Application of the Rotating Cylinder Hull Cell To the Measurement of Throwing Power and The Monitoring of Copper Plating Baths

By C. Madore, D. Landolt, C. Haßenpflug and J.A. Hermann

The Rotating Cylinder Hull (RCH) cell consists of a rotating cylindrical cathode having non-uniform primary current distribution. It permits Hull-cell-type experiments under uniform and well-controlled mass-transport conditions. This study presents practical applications of the RCH cell in copper plating. The RCH cell is employed for measuring the throwing power of a copper pyrophosphate electrolyte as a function of bath composition and electrode rotation rate. Measured data are compared to theoretical simulations of current distribution. Because it permits high mass transport rates, the RCH cell is shown to be well suited for study of the effect of additives and impurities present in small concentrations. Measurements carried out with typical industrial bath compositions confirmed that the RCH cell can be advantageously used for monitoring the performance of industrial plating baths.

The classical Hull cell[1] is a trapezoidal structure in which the cathode is placed at an oblique angle with respect to the anode. The Hull cell allows exploration of the variations in the appearance of an electrodeposit over a wide range of current densities along the cathode surface to determine optimal electroplating conditions. It is being used for the development of plating electrolytes and for monitoring the operation of industrial plating baths.

A shortcoming of the classical Hull cell is that mass transport conditions are poorly controlled. It is normally operated under free convection conditions, but in some cases, solution agitation is provided by gas bubbling near the cathode, by a magnetic stirrer or a reciprocating paddle.

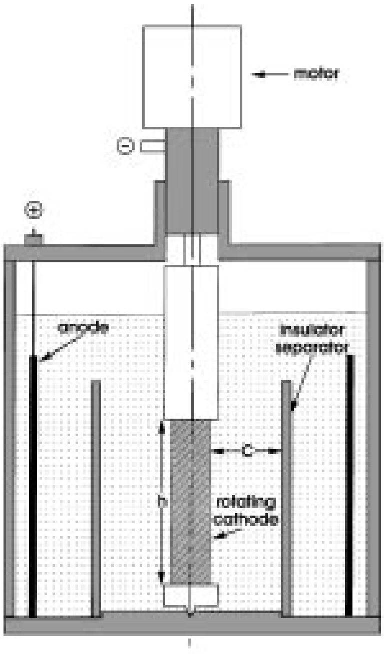

Fig. 1—Schematic of the RCH cell.

For many plating processes, mass transport is a crucial step, for example, in the presence of leveling agents and impurities, or in alloy plating, when one of the components is present in small concentrations. In such cases, the interpretation of a Hull cell plate does not yield sufficient information and experiments performed under well-controlled mass transport conditions are needed.

Recently, a new type of Hull cell, the Rotating Cylinder Hull (RCH) cell, has been developed.[2-4] This cell is well suited for the study of plating processes involving critical mass-transport steps. The RCH cell has a primary current distribution similar to that of the traditional Hull cell, but in addition, well-defined and uniform mass-transfer conditions are achieved by using a rotating cylindrical cathode. In this study, the practical usefulness of the RCH cell for bath control under industrial conditions was evaluated. On the one hand, the RCH cell is used to determine the throwing power of a copper pyrophosphate electroplating bath under different convection conditions. On the other, application of the RCH cell for monitoring additive efficiency and for investigating electrolyte sensitivity to metallic contaminants is being studied.

Description

A schematic of the RCH cell used in this study is shown in Fig. 1. The cylindrical cell, made of Plexiglas™, is 135 mm in height and 120 mm in diameter and contains one liter of electrolyte. The motor shaft and the rotating cylinder assembly are held by a Teflon™ guide attached to the top endplate. The cathode is a hollow metal cylinder 6 cm in length and 1.5 cm diameter, with a surface area of 28.3 cm^2, immersed to a depth of about 4 cm. The cathode surface is recessed by 0.25 cm with respect to the insulating sleeves to prevent the current density at the near edge going to infinity.[2] A cylindrical Plexiglas™ separator, 85 mm high and 55 mm inner diameter, is fixed concentrically with the rotating cylinder at the bottom endplate. Its top is located one cm above the upper edge of the cathode. The cylindrical anode is placed outside the insulating separator. All the current between anode and cathode flows through the open space at the top of the separator. The current density, therefore, is maximum at the top end of the cathode and diminishes continuously toward its lower end. The motor controls the cylinder rotation speed between 0 and 4000 rpm. The

