capillary arrangement is used, high potential gradients parallel to the electrode surface near the electrode-insulator boundary still lead to errors. Furthermore, due to fast dissolution of the anode, the wall of the capillary may soon protrude from the surface. It has to be concluded that direct steady state potential measurements under high current density conditions are not possible. Certain electrode geometries such as cylindrical or spherical arrangements allow reasonable

⁴ In this paragraph current distribution due to mass transfer is not considered. Near the limiting current, current distribution is no longer described by Laplace's equation alone, but local mass transfer values become determining (5).

estimates of ohmic contributions, but, in view of their large value, such a procedure does not recommend itself at very high current densities, particularly since the conductance may vary considerably near the electrode. A similar comment applies to a procedure where several reference electrodes are placed at various distances from the working electrode and the ohmic part of the measured potential values is eliminated by extrapolation to zero distance (11). When using a fast transient method, the geometrical position of the reference tip is less critical, but due to the high rate of charging and discharging processes, subtraction of ohmic contributions from the measured potential value becomes difficult.

Anode Positioning: Due to rapid dissolution, the anode has to be readjusted continuously during a measurement or the amount of dissolved material has to be kept small. Continuous electrode adjustment is used in commercial ECM machines. In the present study only small amounts of material were dissolved, thereby maintaining the plane parallel electrode configuration. The use of this method is possible because at high flow rates steady state mass transfer conditions are reached in a short time, as shown theoretically by Siver (12). Assuming a stagnant diffusion layer the thickness of which is determined by convection, the author finds that for an applied constant current density smaller than the limiting current a steady state is approached when

$$\frac{Dt}{\delta^2} \geq 2 \quad [8]$$

where D = diffusion coefficient, δ = diffusion layer thickness, t = time. Condition [8] corresponds well to results reported by Hale (13) who

numerically solved the unsteady state mass transfer equation, including convection terms for a rotating disk electrode. The average value of the thickness δ of the diffusion layer is related to the average Nusselt number Nu by

$$Nu = \frac{D_h}{\delta} \quad [9]$$

The value of δ to be used in Eq. [8] can therefore be estimated from known mass transfer relations, such as Eqs. [6] and [7].

If the applied current density is larger than the theoretical limiting current density,⁵ zero concentration of the reacting species at the electrode surface is reached after a transition time τ which is always smaller than the time t satisfying condition [8]. In the extreme case where the applied current density exceeds the limiting current density by at least a factor of 10, the transition time t may be predicted by the well known Sand equation (12).

The foregoing discussion demonstrates the impossibility of designing an experimental system satisfying all requirements. A compromise has to be made in each case, depending on the type of information desired. The use of fast transient measurements may be advisable in many instances, but not the same type of information is obtained as in steady state experiments. In the present study, an experimental arrangement was designed for steady state measurements in experiments of short duration.

⁵ In a dissolution process a limiting maximum concentration of reaction products might be reached at the electrode surface. Passivation might then set in after a transition time τ .

EXPERIMENTAL FLOW SYSTEM

An apparatus has been built which allows to perform electrochemical measurements under defined hydrodynamic conditions at linear flow rates along the electrodes of 1 to 25 m/sec. Figure 1 shows a diagram of the flow system. The electrolyte is pumped continuously through the electrochemical cell (C) by means of a regenerative turbine pump (T) made of "Hastelloy C."⁶ The maximum pressure at the cell inlet is approximately 150 psi, which results in a volume flow of 1.65 GPM through the cell. The flow rate through the cell (C) is measured by means of a magnetic flow meter (F)⁷ and regulated with two needle valves in connection with a bypass (Q). Stainless steel pipes are used throughout the system. An electrolyte reservoir (R) made of polyethylene typically contains 10 to 20 gallons of solution. The electrochemical cell is made of epoxy resin. It is shown in Figs. 2 and 3. The electrolyte flows in a rectangular channel (d) of 0.5 x 8 mm cross section and 120 mm length. Two glass windows (e) serve as side wall and allow optical observation of the interelectrode gap. They are held in place by two stainless steel plates (f). The cell is sealed by O-rings (C) embedded in the cell body. The flow channel contains a hydrodynamic entrance length of 77 hydraulic diameters, which serves to establish a fully developed velocity profile at the electrodes (2). Capillaries (b) are drilled into the cell wall near the two electrodes.

