JOURNAL OF APPLIED ELECTROCHEMISTRY 3 (1973) 113–121

Prediction of metal distribution in electroplating systems

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Received 6 September 1972

Three methods of approximation were developed to predict the metal distribution in electroplating systems. The results were compared with Watson's experimental data for the Watts-nickel (close to 100% current efficiency), tin-nickel (alloy deposition, also close to 100% current efficiency), and the standard chromium (approximately 20% current efficiency) systems. Method 1 predicted too uniform a distribution whereas Methods 2 and 3 showed good agreements with all three systems.

The same experimental data were also used to evaluate three predictive methods frequently used in the literature. The primary current distribution and an empirical formula by Hull were found to be inadequate in describing these systems. The secondary current distribution which involved a great deal of numerical analysis showed a considerable improvement.

Key to Symbols Used in Text

a	A Tafel parameter.
b	Tafel slope.
d	Length of cathode in a Hull cell.
E	Current efficiency of the metal deposition reaction.
F	Faraday's constant.
f_1	A weighting factor for overpotential effects.
f_2	A weighting factor for ohmic effects.
I	Total applied current in a Hull cell.
i	Current density.
i_{avg}	Average current density.
i_{H}	Current density calculated by Hull's empirical formula.
i_{P}	Primary current density.
i_{S}	Secondary current density.
i_{t}	Total applied current density.
i_1,i_2,i_3	Current densities calculated by Methods 1, 2 and 3.
L	A characteristic length.
l	Length of the local current stream line.
l_{avg}	Average distance between cathode and anode in a Hull cell.
l_{min}	Minimum distance between cathode and anode in a Hull cell.
M	Ratio of thickness of metal deposits.
n	Number of electrons transferred in an electrochemical reaction.
P	Ratio of primary current density.
R	Universal gas constant.
T	Temperature.
x	The distance along the cathode from the high density end in a Hull cell.
α	Transfer coefficient.
η	Electrode overpotential.
η_{a}	Magnitude of anodic overpotential.
η_{c}	Magnitude of cathodic overpotential.
κ	Specific conductance.
ρ	Specific resistance.

Subscripts

m	Refers to metal deposition reaction.
s	Refers to side reaction.

1. Introduction

Metal distribution is a very important consideration in electroplating systems. The uniformity of metal deposits depends on many factors. Among these are the geometry and size of the electroplating cell, the applied voltage, the properties of the solution, the electrode kinetics and the current efficiency. In order to be able to predict the metal distribution, the relative importance of these factors must be established. Efforts in the literature have followed two main courses. These are the fundamental approach based on transport processes in electroplating systems [1] and the empirical correlations using the concept of throwing powers [2, 3]. Both approaches have their merits as well as disadvantages. The fundamental approach is in principle completely general. However, due to the very complex nature of the transport phenomena involved in most practical systems, applications have so far been restricted to only a few simple cases. On the other hand, the empirical approach has been favored by most electroplaters. Unfortunately, due to the lack of physical significance in throwing power values, the result is highly specific and is only applicable to individual cases with little chance for generalization.

In this paper, the various factors influencing the metal distribution are briefly reviewed. To bridge the gap between the theoretical and empirical approaches, several methods are developed to predict the metal distribution in a Hull cell [4]. The results are then compared with the experimental data reported by Watson [5].

2. Factors Influencing Metal Distribution in Electroplating Systems

For many electroplating systems, the concentration of metal salt in the solution is sufficiently high for mass transfer effects to be small. For a hypothetical system involving only one electrode reaction with no electrode polarization and mass transfer effects, the plating process is controlled completely by the ohmic resistance in the solution and the resulting current distribution is known as the primary current distribution [6]. For the case where electrode polarization is included, the current distribution is called the secondary current distribution. In both cases, the current distribution is obtained by first solving the Laplace equation which governs the potential in the solution [1].