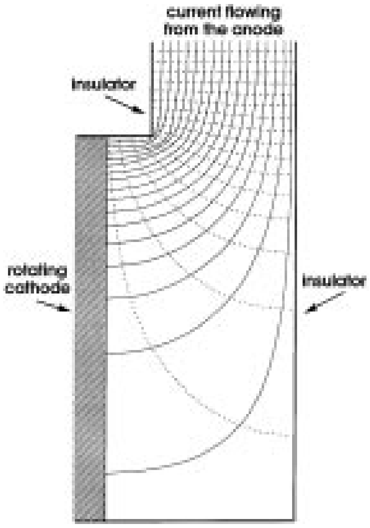

Fig. 2—Equipotential (dotted) and equiflux (solid) lines between the rotating cathode and the insulating separator. Current density is maximum at upper end of cathode.

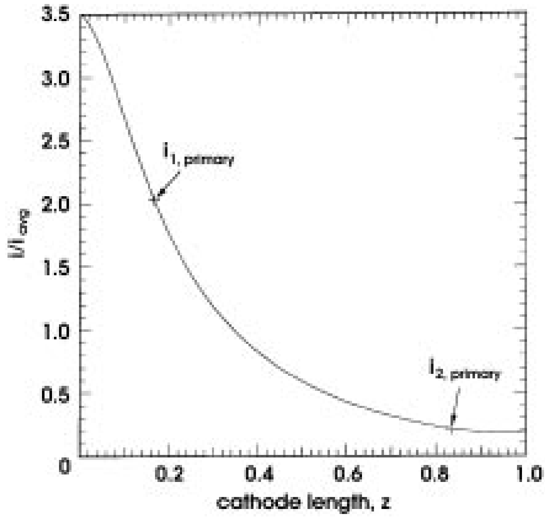

Fig. 3—Primary current distribution along the cathode of the RCH cell.

electrical contact between the rotating electrode and the current source is provided by a silver friction contact. A more detailed description of the RCH cell used in this study has been given elsewhere.[4]

Current Distribution

Current distribution in electrochemical cells depends on cell geometry, electrolyte conductivity, the reaction kinetics at the cathode and mass-transport conditions. The relative importance of these factors depends on process conditions. The so-called primary current distribution applies when electrode kinetics are fast. Current distribution in that case depends only on the cell geometry and is the least uniform. The primary current distribution can be theoretically calculated by solving Laplace's equation for a given cell geometry, assuming a constant potential along the two electrodes.

In the RCH cell, the primary current distribution depends mostly on the ratio of the cathode height *h* to the distance between the cathode and the insulating separator *c*.[2] With a ratio *h/c* = 3, the geometry can be optimized to obtain a primary current distribution similar to that of the classical Hull cell. A schematic of the equipotential and flux lines between the insulating separator and the cathode obtained by solving Laplace's equation is shown in Fig. 2. The primary current distribution along the cathode length is shown in Fig. 3. The numerically calculated curve can be described by the analytical expression (1) proposed previously.[2]

$$\frac{i(z)}{i_{avg}} = \frac{0.535 - 0.458z}{(0.0233 + z^2)^{1/2}} + 8.52{*}10^{-5} \exp(7.17z) \qquad (1)$$

where *z* is the dimensionless distance along the cathode from the lowest current density side, i_z the local current density and i_{avg} the average current density.

When charge transfer kinetics are of importance, secondary current distribution conditions apply. In this case, current distribution on the cathode can be calculated by replacing the constant potential boundary condition by a kinetic expression relating the potential in the solution to that in the metal. For many plating processes, Eq. (2) adequately describes the electrode kinetics.