⁶Model 5SC2129 HC, Roy E. Roth Company, Rock Island, Illinois.

⁷Model 346 921516 with signal converter Model 460-1, Brooks Instrument Division, Hatfield, Pennsylvania.

They provide for potential measurements against a reference electrode. Calomel reference electrodes⁸ used in the present study were placed in a small glass container and connected to the capillaries by means of a short tygon tubing. The electrochemical cell is connected to the stainless steel piping system by means of an O-ring sealed flange at the entrance and a short piece of tubing at the exit. The electrodes are of rectangular shape, 0.53 by 3.17 mm (area = 1.67 mm²). They are cast into a cylindrical epoxy insert (a). The arrangement allows suppression of edge effects which might arise if there is a finite gap between metal and epoxy. The epoxy insert contains a flat shoulder, which allows the electrode surface to be easily positioned flush with the channel wall. The critical distance between shoulder and surface plane is obtained by mechanical grinding and polishing of the epoxy insert in a stainless steel holder of the desired dimensions. The electrode inserts are attached to the cell by means of three set screws, and sealed by means of an O-ring (c). The described arrangement allows easy and reproducible exchange of electrodes between experiments. During the metal dissolution experiments described here, the short dimension of the electrodes was oriented parallel to the flow direction. This way, temperature differences along the electrodes and the influence of catholically generated gas bubbles on the anode were kept to a minimum.

Mass transfer conditions corresponding to the described arrangement were estimated from the relations given in the previous paragraph. Estimated values of the average diffusion layer thickness (mass

⁸Fiber Junction Reference Electrodes, Beckman, Inc., Fullerton, Cal. 92634.

transfer entry region) ranged from 4×10^{-4} cm at a flow rate of 100 cm/sec to 8×10^{-5} cm at a flow rate of 2500 cm/sec.⁹

The electrical current was drawn from a constant current power supply¹⁰ having a maximum output of 3 amperes. At the start of an experiment the constant current was switched from a dummy circuit having negligible impedance to the cell circuit by means of a mercury wetted contact relay switch.¹¹ The relay was actuated by means of a pulse generator. It was switched back automatically after a preset time period by means of a flip flop circuit. The relay could be actuated manually if experimental times longer than two seconds were desired. Experiments usually lasted between 40 msec and a few seconds, depending on current density. A charge of 25 coulomb/cm² was passed which corresponds to an average dissolution of copper in the order of 10 μ . It was assumed that dissolution of such a small amount would not change the hydrodynamic conditions significantly. The experimental times were long enough, on the other hand, that a steady state could be reached during each run.

Anode and cathode potentials were measured against saturated calomel electrodes. The measured values which included large ohmic contributions were recorded simultaneously with overall cell voltage and current by means of a light beam oscillograph.¹² The oscillograph had a frequency response of 1000 cps. The input impedance of the preamplifiers was 100 k Ω . This value is low for precise potential measurements

⁹ It was assumed here that $D = 10^{-5}$ cm²/sec, $v = 10^{-2}$ cm/sec.

¹⁰ Type C 618 Electronics Measurements Company, Inc., Eatontown, New Jersey.

¹¹ Type HG 1003, C. P. Clare and Company, Chicago, Illinois.

¹² Series 2300, Brush Instr. Div., Cleveland, Ohio.

against reference electrodes. It was sufficient, however, for the present study where gross effects were measured only. Each experimental run was started with a freshly prepared anode. Anode preparation consisted of grinding the surface on 0000 emery paper and then polishing it mechanically on 1μ diamond powder, using conventional metallographic equipment. Residual scratches in the copper surface after the polishing operation were less than 0.3μ deep as determined from interference micrographs and from electronmicrographs of carbon replicas. The electrodes were cleaned with acetone and detergent. They were pre-electrolyzed cathodically at 100 mA/cm^2 for approximately 3 minutes in a solution of 1 N NaOH. After an experimental run, the anode was removed from the cell immediately. It was rinsed with distilled water and dried with acetone. The surface texture was then examined microscopically.

