## LIST OF SYMBOLS

- rotating disk hydrodynamic constant (0.51023)
- $C_{
  m i}$  $ar{C}_{
  m i}$ normalized concentration of species i
- concent. of species i (mol/cm<sup>3</sup>)
- $\hat{D}_{j}$ diffusion coefficient of species i (cm<sup>2</sup>/s)
- F Faraday's constant (96,487 C/eq)
- total cathodic current density (A/cm<sup>2</sup>)  $i_{
  m tot} K_{
  m i}$
- dissociation constant of species i cathodic rate constant for species i
- $k_{
  m i} N_{
  m j}$
- dimensionless molar flux Ν
- molar flux (mol/cm<sup>2</sup>-s) R
- universal gas constant, 8.3143 J/mol-K  $R_{i}$ homogeneous reaction rate (mol/cm<sup>3</sup>-s)
- time (s)
- T absolute temperature, K
- V absolute value of the cathodic potential (volts) with respect to NHE
- dimensionless distance from electrode  $\boldsymbol{x}$
- distance from electrode (cm) 2

#### Greek Characters

- cathodic transfer coefficient αi
- coefficients defined after Eq. [11] ß
- δ mass-transfer boundary layer defined by Eq. [7]
- current efficiency of alloy deposition η
- fraction of surface available for discharge of metal-A hydroxide ions
- kinematic viscosity (cm<sup>2</sup>/s)
- disk rotation speed (rad/s) ω

### Superscript

bulk b

- surface s
- cathodic c

### REFERENCES

- 1. A. Brenner, "Electrodeposition of Alloys," Vol. II,
- D. 222, Academic Press Inc., New York (1963).
   S. Glasstone and T. Symes, *Trans. Faraday Soc.*, 23, 213 (1927); 24, 370 (1928).

- 3. A. T. Vagramyan and T. A. Fautueva, This Journal, 110, 1031 (1963).
- 4. M. J. Nicol and H. I. Phillip, J. Electroanal Chem., 70, 233 (1976).
- 5. H. Dahms and I. M. Croll, This Journal, 112, 771 (1965).
- 6. L. T. Romankiw and I. M. Croll, in "Electrodeposition Technology, Theory and Practice," L. T. Romankiw Editor, p. 285, The Electrochemical Society Soft-bound Proceedings Series, PV 87-17, Pennington, NJ (1987).
- 7. L. T. Romankiw, in "Electrodeposition Technology, Theory and Practice," L. T. Romankiw, Editor, p. 301, The Electrochemical Society Softbound Proceedings Series, PV 87-17, Pennington, NJ (1987). 8. L. G. Sillen, Q. Rev., XIII, 146 (1959). 9. "The NBS Tables of Thermodynamic Properties," J.
- Phys. Chem., Ref. Data, Vol. II, Suppl. 2 (1982).
  10. J. O'M. Bockins, D. Drazic, and A. R. Despic, Electro-
- chim. Acta, 4, 325 (1961). 11. J. Matulis and R. Slizys, ibid., 9, 1177 (1964).
- L. Harris, *This Journal*, **120**, 1034 (1973).
   A. Ives, J. Edington, and G. Rothwell, *Electrochim. Acta*, **15**, 1797 (1970).

- Acta, 13, 1797 (1970).
  14. J. Horkans, This Journal, 128, 45 (1981).
  15. P. Andricacos, C. Arana, J. Tabib, J. Dukovic, and L. T. Romankiw, *ibid.*, 136, 1336 (1989).
  16. J. Newman, "Electrochemical Systems," Prentice-Hall, Englewood Cliffs, NJ (1973).
  17. Horkans, This Journal, 126, 1861 (1979).
- J. Horkans, This Journal, 126, 1861 (1979).
   L. G. Sillen, "Stability Constants of Metal-Ion Complexes," ACS Special Pub., No. 17, (1964), Special
- Pub. No. 25, (1971), London Chem. Society.
  19. A. Bard, R. Parsons, and J. Jordan, "Standard Potentials in Aqueous Solutions," IUPAC, Marcel Dekker Inc., 1985.
- 20. S. Biallozor and M. Leider, Surf. Technol., 21, 1 (1984).
- A. J. Bard, "Encyclopedia of Electrochemistry of the Elements," Vol. II and Vol. III, Marcel Dekker Inc., New York (1975).