Table 1
Kinetic and Mass-Transport Parameters For Pyrophosphate & Sulfate Electrolytes

	κ(S/cm)	**ß$_c$(mV)**	**i$_{lim}$(mA/cm^2)**
Pyrophosphate	0.18[a]	116[b]	93[c]
Sulfate	0.26[d]	45[d]	395[d]

[a] From Ref. 6; [b] from Ref. 7; [c] 600 rpm [d] from Ref. 3

$$i = -i_o \exp\left(\frac{-V}{ß_c}\right) \qquad (2)$$

where i_0 is the exchange current density, V the overvoltage and $ß_c$ the cathodic Tafel coefficient. The secondary current distribution is always more uniform than the primary current distribution. The relative importance of kinetics for the current distribution can be characterized by the Wagner number, which represents the ratio of the polarization resistance at the electrode surface to the ohmic resistance of the electrolyte. For Tafel kinetics, the Wagner number is

$$Wa = \frac{dV/di}{\rho_e L} = \frac{ß_c \kappa}{i_{avg} L} \qquad (3)$$

where ρ_e is the electrolyte resistance, κ is the electrolyte conductivity and *L* is a characteristic length. In the present RCH cell, the length *L* corresponds to the height of the cylinder and has a value of 6 cm.

When concentration gradients are important, tertiary current distribution conditions prevail. For the calculation of tertiary current distribution, the boundary conditions (2) may be replaced by Eq. (4).

$$i = -i_o \left(\frac{C_s}{C_b}\right) \exp\left(\frac{-V}{ß_c}\right) \qquad (4)$$

The ratio C_s/C_b expresses the decrease of reactant concentration at the cathode surface as a result of mass-transport limitations. Equation (4) can be written more conveniently in terms of the measurable quantity i_{lim}, the limiting current density of the reacting species.

$$i = -i_o \left(1 - \frac{i}{i_{lim}}\right) \exp\left(\frac{-V}{ß_c}\right) \qquad (5)$$

For a rotating cylinder electrode, the value of i_{lim} can be calculated by Eq. (6), after Eisenberg, Tobias and Wilke.[5]

$$i_{lim} = 0.0791nFCU^{0.7}d^{-0.3}\nu^{-0.344}D^{0.644} \qquad (6)$$

where *n* is the charge transfer number, *F* is the Faraday constant, *d* is the cylinder diameter (cm), *U* is the peripheral velocity at the rotating cylinder (cm/sec), *ν* is the kinematic viscosity of the electrolyte (cm^2/sec) and *D* is the diffusion coefficient (cm^2/sec). The tertiary current distribution in the RCH cell depends on the value of the Wagner number and the ratio $i/_{lim}$. For a ratio $i/_{lim} = 1$, the current distribution is uniform and controlled entirely by mass transport.

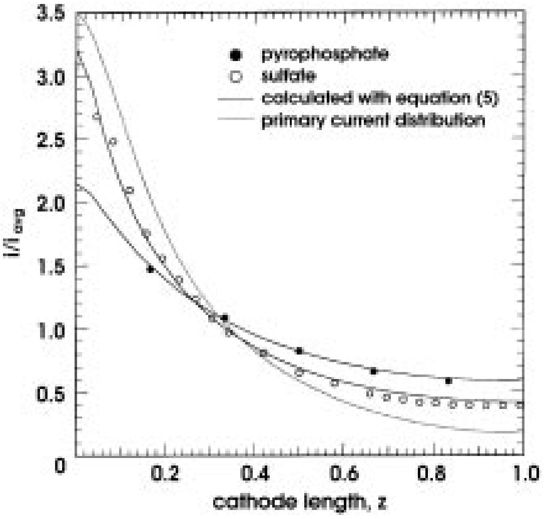

Fig. 4—Measured and calculated current distributions along the cylindrical cathode for pyrophosphate and sulfate electrolytes.