RESULTS

Current voltage relationships: Typical voltage transients observed in constant current dissolution experiments are shown in Figs. 4 and 5. Constant values of all measured voltages were reached within the time resolution limit of the oscillograph (2-5 milliseconds, depending on amplitude) under conditions corresponding to the experiment given in Fig. 4. The transient illustrated by Fig. 5 showed a step at a voltage value comparable to the steady state value of the experiment of Fig. 4, which was performed at the same current density of 50 A/cm^2 but at a higher flow rate in Fig. 5. A second voltage rise occurred after a few milliseconds. After reaching a peak value both anode

potential and cell voltage decayed slowly to a constant value lying in between the initial step value and the peak value. Irregular fluctuations were observed in this region. Experiments performed at different current densities and flow rates showed the decay time of the overshoot of the peak value to decrease with increasing flow rate and with increasing current density. Measured decay time in KNO_3 solutions varied from approximately 180 msec at a current density of 50 A/cm^2 and a flow rate of 100 cm/sec, to approximately 13 msec at 150 A/cm^2 and 2500 cm/sec. No systematic study of the phenomenon has been undertaken, however. After switching off the current, the measured voltage values decayed immediately to zero. A detailed study of this decay with time resolution in the micro-second range is in progress.

In all KNO_3 solutions studied, anode potential and cell voltage transients of the types shown in Figs. 4 and 5 were observed. Transients observed in sulfate solutions also showed the general behavior of Figs. 3 and 4, but the second voltage rise was about twice as high. In addition, they exhibited slow periodic fluctuations of many volts under certain conditions of current density and flow rate. Periodic fluctuations associated with passivation phenomena have been reported in the literature for experiments performed in stagnant solutions (10). No attempt has been made here to investigate the observed phenomena further.

The cathode potential trace in Fig. 5 shows a slight increase during the first few milliseconds, but a steady state is reached soon. Fast oscillations were observed at low flow rates and high currents.

The relation of these oscillations to characteristics of the cathodic gas evolution is currently being studied by stop motion photography.

Measured values of anode and cathode potential under different flow conditions during copper dissolution in 2 M KNO_3 are plotted versus current density in Fig. 6. The given values represent steady state values in the case of transients of the type shown in Fig. 4, or peak values in the case of transients of the type of Fig. 5. Because the measurements contain large ohmic contributions, the absolute potential values of Fig. 6 have no significance. Figure 6 illustrates, however, the fact that the occurrence of the steep rise in the anode potential depends strongly on both current density and electrolytic flow rate. Variations in the cathode potential are less pronounced. Most of the observed deviation from linearity is probably due to partial coverage of the cathode with gas bubbles and to changes in overall current distribution coincident with the drastic rise of the anode potential. It has been mentioned above that anode potential and cell voltage transients behave analogously. In Fig. 7 cell voltage measurements in different solutions are compared. All three solutions studied, namely 2 M KNO_3 , 0.4 M KNO_3 and 0.2 M K_2SO_4 , exhibited a similar current-voltage behavior. The voltage jump was larger in the sulfate solution and for given flow conditions it occurred at lower current densities.

Surface textures: Surface textures resulting from anodic dissolution were strongly dependent on the relative value of the applied current density, with respect to the current density corresponding to the voltage jump discussed above. Etching was observed in connection with voltage transients of the type of Fig. 4, pitting and brightening in connection with transients of the type of Fig. 5. Photomicrographs of

representative samples obtained in 2 M KNO_3 solution at a current density of 50 A/cm^2 at flow rates of 2500 and 400 cm/sec are given in Figs. 9 and 10, respectively. At the high flow rate, the local dissolution rate seems to depend on crystallographic parameters and the grain structure of the anode is clearly visible after dissolution.¹³ The surface appears dull, and steps and etch pits can be observed within each grain. Reduction of the electrolyte flow rate to 1000 cm/sec resulted in a similar surface structure with less microroughness. Figure 10 shows a surface obtained at 400 cm/sec (voltage transient of the type shown in Fig. 5). This surface appears bright and contains round pits which are located preferentially, although not exclusively, along grain boundaries. Further decrease of flow rate to 100 cm/sec resulted in a strongly pitted surface of considerable microroughness between pits. Surfaces obtained under identical conditions in 0.4 M KNO_3 solutions showed the same characteristics as those discussed. The appearance of the surfaces after dissolution in potassium sulfate solutions was less clear cut, although the same general pattern, i.e., etching and pitting was observed. It may be added that in all cases the transition from the dull to the bright surface finish could be accomplished by changing current density or flow rate. The study of surface textures under different experimental conditions suggested that the best surface appearance was obtained in the immediate vicinity of the voltage jump.