# The Effect of Base Metal lons on the Electrochemical and Structural Characteristics of Electrodeposited Gold Films

P. Bindra\* and D. Light

International Business Machines Corporation, Endicott, New York 13760

#### P. Freudenthal

Rockefeller University, New York, New York 10021

### D. Smith

IBM T. J. Research Center, Yorktown Heights, New York 10598

#### ABSTRACT

It has long been known that gold deposits obtained from Co and Ni-containing electrolytes are generally hard, while Pb and Tl-containing electrolytes tend to give soft gold deposits. Yet the mechanism by which these additives affect the grain size is not fully known. This study was undertaken to investigate the effect of base metal inclusions on the deposition characteristics and the microstructure of electrodeposited gold films. The kinetic and mechanistic aspects of the gold deposition reaction were investigated using linear sweep voltammetry on a rotating disk electrode. A combination of electron microscopy and electron diffraction techniques was used to characterize the microstructure.

Gold is used extensively in the electronics industry because of its unique combination of physical properties. Electrodeposited soft gold films generally are of high purity and provide good electrical conductivity, as well as high corrosion resistance. Hard gold deposits show very low porosity and high wear resistance and as such are most suitable for sealed contacts (1) and separable connectors. Soft gold electrodeposits represent excellent bonding substrates. The importance of these properties to the electronics industry has resulted in several fundamental studies of electroplated gold films in recent years (2-6). Such studies have demonstrated that gold deposits obtained from cobalt- and nickel-containing electrolytes are hard, while lead- and thallium-containing electrolytes give soft gold deposits. The hardness of electroplated hard gold has been attributed to its small grain size (7), yet the mech-\* Electrochemical Society Active Member.

anism by which these additives affect the grain size is not fully understood. Further, there is a definite paucity of data concerning the role of base metal ions such as Co, Ni, Tl, and Pb in affecting the fundamental processes involved in the electrodeposition of gold (2).

Review of the literature indicates that kinetic studies have been confined to additive-free gold solutions. Cheh and Sard (8) used galvanostatic techniques on a rotating disk electrode to study the morphology of gold deposits from various electrolytes. MacArthur (9) employed voltammetric and galvanostatic techniques and postulated two reduction pathways in alkaline cyanide solution. One reduction pathway, at low overpotentials, involves (AuCN)ads as the reactive species. The other, at high overpotentials, involves a direct charge transfer to the soluble Au(CN)2-. McIntyre and Peck (10) investigated gold deposition in the presence of heavy metal ions (including Pb and Tl), but

a

they limited themselves to the depolarization effect primarily. Recently, Eisenmann (11) studied the kinetics of gold deposition from two commercial hard gold baths and a soft gold bath containing lead ions.

Although base metal ions affect the kinetics as well as the microstructure of gold films, there is no indication that a unifying study of the two effects has been attempted. This study was undertaken to investigate the effect of base metal additives on the deposition characteristics and the microstructure of electrodeposited gold films. The kinetic and mechanistic aspects of the gold deposition reaction, with and without base metal ions, were investigated using linear sweep voltammetry on a rotating disk electrode. A combination of electron microscopy and electron diffraction techniques was used to characterize the microstructure.

#### Experimental

Electrochemical measurements.-Electrochemical measurements were performed in a glass cell under conditions of controlled mass transport using the rotating disk electrode technique. The working electrode was a 0.458 cm<sup>2</sup> gold disk embedded in a Teflon cylinder. The rotating disk electrodes and the rotator were obtained from Pine Instruments. The electrode was polished to a near-mirror finish using progressively finer grades of alumina as the abrasive. It was then degreased with alcohol and thoroughly rinsed with triply distilled water before use. The counterelectrode was a large-surface-area gold foil, and the potential was monitored with respect to a saturated calomel reference electrode (SCE) separated from the bulk solution by a Luggin capillary. Potentiostatic control of the working electrode was achieved using a PAR 173 Potentiostat in conjunction with a PAR 175 Universal Programmer. The data were recorded on a Yokagawa X-Y-t recorder.