The primary current distribution depends only on the geometry of the system. Generally, the current densities are lower for the less accessible parts of the electrode. The most important series of papers on this subject are those by Kasper [7] who calculated the primary current distribution for a variety of geometrical arrangements. For the Hull cell, the primary current distribution was reported by Rousselot [8], and also by Watson [5]. For the more complex case involving three-dimensional electrodes, the primary current distribution was measured by Rousselot using analogical methods [9]. In addition, Gilmont and Walton [10, 11] studied both the metal distribution and polarization behaviour using a special plating cell with curved anodes.

The general effect of electrode polarization is to make the current distribution more uniform. The secondary current distribution depends also on the geometry of the electroplating system and, in addition, on two dimensionless parameters which were first discussed by Gardam [12] and were studied in great detail later by Hoar and Agar [13]. Depending on whether the electrode polarization law is linear or logarithmic, the two parameters are

$$\left(\frac{L}{\kappa}\right)\left(\frac{\mathrm{d}i}{\mathrm{d}\eta}\right) \text{ and } \frac{i_{\mathrm{avg}}(1-\alpha)\,nFL}{RT}$$

where L is a characteristic length of the system, κ is the conductivity of the solution, i is the current density, η is the electrode overpotential, i_{avg} is the average current density, α is the transfer coefficient, and n,F,R and T have their usual meanings. The term $RT/(1-\alpha)nF$ is also known as the Tafel slope, which is frequently designated by the letter b. The smaller these parameters are, the more uniform is the current distribution. This conclusion is in general agreement with experimental observations. Additional discussion and applications of these parameters were given by Wagner [14], Newman [1], and Cheh [15].

For systems involving only one reaction, the metal distribution is identical to the current distribution. However, in many practical plating systems, more than one electrode reaction is involved. In these cases, the metal distribution is the same as the current distribution of the deposition reaction which in turn equals to the product of the total current density i_t and the current efficiency of the deposition reaction E. Both i_t and E may be functions of position on the electrode surface. The effect of current efficiency on the metal distribution was also noted by Gardam [12]. However, no definite conclusions were drawn.

3. Theoretical Models

3.1. *Methods of approximation for systems with 100% current efficiency*

3.1.1. *Method 1.* Consider the case that an external voltage is applied to a rectangular cell where two electrodes occupy completely the two opposite walls. The applied voltage is then equal to the sum of the magnitudes of the anodic and cathodic overpotentials and the ohmic drop in the solution, i.e.

$$\Delta E = \eta_a + \eta_c + i\rho l \qquad (1)$$

where ΔE is the applied voltage, η_a and η_c are the magnitudes of anodic and cathodic overpotentials, ρ is the specific resistance of the solution and l is the distance between the cathode and the anode.

For many plating systems, the cathodic overpotential can be described adequately by the Tafel equation and the anodic overpotential is negligibly small [16]. Equation (1) can then be rewritten as

$$\Delta E = a + b \log i + i\rho l \qquad (1a)$$

where a is a Tafel parameter. For given values of ΔE and l, the current density can now be calculated. This equation is in principle applicable to cells with any geometrical arrangement provided that l is modified to represent the stream line for local current. Difficulty arises in practical cases where l is usually unknown.

The approximation adopted in this method to estimate the current distribution in a Hull cell is to replace l by the actual distance between the electrodes as shown in Fig. 1. The prediction of current distribution based on this method is presented in a later section. However, it is important to mention here that the predicted current distribution from this method is always more uniform than the actual experimental value.

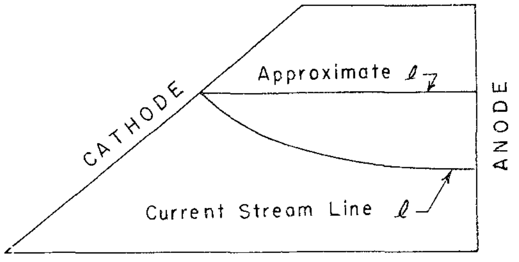

Fig. 1. Approximate l for the current stream line in a Hull cell.