¹³The large grains visible on Fig. 9 appear highly distorted. this is due to the fact that the electrodes (99999 copper) were made from extruded wire. Chemical etching confirmed the distorted structure.

DISCUSSION OF RESULTS

Current cell voltage relationships: The behavior of measured anode potentials illustrated by Figs. 4 and 5 suggests that passivation phenomena occurred under certain conditions. Visual evidence obtained both in experiments performed in stagnant solution and under forced convection conditions indicated that passivation coincided with the formation on the anode of a thick layer consisting of loosely attached amorphous material. During dissolution in nitrate solution under forced convection, the anodic layer seemed to disappear in a few milliseconds after current was shut off. This was evidenced by studying potential transients by means of an oscilloscope, while two consecutive current pulses at various time intervals were applied to the cell. The anodes, after being taken out of the solution at the end of a dissolution experiment in nitrate solution, appeared bright and no solids were adhering to the metal.¹⁴ Electrodes examined after dissolution in sulfate solutions often were partly covered by anode films. No correlation between the pattern of film coverage and flow direction was observed in sulfate solutions. The composition of anodic films and the apparent valence of the dissolution process are being studied by Kinoshita (14). Distinct changes which coincide with the transition from active to passive dissolution have been observed.

It was mentioned above that exact values of the electrode potentials could not be measured with the present arrangement. There is

¹⁴ Some solid material adhering to the epoxy downstream from the anode was found occasionally.

evidence, however, born out by the results shown in Fig. 7, that the prevailing values of anode and cathode potentials were relatively low, compared to the voltage difference due to the ohmic resistance of the solution, as long as the experiment was performed at a current density smaller than the passivation current density, i.e., for experiments performed in the active dissolution region.

Cell voltages corresponding to steady state values during active dissolution yielded straight lines when plotted against current density, up to current density values of 50 to 150 A/cm² depending on the composition of the solution. Equivalent specific resistances ρ_i^* ¹⁵ were calculated by dividing the least square fit slopes of the straight lines by the electrode width. The ratios of the values obtained for different solutions were then compared to the ratios of the specific resistances of these solutions. A close correspondence between experimental and theoretical ratios has been observed: Experimental values obtained were $\rho_1^* = 4.37\Omega\text{cm}$, (2M KNO₃), $\rho_2^* = 17.7\Omega\text{cm}$ (0.4M KNO₃), $\rho_3^* = 19.5\Omega\text{cm}$ (0.2M K₂SO₄). Literature values for the specific resistance at 25°C are $\rho_1 = 6.31\Omega\text{cm}$ (2M KNO₃) (27), $\rho_2 = 24.14\Omega\text{cm}$ (0.4M KNO₃) (28), $\rho_3 = 24.70\Omega\text{cm}$ (0.2M K₂SO₄) (28). Corresponding ratios then become $\rho_2^*/\rho_1^* = 4.05$, $\rho_2/\rho_1 = 3.83$, $\rho_3^*/\rho_1^* = 4.46$, $\rho_3/\rho_1 = 3.91$.

Linear current-voltage relationships dominated entirely by the ohmic resistance of the solution have been reported in the literature for conditions corresponding to ECM (21, 22). Cole and Hopfield (26) explained observed deviations from linear current voltage behavior by

¹⁵ The effective specific resistance ρ_i^* is always smaller than ρ_i because the actual cross section of the flux in the solution is larger than the electrode area.

a model which considered the influence of cathodically generated gas bubbles on the ohmic resistance of the solution. Attempts aimed at measuring actual anode potentials during anodic dissolution under ECM conditions have been reported (21,22), but no reliable results were obtained.

The current-voltage curves given above demonstrate that passivation may lead to an increase in the anode potential of many volts. In this case, the ohmic resistance of the bulk solution can no longer be considered the only important resistance of the system. Local current distribution may, therefore, change significantly at the transition point between active and transpassive dissolution.

Passivation has been mentioned (25) as playing a role in improving dimensional accuracy during ECM, but the statement was based mainly on observations made at low current densities. The present investigation confirms that passivation phenomena play a decisive role in determining local metal dissolution rates under ECM conditions.