Determination of Throwing Power

The throwing power of a plating electrolyte characterizes the uniformity of the thickness of the deposited metal. More specifically, the actual thickness of an electrodeposit obtained at different distances from the counter-electrode is compared to that expected theoretically for negligible electrode polarization and 100 percent current efficiency. Most often, the throwing power is measured in the Haring-Blum cell, which consists of a central anode and two equipotential cathodes at unequal distances r_1 and r_2. For a distance ratio of $R = r_1/r_2$ and a measured deposit thickness ratio (or mass ratio) of $M = m_1/m_2$, the throwing power (TP) can be calculated from equation (7):

$$\mathrm{TP} = \frac{\mathrm{R} - \mathrm{M}}{\mathrm{R} - 1}\ 100\ (\%) \tag{7}$$

Because of its non-uniform current distribution, the RCH cell can be used for determination of throwing power in a way similar to that of the Haring-Blum cell. Contrary to the latter, the RCH cell allows one to evaluate the effect of mass transport on throwing power. To determine throwing power with the RCH cell, deposit thickness is measured at two predetermined locations on the cylinder cathode, differing in local current density, and corresponding to the distances r_1 and r_2 from the upper edge. From the thickness measurements, the ratio M is calculated. For the RCH cell, the ratio R, appearing in Eq. (7), corresponds to the current density ratio computed for primary current distribution: $R = i_{1,primary}/i_{2,primary}$. The local current densities $i_{1,\,primary}$ and $i_{2,\,primary}$ are taken at distances r_1 and r_2, respectively. They can be read from Fig. 3 or evaluated from Eq. (1).

In this study, all deposits used for the determination of throwing power were measured at a distance of one cm from the upper and lower ends of the cathode. The value of R, therefore, is:

$$\mathrm{R} = \mathrm{i}_{1,\,\mathrm{primary}}/\mathrm{i}_{2,\,\mathrm{primary}} = 9.5 \tag{8}$$

By measuring the thickness at one cm from the end, possible edge effects are avoided. The throwing power corresponding to the described procedure for the RCH cell used is given by Eq. (9).

$$\mathrm{TP} = 111.8 - 11.8\ \mathrm{M}\ \ (\%) \tag{9}$$

For a uniform deposit thickness (representing the limiting case for secondary or tertiary current distribution, respectively) $M = 1$ and $TP = 100$ percent. On the other hand, for negligible electrode polarization (primary current distribution) at constant current efficiency, $M = R$ and $TP = 0$ percent. It may be noted that although the two limiting values of throwing power are the same as in the Haring-Blum cell, the numerical values for intermediate conditions depend on the distances chosen for r_1 and r_2 and, therefore, are usually not the same. For this reason, only throwing power values obtained under identical geometrical conditions can be compared quantitatively. In this study, all throwing power values were calculated by Eq. (9) and refer to the same geometrical conditions.

Current Distribution and Throwing Power

Copper pyrophosphate electroplating baths are widely used in industrial applications where good throwing power, tensile strength, and ductility are important, such as electroforming and the plating of through-hole interconnections in high-reliability circuit boards. The properties of electrodeposits plated from pyrophosphate baths are sensitive to mass-transport conditions prevailing during deposition, and experimental studies, therefore, should be performed under well-defined hydrodynamic conditions. In a first series of experiments, the current distribution on the RCH cathode and the corresponding throwing power were determined for an industrial copper pyrophosphate electrolyte. For comparison, a copper sulfate electrolyte was also studied. The electrolytes contained no leveling agent. The pyrophosphate electrolyte had the following composition:

copper, Cu^{+2}	20g/L
pyrophosphate, $(P_2O_7)^{-4}$	160 g/L
additive A	5 mL
pH	8.3
temperature	40 °C

The composition of the sulfate electrolyte was:

copper, Cu^{+2}	32 g/L
sulfuric acid (96%)	50 mL
temperature	25 °C

In both cases, copper was deposited galvanostatically at an average current density of 20 mA/cm^2. The cylinder rotation rate was 600 rpm for the pyrophosphate electrolyte and 1250 rpm for the sulfate electrolyte. To avoid any effect of aging, all experiments were carried out with freshly prepared electrolytes. The metal thickness distribution along the rotating cylinder was measured by X-ray fluorescence.[3]

In Fig. 4, the experimentally measured and theoretically calculated current distributions along the cylinder cathode are shown for the pyrophosphate and sulfate electrolytes. Also given is the curve for primary current distribution, corresponding to Eq. (1). To calculate the current distribution of the pyrophosphate and sulfate electrolytes, the kinetic parameters listed in Table 1 were used.