3.1.2. *Method 2.* In order to make the predicted current distribution less uniform, it was decided in a somewhat arbitrary manner to shift the calculation more towards the primary current distribution. This was performed by giving both the primary current distribution and Method 1 reasonable proportions of their contributions. Based on the concept of the lever rule, the following expressions were chosen to estimate the current distribution,

$$i_2 = \frac{i_1 f_1 + i_P f_2}{f_1 + f_2} \qquad (2)$$

with

$$f_1 = a + b \log i_{avg} \qquad (3)$$

and

$$f_2 = i_{avg} \rho l_{min} \qquad (4)$$

where i_2 is the calculated current density based on this method, i_1 is the current density calculated from Method 1, i_P is the primary current distribution in a Hull cell, and l_{min} is the minimum distance between the anode and cathode. f_1 and f_2 are weighting factors representing the voltage drops due to electrode polarization and solution resistance. The choice of l_{min} instead of the average distance is somewhat arbitrary, the rationale being that part of the ohmic effect has already been accounted for in calculating i_1.

The current distribution calculated by this method agrees well with experimental data.

3.1.3. *Method 3.* In order to calculate i_2, Method 1 must first be used to obtain i_1 and the whole procedure is somewhat cumbersome. In addition, since i_1 is itself a combination of polarization and ohmic effects, the basis of postulating Equations (2) to (4) was reasonable but not rigorous. To simplify the procedure for calculation, it is proposed here to replace i_1 in

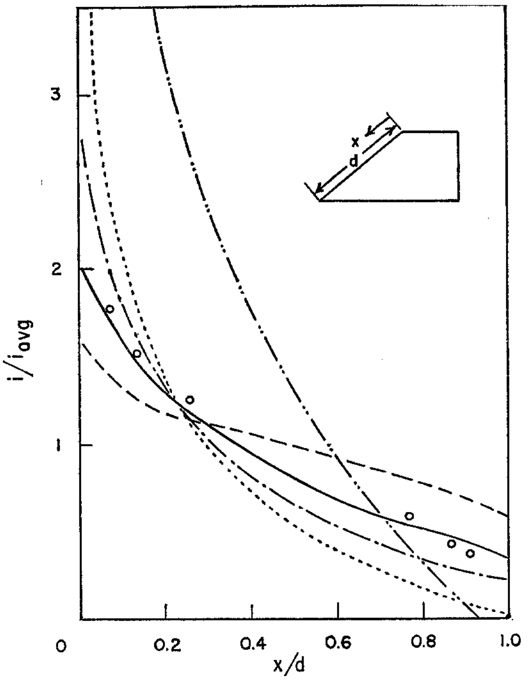

Fig. 2. Current distribution in a Watts-nickel system. ($i_{\text{avg}} = 2{\cdot}15 \times 10^{-3}$ A cm^{-2}).

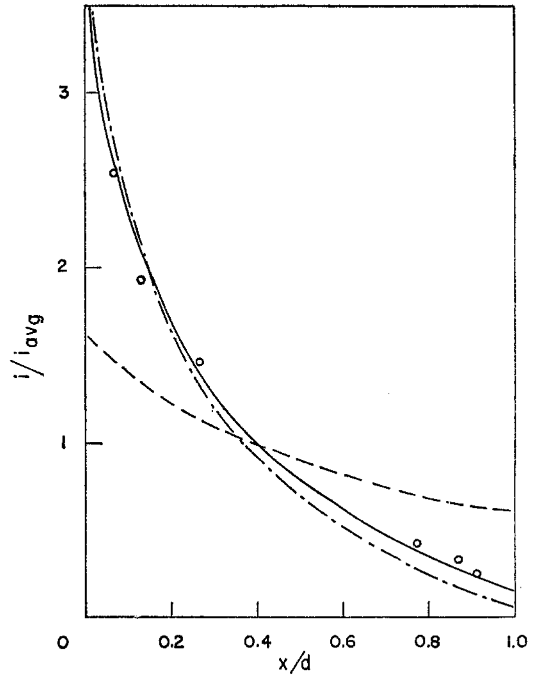

Fig. 3. Current distribution in a Watts-nickel system. ($i_{\text{avg}} = 10{\cdot}8 \times 10^{-3}$ A cm^{-2}).