The results given in Figs. 6 and 7 demonstrate that the onset of passivation is determined by flow rate and current density. The results strongly indicate that, in the systems investigated here, the onset of passivation is controlled by mass transfer. The fact that in both nitrate solutions studied (Fig. 7) passivation occurred in the same range of current density suggests that the transport of anions was not a controlling factor. An anion limited dissolution mechanism is expected if a net consumption of anions at the anode occurs, e.g., by complex formation of dissolved metal ions. Such a mechanism has been reported for the dissolution of gold in chloride solutions (33) and a

similar but more complex case is represented by the dissolution of copper in chloride solution, where under some conditions formation of stable cuprous chloride complexes is possible (30,33). If non-complexed metal ions are produced during the dissolution process, accumulation of anions in the vicinity of the anode is necessary in order to maintain electroneutrality.

At a high dissolution rate, the product of the metal ion concentration and anion concentration may exceed the solubility product. This may lead to precipitation of salt crystals. Initiation of passivity by salt precipitation has been described by W. J. Muller (31). A critical review of more recent literature dealing with the phenomena has been given by T.R. Hoar (32). The fact that, in our experiments, the onset of passivity was independent of concentration in nitrate solutions, but occurred at lower current densities in the sulfate solution, is qualitatively consistent with the above mechanism, since copper sulfate has a lower solubility than copper nitrate.

A semiquantitative test of the theory is illustrated by the results of Fig. 8, in which Nusselt numbers derived from the experimentally observed passivation current densities were compared with those predicted from the known mass transfer relations [3] and [9]. A band of possible values of the passivation current density i_p was estimated from Fig. 7. Nusselt numbers corresponding to these values were calculated by assuming a concentration driving force corresponding to the saturation concentration c_s of copper nitrate and copper sulfate, respectively. The experimental Nusselt number is then given by

$$Nu_p = \frac{i_p D}{2Fc_s D}. \quad (10)$$

The value of D was assumed to be 10^{-5} cm²/sec. It has to be regarded as an order of magnitude estimate of an effective diffusion coefficient of copper ion including the influence of migration and of possible changes in physical properties in the vicinity of the anode. Values for the saturation concentration c_s were estimated from solubility data given in (15) and (16) to be 7 mole/liter for copper nitrate and 1.5 mole/liter for copper sulfate (25°). The influence of the presence of potassium ions on the value of c_s was neglected, since due to migration, their concentration at the interface is much smaller than that of copper ions. A reasonable order of magnitude agreement between experimental and predicted passivation current densities was obtained (Fig. 8). The observed agreement indicates that in the systems studied here, the application of a model which considers maximum possible mass transfer rates of dissolution products leads to valid predictions of the conditions, which correspond to the onset of passivation.

Surface textures: The results reported in the previous section indicated that the surface texture resulting from anodic dissolution depended strongly on whether dissolution occurred in the active or transpassive mode. As to which dissolution mode prevailed at a given current density depended on mass transfer conditions. The findings of the present investigation are thus comparable to results reported in recent studies about the conditions leading to electropolishing (17, 18, 19, 20). While the detailed mechanism leading to polishing is disputed, it is well established now that passivation

phenomena play a dominant role. The current density leading to passivation (sometimes referred to as limiting current density in the literature) is determined by mass transfer. Obtaining polished surfaces during ECM has been reported by various authors (21, 22, 23). The fact that, under appropriate operating conditions, a very low surface roughness can be obtained allows the application of ECM to technical surface finishing operations (24). No current potential curves indicating passivation have been reported so far for conditions corresponding to ECM. In view of the results obtained in the present study and of some findings reported in the literature (25, 29), it seems very probable that passivation phenomena play an important role in practical ECM, not only with respect to dimensional accuracy (see above) but also with respect to obtainable surface finish. The present study confirms and extends a general observation (20) valid for metal dissolution at conventional current densities, that active dissolution leads to etched surfaces while transpassive dissolution often results in anodic brightening, pitting or polishing.

Many questions remain unanswered by the present study such as, e.g. why pitting is observed at all under the present experimental conditions which would seem highly unfavorable for dissolution within pits, not only from a point of view of local current distribution, but also from a point of view of mass transfer. The role of the metallurgical factors in determining how etching and pitting proceed or the influence of the chemical composition of the electrolyte on the nature of anodic films formed are other areas which need more research. A study of the dissolution of copper single crystals under conditions comparable to those of the present study has recently been initiated at this laboratory.