The data of Fig. 4 show good agreement between calculated and measured current distributions for both electrolytes. The pyrophosphate electrolyte has a more uniform current distribution than the sulfate electrolyte and, there-

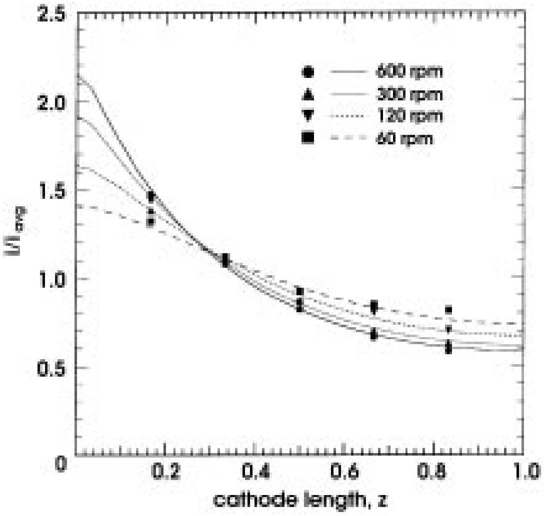

Fig. 5—Measured and calculated current distributions along the cylindrical cathode for the pyrophosphate electrolyte without leveling agent.

fore, should have a higher throwing power. The throwing power values, calculated with Eq. (9) are 82 and 72 percent, respectively, for the two experiments in qualitative agreement with expectation. The better throwing power of the pyrophosphate electrolyte can be explained by slower deposition kinetics (higher value of β_c) and a smaller limiting current. This is consistent with the fact that the Wagner number and the limiting current ratio differ between the two electrolytes. Wa = 0.2, i_{lim} = 0.21 for pyrophosphate and Wa = 0.1, i_{lim} = 0.05 for sulfate. The data of Fig. 4 confirm that the throwing power measured in the RCH cell can be used in practice as a measure of the uniformity of current distribution.

Application to Electrolyte Optimization

The influence of different operating parameters, such as agitation, bath composition, pH and temperature on the throwing power of an industrial pyrophosphate electrolyte was studied. A series of measurements was aimed at investigation of the effect of agitation. For this, the cylinder rotation rate was varied from 60 to 600 rpm, corresponding to a linear velocity of the cathode surface, with respect to the electrolyte, of 2.8 to 28.3 m/min, respectively. An average current density of 20 mA/cm^2 was applied in all experiments. The measured and calculated current distributions are given in Fig. 5. The results indicate a marked effect of rotation rate on current distribution, the latter becoming more uniform as the rotation rate is decreased, because of closer approach to the limiting current. The least uniform current distribution at 600 rpm yields a throwing power of 82 percent, while at 60 rpm a throwing power of as high as 93 percent is observed. Unfortunately, at low rotation rates, the deposit quality was not good. Indeed, it is a well-known fact that electrodeposition at current densities close to the limiting current density can lead to rough and dendritic deposits.