All solutions were made from Analar grade chemicals, with triply distilled water, and were deaerated by bubbling with argon before and during the measurements. The buffer solution used to establish the underpotential deposition ranges for the base metal ions was purified further by conventional pre-electrolysis for about 15h at 5 mA cm<sup>-2</sup>.  $K_2C_2O_4$  and KAu (CN)<sub>2</sub> were used without further purification.

Plating procedure.—The gold deposits examined in this study were plated from an oxalate bath with a phosphate buffer. The basic formulation of the bath, excluding base metal additives, was as follows: 0.04M KAu(CN)2; 0.2-0.87M K<sub>2</sub>C<sub>2</sub>O<sub>4</sub>; 0.123*M* KH<sub>2</sub>PO<sub>4</sub>; 0.057*M* K<sub>2</sub>HPO<sub>4</sub>. The plating was carried out at 65°C using a rotating cathode. For transmission electron microscopy (TEM) sample preparation, the cathode was a detachable copper foil, which was 2 mm thick, with an exposed area of 0.58 cm<sup>2</sup>. The cathode assembly is shown schematically in Fig. 1. The anode was a 10 cm<sup>2</sup> gold foil. The cathode was rotated at 900 rpm and the plating performed both potentiostatically and galvanostatically. For scanning electron microscopy (SEM) samples, the cathode was a detachable, cylindrical copper slug. Only the face of the slug was exposed to the solution. The exposed area was 0.636 cm<sup>2</sup>.

Specimen preparation for TEM examination.—After gold deposition the copper substrates were dissolved in nitric acid. The gold films were washed in distilled water and isopropanol, and mounted on grids. The final stage of preparation was ion milling to a thickness of approximately 1000 angstroms.

The scanning electron microscopy was done on specimens in the as deposited condition.

#### **Results and Discussion**

*Cyclic voltammetry.*—Linear sweep voltammetry has been used in an attempt to establish details of the gold deposition reaction in oxalate media. Some of these details tend to be obscured in the complete plating solution; therefore cyclic voltammetry measurements were first performed in components of the base electrolyte separately. A typical voltammetry curve for gold in the phosphate buffer solution is presented in Fig. 2(a). This curve displays a large number of anodic and cathodic current peaks and



Fig. 1. Cathode assembly schematic

shoulders, compared with the curves obtained in acid or alkaline electrolytes (12, 13). For the gold/alkaline solution interface, it has been established (14) that the initial anodic film formation begins at some 0.7 to 0.8V negative compared to that for the start of anodic film formation in acid electrolytes (15). Figure 2(a) shows that this is also true for gold in phosphate buffer solution. Another point to note in Fig. 2(a), from the point of view of gold deposition, is that hydrogen evolution commences at -0.8V vs. SCE. The thermodynamic reversible potential for the hydrogen electrode in this electrolyte (pH = 6.5) is -0.64V vs. SCE.

Figure 2(b) shows the voltammetry curve obtained with a gold electrode in phosphate buffer solution to which has been added 0.87*M* potassium oxalate. The addition of oxalate to the electrolyte raises the pH slightly. The pH was adjusted to 6.5 by adding  $H_2PO_4^-$  to the solution. It is clear from Fig. 2(b) that oxalate oxidation in the buffer occurs at +0.2V vs. SCE. This is negative of the reversible potential for the redox couple Au<sup>+</sup>/Au<sup>3+</sup> in cyanide medium, suggesting that oxalate electrolyte would prevent the formation of Au<sup>3+</sup>, which is detrimental to gold deposition efficiency. While oxalate reduction is also thermodynamically possible (16) in the negative potential range scanned, it either does not occur on gold at pH 6.5 or it is obscured by the hydrogen evolution reaction.