CONCLUSIONS

The present work demonstrates the feasibility of studying an electrochemical process proceeding at a current density of many amperes per square centimeter under controlled hydrodynamic conditions. A rectangular flow channel cell operated under fully developed turbulent flow conditions has been found to be well suited for this investigation. Steady state mass transfer rates corresponding to an equivalent diffusion layer thickness of the order of 10^{-4} cm have been realized.

A study of copper dissolution in KNO_3 and K_2SO_4 solutions has shown two distinct dissolution modes. Active dissolution resulting in etched surfaces occurred at relatively low overpotentials. Observed dissolution rates were well within the limits estimated from known mass transfer relations for the transport of cupric ions away from the surface. Transpassive dissolution proceeded at higher anode potentials, leading to pitting and brightening. Current densities applied during transpassive dissolution were up to ten times higher than the minimum current density leading to passivation; the latter is believed to correspond to the highest rate at which cupric ions may be removed from the anode by convective diffusion. It appears therefore, that a large part of the oxidized copper was transported away from the anode in the form of solid dissolution products formed at or near the anode. It is probable that a similar transport mechanism is involved in many practical ECM operations.

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FIGURE CAPTIONS

Figure 1. Flow apparatus for high current density metal dissolution studies. C = flow channel cell, T = regenerative turbine pump, R = storage tank, F = magnetic flow meter, M = pressure gauge, Q = bypass to flow regulation through cell, N = needle valve, B = ball valve, I = deionized water for cleaning, Z, D = drain.

Figure 2. Experimental cell for metal dissolution studies at high current densities.

a = copper electrodes cast into epoxy resin
b = backside capillary for potential measurements
c = O-ring seal
d = flow channel
e = glass side wall
f = stainless steel plate
g = flange for connection to stainless steel piping system
h = bolts
k = teflon insert

Figure 3. Cross section of experimental cell. Captions - see Figure 2.

Figure 4. Oscillograph trace typical for active dissolution region.

(1) = current
(2) = cell voltage
(3) = anode potential
(4) = cathode potential

Figure 5. Oscillograph trace typical for transpassive dissolution region.

(1) = current
(2) = cell voltage
(3) = anode potential
(4) = cathode potential

Figure 6. Measured potential values during copper dissolution in 2 N KNO_3 at various flow rates.

———— anode potential

----- cathode potential

electrolyte flow rates 100 cm/sec; 400 cm/sec;
1000 cm/sec; 2500 cm/sec.

Figure 7. Current cell voltage relationships during copper dissolution in nitrate and sulfate solutions

———— least square fit of values for active dissolution and initial step values for transpassive dissolution for all flow rates.

— — — — 2 M KNO_3 passive

----- 0.4 M KNO_3 passive

———•—— 0.2 M K_2SO_4 passive

Passivation: electrolyte flow rate $\diamond = 100/\text{sec}$;

$\square = 400 \text{ cm/sec}$, $\triangle = 1000 \text{ cm/sec}$, $\bigcirc = 2500 \text{ cm/sec}$.

Figure 8. Semiquantitative tests of theory predicting onset of passivation by salt precipitation. Curve - theoretical prediction of limiting mass transfer rate by equations [3] and [7]. Vertical ranges onset of passivity as determined from experiments illustrated in Fig. 7, solid lines - KNO_3 solution, broken lines, K_2SO_4 solution.

Figure 9. Etched surface texture after dissolution of 99999 copper in the "active" state (2 M KNO_3 , 50 A/cm^2 , 2500 cm/sec .)

Figure 10 Polished and pitted surface texture after dissolution of 99999 copper in the "passive" state (2 M KNO_3 , 50 A/cm^2 , 400 cm/sec .)

XBL 681-1568A

Fig. 1

Fig. 2

XBL688-3499

XBL688-3498

Fig. 3

XBL688-3502

Fig. 4

XBL688-3503

Fig. 5

X00. 081-1507A

Fig. 6

XBL688-3500

Fig. 7

XBL688-3501

Fig. 8

XBB 682-589-A

Fig. 9

XBB 681-208-A

Fig. 10

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