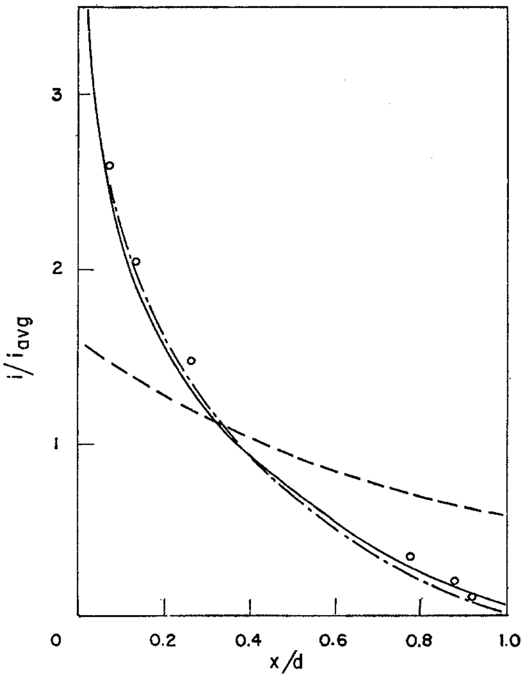

Fig. 4. Current distribution in a Watts-nickel system. ($i_{\text{avg}} = 43{\cdot}1 \times 10^{-3}$ A cm^{-2}).

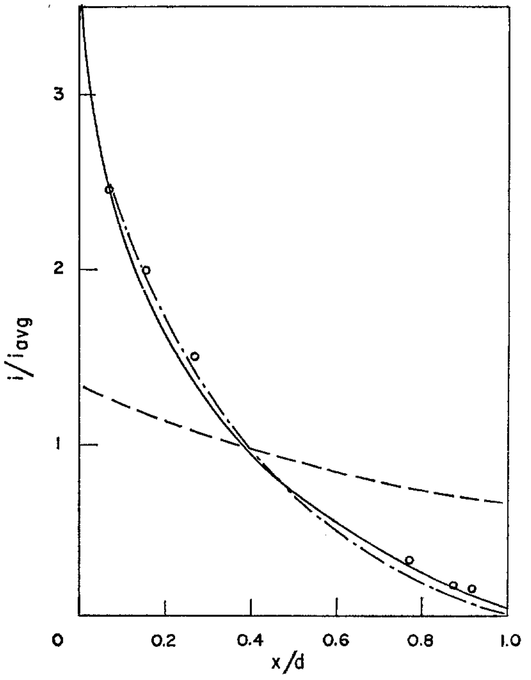

Fig. 5. Current distribution in a Watts-nickel system. ($i_{\text{avg}} = 108 \times 10^{-3}$ A cm^{-2}).

Legends for Figs. 2 to 9: ○ Experimental; — — — — Method 1; ———— Methods 2 and 3; - - - - - - - - primary current distribution; —·—·—· secondary current distribution; —··—··— Hull's empirical formula.

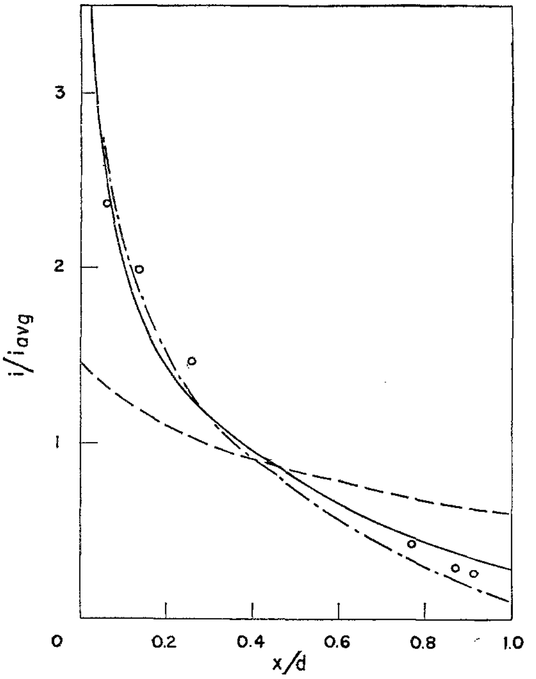

Fig. 6. Current distribution in a tin-nickel system. ($i_{avg} = 10{\cdot}8 \times 10^{-3}$ A cm^{-2}).