To compare experimental and theoretical current distributions, limiting current densities were estimated by measuring polarization curves on a rotating disk electrode and fitting them to Eq. (5). From the data, the corresponding limiting current densities for the cylindrical electrode were calculated, taking into account the different hydrodynamic conditions. The values thus obtained are listed in Table 2. They were used for the numerical calculation of the theoretical curves of Fig. 5, corresponding to tertiary current distribution. Also indicated in Table 2 are the throwing power values determined from the experimental measurements and from the theoretical curves. The good agreement between measured and calculated throwing power indicates that the model used describes well the influence of mass transport on current distribution, despite the fact that the actual reaction mechanism of copper deposition from pyrophosphate may involve several steps.[8]

In another series of experiments, the effect of electrolyte composition on throwing power was studied. An average current density of 20 mA/cm^2 and a constant rotation rate of 600 rpm were applied throughout. At first, the influence of a leveling agent was studied, using concentrations of 2.5 and 7.5 mL/L. This yielded throwing power values of 72 and 67 percent, respectively, that are smaller than the value of 82 percent, measured without a leveling agent. The less uniform current distribution in the leveling agent-containing electrolyte indicates that copper deposition was relatively more inhibited by the leveling agent at low current densities than at high current densities, where the flux of leveling agent becomes mass-transport controlled. The particular leveling agent used apparently has a negative effect on the throwing power on a macroscopic scale, although it improves the smoothness of deposits on a microscopic scale.

An increase of the pyrophosphate concentration from 140 to 180 g/L was found to lead to an improvement of the throwing power from 68 to 86 percent. This can be explained by assuming that a high pyrophosphate concentration favors copper complex formation, slowing the deposition rate and leading to a higher Wagner number. An increase or a decrease in the Additive A concentration from its usual concentration of 5 mL/L lowered the throwing power slightly. It was observed, however, that the additive used has a minor influence on the throwing power in comparison with the effect of

Table 2
Limiting Current Densities, Ratio i_{lim} & Throwing Power for Pyrophosphate Electrolyte

Rotation rpm	i_{lim} mA/cm^2	i/i_{lim}	Throwing power % theoretical	Throwing power % experiment
600	93	0.21	82	82
300	59	0.34	85	86
120	40	0.50	88	88
60	31	0.65	92	93

Table 3

Component	Electrolyte A TP 72%	Electrolyte B TP 64%	Electrolyte C TP 91%
Cu (g/L)	20	20	20
Pyrophosphate (g/L)	160	140	180
Additive A (mL/L)	5	5	2
Leveling agent (mL/L)	2.5	7.5	2.5
pH	8.3	8.8	7.8

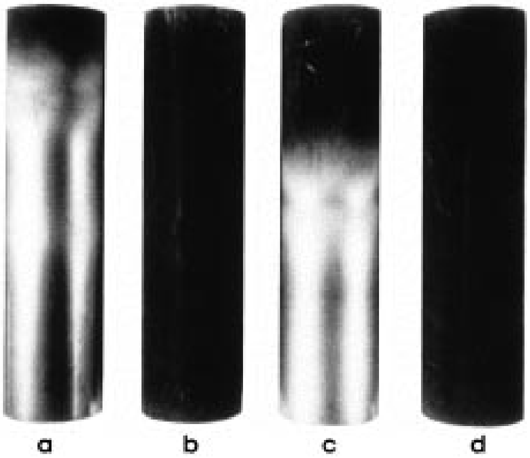

Fig. 6—Rotating cylinder Hull cell tests for copper deposited from the pyrophosphate electrolyte (I) containing metallic impurities. Deposition conditions: (a) 20 mA/cm², 600 rpm; (b) 20 mA/cm², 60 rpm; (c) 40 mA/cm², 600 rpm; (d) 40 mA/cm², 60 rpm.

the leveling agent and of the pyrophosphate content. An increase in pH from 8.3 to 8.8 caused the throwing power to decrease from 82 to 60 percent, while an increase of the temperature from 40 to 60 °C changed the throwing power from 72 to 63 percent.

The different results show that the throwing power of the industrial copper pyrophosphate electrolyte studied is influenced by the cylinder rotation rate and, in diminishing order, the pH, the pyrophosphate concentration, the leveling agent concentration and the temperature. The different data could be used to improve the throwing power of the original electrolyte from 72 to 91 percent. The influence of electrolyte composition on throwing power for three typical electrolyte compositions is shown in Table 3.

Application to Bath Control

Control of additive concentration and efficiency in industrial plating baths is of great importance for maintaining satisfactory deposit quality. Additives that include leveling and brightening agents are usually added to the electrolyte at very low concentration. Because their effectiveness is influenced by mass transport, the RCH cell is a promising tool for monitoring additives.