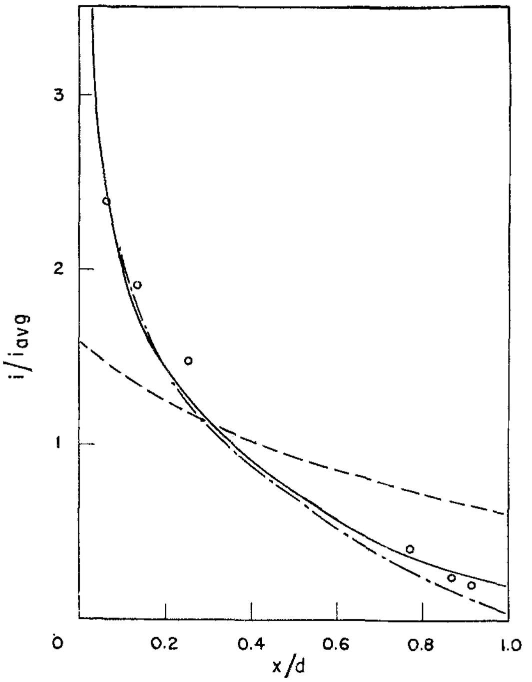

Fig. 7. Current distribution in a tin-nickel system. ($i_{avg} = 25{\cdot}8 \times 10^{3}$ A cm^{-2}).

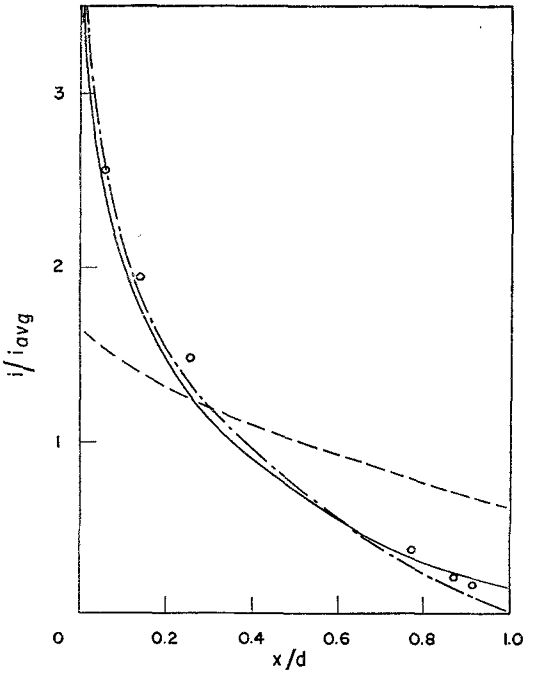

Fig. 8. Current distribution in a tin-nickel system. ($i_{avg} = 43{\cdot}1 \times 10^{-3}$ A cm^{-2}).

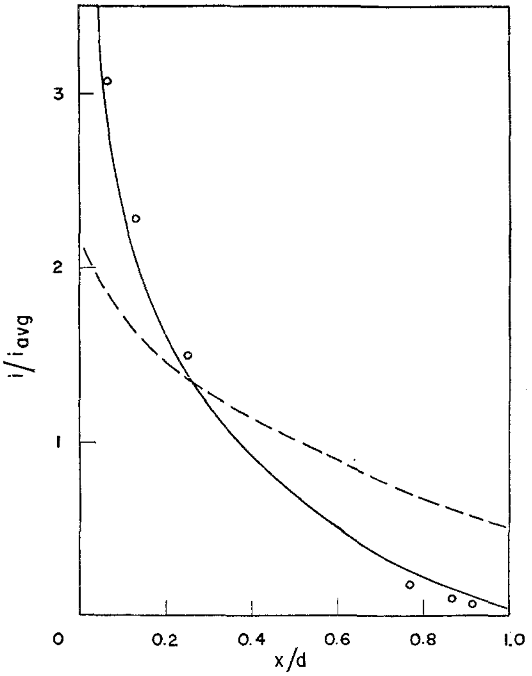

Fig. 9. Current distribution in the standard chromium system. ($i_{avg} = 161 \times 10^{-3}$ A cm^{-2}).

Equation (2) by i_{avg} and l_{min} in Equation (4) by l_{avg}, i.e.

$$i_3 = \frac{i_{avg}f_1 + i_P f_2}{f_1 + f_2} \tag{5}$$

with

$$f_1 = a + b \log i_{avg} \tag{6}$$

and

$$f_2 = i_{avg}\rho l_{avg} \tag{7}$$

Application of this method showed that there was practically no difference between the values of i_2 and i_3.

3.2. *Methods of approximation for systems with one side reaction*

For the more general cases where one side reaction may occur, the current-overpotential behaviour for both the deposition reaction and the side reaction are assumed to obey the Tafel equation, i.e.

$$\eta_{c,m} = a_m + b_m \log i_m = a_m + b_m \log i_t E \tag{8}$$

and

$$\eta_{c,s} = a_s + b_s \log i_s = a_s + b_s \log i_t(1-E) \tag{9}$$

where subscript m refers to the metal deposition reaction and s refers to the side reaction. It is worth noting that it is i_m and not i_t which is equivalent to the metal distribution. At any position on the electrode surface,

$$\eta_{c,m} = \eta_{c,s} \text{ and } i_t = i_m + i_s \tag{10}$$

In most practical systems, it is customary in the literature to report the overpotential versus the applied current density, instead of Equations (8) and (9). However, it is obvious that a_m and b_m as well as a_s and b_s can be obtained by solving Equations (8) to (10) provided that E is a known function of i_t.

Method 1 can easily be extended to include the present case. This is accomplished by replacing the $(a+b \log i)$ term in Equation (2) by Equation (8).

Two modifications are needed in order to use Methods 2 and 3. First, i_1 and i_{avg} are replaced by the deposition currents $i_{1,m}$ and $i_{avg,m}$. A slightly more complicated modification is needed for f_1. Recalling that f_1 is a weighting factor arising from electrode kinetics, f_1 is therefore a function of the relative irreversibility between the deposition reaction and the side reaction. For instance, if the deposition reaction is more reversible than the side reaction, the fraction for the deposition current density is higher at higher total current density. Consequently, the metal distribution is even more non-uniform than the primary current distribution. Since the relative irreversibility is largely characterized by the values of b_m and b_s, we postulate that,

$$f_1 = \eta_{c,m} + \frac{b_m - b_s}{b_m}(1-E)\eta_{c,s} \tag{11}$$

This equation reduces to Equation (6) when either $b_m = b_s$ or $E = 1$.

4. Results and Discussion

Experimental metal distribution data of several plating systems in a Hull cell have been reported by Watson [5]. In order to have a good representation for different systems, the Watts-nickel, tin-nickel and chromium systems were chosen to test our methods. The Watts-nickel and tin-nickel systems are both close to 100% current efficient, the major difference being that pure nickel is deposited in the Watts-nickel bath whereas an alloy is deposited in the tin-nickel system. Although the composition of the tin-nickel alloy should vary along the cathode, the system was treated by Watson as a single metal with no information given on the alloy composition. The current efficiency for the chromium system is approximately 15–30% with the side reaction being hydrogen evolution [17].

The measured local deposit thickness reported by Watson was converted to current density units. In these calculations, a 100% current efficiency was assumed for both the Watts-nickel and tin-nickel systems whereas data on the current efficiency versus applied current density reported by Morisset *et al.* (17) were used for the chromium system. The results are presented in Figs. 2 to 9. The polarization parameters a and b for the electrode reactions and the specific conductances were available from the literature [5, 18, 19]. These are summarized in Table 1. The side reactions for both the Watts-nickel and tin-nickel systems were neglected in our calculations. The results of our methods are also shown in

Table 1. Tafel parameters and specific resistances

System	*a* *volts*	*b* *volts*	ρ Ω *cm*	*References*
Watts-nickel	0·256	0·09	11·6	[5]
Tin-nickel	0·234	0·094	4·32	[18]
Standard chromium	0·85	0·105 (b_m) 0·252 (b_s)	1·45	[19]

Figs. 2 to 9. Results of Methods 2 and 3 were so close that only single curves are shown in all the figures.