The data of the previous section suggest that throwing power is not a sufficiently sensitive measure of additive effectiveness. A better control of the efficiency of additives is obtained by optical observation of the deposit. Indeed, because well-controlled, uniform mass-transport conditions prevail in the RCH cell, deposit appearance along the length of the cathode at different rotation rates is generally very reproducible and sensitive to additives. This is in contrast with the conventional Hull cell, where it is sometimes difficult to assign the appearance of the deposit to specific operating conditions. In the RCH cell, on the other hand, the degree of brightness of the deposit can be easily correlated with additive concentration, current density and electrolyte agitation. For example, with the industrial pyrophosphate electrolyte used in this study, a significant decrease in deposit brightness was observed after an active charcoal treatment for decreasing the leveling agent concentration. Similarly, the RCH cell can be used for monitoring the effect of contaminants. Indeed, copper pyrophosphate electrolytes are very sensitive to contaminants, such as cyanide, chloride, oil and low concentrations of ions of lead, zinc, iron, nickel, etc. In the conventional Hull cell, the effect of contaminants present at low concentrations is often difficult to detect. To investigate the potential usefulness of the RCH cell for observing the presence of contaminants at concentrations in the range of 50–100 ppm, copper was electrodeposited from industrial pyrophosphate electrolytes containing different metallic impurities, as shown in Table 4.

Table 4

Electrolyte ppm	I	II	III
Pb	886	88.4	36.9
Zn	125	-	9
Fe	24.2	167	13.8
Ni	13	20	14.7
Au	-	6.9	8.2
Cl^-	-	-	55

In practice, the work pieces plated with electrolyte (I) showed gray/black deposits on parts exposed to relatively high current densities. Verification in the RCH cell yielded a deep black, amorphous deposit over the whole length of the cylinder at a rotation speed of 60 rpm, but a bright deposit on the low-current-density side of the cathode at a rotation speed of 600 rpm (Fig. 6). Treatment of the electrolyte with activated charcoal produced no improvement in appearance, suggesting that the poor morphology is indeed caused by the metallic impurities, not by the leveling agent.

Electrolyte (II) is a bright copper electrolyte containing additives. The rotating cylinder cathode showed a bright, dark-red deposit at 600 rpm. Treatment with activated charcoal to reduce the leveling agent content yielded a matte deposit over the whole cylinder. Subsequent addition of the leveling agent restored a bright deposit. In this case, sufficient leveling agent yields bright deposits even in the presence of impurities.

The third electrolyte tested (III) was a leveling-agent-free bath with very low concentration of metallic impurities. An experiment with the conventional Hull cell was unsuccessful in revealing any effect as a result of their presence in the electrolyte. In the RCH cell at 600 rpm, however, a dark deposit on the high-current-density side of the cathode was observed. The reaction rate of impurities present at low concentration are fully controlled by mass transport. Because of a high mass-transport rate, the RCH cell apparently can detect small concentrations of impurities before they become a problem in the industrial plating cell.

Conclusions

This study has shown that the recently developed RCH cell, which has a highly non-uniform primary current distribution and well-controlled uniform mass-transport rates, is a useful tool for optimizing and maintaining industrial plating electrolytes. By comparing theoretically calculated secondary and tertiary current distributions for copper deposition from a pyrophosphate electrolyte with experimental measurements, the theoretical basis of throwing power measurements with the RCH cell has been proposed. It follows that the RCH cell is well-suited for determination of the throwing power of plating electrolytes under controlled hydrodynamic conditions. Using a pyrophosphate electrolyte as example, the importance of mass-transport effects for throwing power was demonstrated. Experiments with commercial additives and leveling agents yielded evidence for the sensitivity of RCH cell tests to the presence of such substances in small concentrations. Because of a high mass-transport rate, RCH cell tests have been found useful for monitoring the effect of small amounts of metallic impurities in industrial plating baths.

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