The results of three additional methods frequently used in the literature are also included in these figures. These are:

Primary current distribution i_P. The primary current distribution is independent of the plating systems and the applied current density. The results are included only in Fig. 2.

Secondary current distribution i_S. The secondary current distribution for the Watts-nickel and tin-nickel systems were obtained by solving the Laplace equation with the appropriate Tafel equations serving as boundary conditions. The local current density was then calculated by

$$i_S = -\frac{1}{\rho}\nabla\phi \tag{12}$$

where ϕ is the potential in the solution. The Laplace equation was solved numerically using finite-difference methods. Results are included in Figs. 2 to 8.

Empirical formula by Hull i_H. A widely used empirical formula to estimate the current distribution in a Hull cell is given by the following expression [4],

$$\frac{i_H}{I} = 27{\cdot}7 - 48{\cdot}7 \log x \tag{13}$$

where I is the total applied current in amperes, x is the distance along the cathode from the high density end in inches and i_H is in A ft^{-2}. Since the cathode area for the Hull cell used by Watson was 0·1 ft^2, Equation (13) can then be rearranged to have the following form,

$$\frac{i_H}{i_{avg}} = 2{\cdot}77 - 4{\cdot}87 \log x \tag{14}$$

Equation (14) predicts too non-uniform a current distribution for the Watts-nickel and tin-nickel systems.

As shown in these figures, the current distribution predicted by Method 1 is much too uniform whereas the results based on Methods 2 and 3 show satisfactory agreements. The average discrepancy (defined as $|(i/i_{avg})_{predicted} - (i/i_{avg})_{expt}|$) between the predicted and experimental value is 0·12 for both Methods 2 and 3.

The primary current distribution failed definitely to describe the systems whereas the secondary current distribution showed a considerable improvement. The average discrepancy for the secondary current distribution is 0·14. The surprising result was that the formula by Hull predicted a more non-uniform current distribution than the primary current distribution.

Based on his metal distribution data, Watson [5] also calculated the throwing power values using the following formula by Field [2],

$$(T_F)_P = \frac{P-M}{P+M-2}\cdot 100 \tag{15}$$

where P is the primary current ratio and M is the metal ratio. The six positions on the cathode where the thickness of metal deposits were measured were chosen such that $P = 5$, 12 and 25. Although Field's formula has been used by many electroplaters, Subramanian [3] pointed out recently that the results using Field's formula can sometimes be misleading. For example, in the nickel–acetate bath with an applied current density of $2{\cdot}15 \times 10^{-3}$ A cm^{-2}, Watson's experimental values of $(T_F)_5$ and $(T_F)_{25}$ are 40 and 64 respectively. From these results, one may easily reach the conclusion that the metal distribution is more uniform for the case where $P = 25$ than for the case where $P = 5$. However, the actual value of M is 6·3 for $P = 25$ and 2·7 for $P = 5$. This possible confusion was removed by Subramanian who suggested the following formula for throwing power,

$$(T_S)_P = \frac{P-M}{M(P-1)}\cdot 100 \tag{16}$$

In Tables 2 to 4, we have summarized the throwing power values from Watson's data as

Table 2. Throwing power values for the Watts-nickel system

Average current density (*A cm*$^{-2}$)		*Field formula* $(T_F)_P$			*Subramanian formula* $(T_S)_P$		
		$P = 5$	$P = 12$	$P = 25$	$P = 5$	$P = 12$	$P = 25$
$2{\cdot}15 \times 10^{-3}$	Experimental	53	64	74	31	23	18
	Method 2	51	64	75	30	23	20
	Method 3	53	66	78	31	25	22
	Laplace equation	25	39	54	12	10	8
$10{\cdot}8 \times 10^{-3}$	Experimental	21	30	39	10	6·6	4·8
	Method 2	23	32	41	10	7·3	5·2
	Method 3	20	31	39	9	7·0	4·9
	Laplace equation	5	8	15	2·2	1·4	1·4
$43{\cdot}1 \times 10^{-3}$	Experimental	7·5	7·0	15	3·1	1·3	1·4
	Method 2	11	14	22	4·5	2·7	2·2
	Method 3	8	13	21	3·5	2·5	2·1
	Laplace equation	−7·8	−12	−8·2	−3·0	−1·9	−0·6
108×10^{-3}	Experimental	6·9	4·4	12	2·9	0·8	1·1
	Method 2	5·3	6·8	9·1	2·2	1·2	0·8
	Method 3	4·4	6·7	9·2	1·8	1·2	0·8
	Laplace equation	−15	−22	−29	−5·7	−3·1	−1·8
	Hull's formula*	−17	−41	−69	−6·2	−5·1	−3·4

* Note that the throwing power values calculated by Hull's formula are independent of the system as well as the applied current density.

well as calculated values from Methods 2 and 3, the secondary current distribution, and Hull's formula. It is clearly shown in these Tables that Methods 2 and 3 compare most favorably with the experimental data. The values were somewhat high for the tin-nickel system. However, it must be recognized that the throwing power is very sensitive to M. Either experimental error, especially at the low current density positions, or systematic error in the theoretical results, will cause a significant change in the value of M which affects the accuracy of the throwing powers. The values based on the secondary current distribution are consistently low whereas the results from Hull's formula fail completely to describe these systems.

Table 3. Throwing power values for the tin-nickel system

Average current density (*A cm*$^{-2}$)		*Field formula* $(T_F)_P$			*Subramanian formula* $(T_S)_P$		
		$P = 5$	$P = 12$	$P = 25$	$P = 5$	$P = 12$	$P = 25$
$10{\cdot}8 \times 10^{-3}$	Experimental	25	34	47	12	8·0	6·6
	Method 2	43	49	63	23	14	12
	Method 3	44	50	61	24	14	11
	Laplace equation	16	30	25	6·8	6·5	2·5
$25{\cdot}8 \times 10^{-3}$	Experimental	17	27	33	7·5	4·6	3·8
	Method 2	30	39	47	15	9·5	6·7
	Method 3	28	39	46	14	9·6	6·4
	Laplace equation	7·7	−1·6	−3·4	3·2	−0·3	−0·3
$43{\cdot}1 \times 10^{-3}$	Experimental	12	16	22	5·0	3·1	2·3
	Method 2	23	31	35	11	7·1	4·1
	Method 3	20	30	37	9·2	6·6	4·5
	Laplace equation	−8·6	−11	−1·6	−3·3	−1·7	−0·1

Table 4. Throwing power values for the standard chromium system

Average current density $(A\ cm^{-2})$		*Field formula* $(T_F)_P$ $P = 5$	$P = 12$	$P = 25$	*Subramanian formula* $(T_S)_P$ $P = 5$	$P = 12$	$P = 25$
	Experimental	−42	−48	−100	−13	−5·7	−4·2
161×10^{-3}	Method 2	−12	−22	−25	−4·3	−3·0	−1·6
	Method 3	−11	−19	−27	−3·8	−2·7	−1·7

5. Conclusions

Experimental metal distribution data for the Watts-nickel, tin-nickel and chromium systems by Watson were used to test three common predictive methods in the literature and to develop new and more accurate models.

The primary current distribution as well as an empirical formula by Hull were shown to be inadequate in describing these systems. The secondary current distribution which was based on the exact solution of the Laplace equation showed a considerable improvement. However, the calculations were rather complex and a great deal of numerical analysis was needed.

Three methods of approximation were developed in this paper. Method 1 predicted too uniform a current distribution whereas Methods 2 and 3 showed good agreements with all these experimental systems. Since Method 3 is considerably simpler to use, it is recommended as a new technique which is both simple and accurate in predicting metal distribution in practical electroplating systems.

Acknowledgement

The authors wish to thank Professor H. B. Linford for his critical review of the manuscript.

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