Figure 2(c) shows the cyclic voltammetry curve obtained



Fig. 2. Cyclic voltammogram for gold in solution at scan rate of 100 mV/s, pH = 6.5,  $T = 65^{\circ}$ C, argon-saturated. Top, in phosphate buffer solution. Middle, in phosphate buffer +0.87M potassium oxalate, electrode area 0.458 cm<sup>2</sup>. Bottom, in 0.04M KAu(CN)<sub>2</sub> in buffered solution containing potassium oxalate, electrode area 0.458 cm<sup>2</sup>.

on a gold electrode in the presence of 0.04M KAu(CN)<sub>2</sub> in buffered oxalate base electrolyte. The potential scan was initiated at -0.2V in the anodic direction. Anodic peak I is attributed to the formation of an insoluble thin layer of AuCN. The integral charge capacity of this peak is  $\sim 5.0m$  C cm<sup>-2</sup>. Assuming a surface roughness factor of 2 and taking the radius of the Au atom as 1.5Å, this charge corresponds to 10 monolayers of the insoluble AuCN layer. Some of the charge in this peak may also be due to the oxidation of the oxalate anion (cf. Fig. 2(b)). During the cathodic scan an anodic peak (peak II) is observed at +0.3V vs. SCE. This peak is almost certainly due to the oxidation of the oxalate anion. Such behavior is typical of organic reducing agents (17, 18). The first indication of gold deposition occurs in the form of a cathodic prewave at  $\approx 0.7$  V. The amplitude of this wave is independent of agitation, and the faradaic charge passed is constant at several potential scan rates. This prewave has been assigned to the following reaction by MacArthur (9)

$$(AuCN)_{ads} + e^- \rightarrow Au + CN^-$$
[1]

The constant charge capacity of the prewave III is about  $3 \text{ mC cm}^{-2}$ , which corresponds to about 7-10 monolayers of AuCN, depending on the packing of the atoms. Cathodic wave III, therefore, is the conjugate of anodic peak I.

Cathodic peak IV is known to correspond to gold deposition via direct charge transfer to  $Au(CN)_2^-$  from the solution (9). The behavior of this peak was examined as a function of scan rate. For this purpose  $(i_p - i_0) vs. (dv/dt)^{1/2}$  has been plotted (Fig. 3) where  $i_0$  is the current in the absence of  $Au(CN)_2^-$  in the solution. A linear relationship was observed, indicating that the reduction of  $Au(CN)_2^-$  is diffusion-limited in this potential region.

The potential sweep was reversed at -1.2V vs. SCE. The very broad anodic peak observed at -0.5V can be attributed to the specific adsorption of CN<sup>-</sup>, which has been released during gold deposition in cathodic peak IV and is still in the close vicinity of the electrode when the potential is reversed. The Au(CN)<sub>ads</sub><sup>-</sup> is oxidized to AuCN at the more anodic potential in anodic peak I.

Interactions of gold with Pb, Tl, Ni, and Co.-To ascertain the effect of base metal additions on the deposition characteristics and the microstructure of electrodeposited gold films, it is necessary first to establish whether these metals will undergo underpotential deposition (UPD) in the buffer solution at pH of 6.5. UPD is the deposition of mono- or submonolayers of certain metal ions on foreign metal substrates at potentials considerably more positive than the corresponding values for the bulk metal. This phenomenon occurs because of the interaction of the metal layers with the more noble substrate. UPD has been studied extensively (19), usually with linear sweep voltammetry. Peaks occur in the voltammetry curves and correspond to the adsorption-desorption of the UPD species and structural changes in the layers. Gerischer et al. (20) have discussed the correlation of the differences in the potential for UPD and that for bulk metal,  $\Delta U_{\rm p},$  with the differences in the work functions of the substrate metal and the UPD metal as bulk phase. Specifically, they have demonstrated that

$$\Delta U_{\rm p} = K \Delta \Phi \qquad [2]$$

where  $\Delta \Phi$  is the difference in work functions of the substrate and adsorbate and *K* is  $\approx 0.5$  V/eV. The UPD species may have some ionic character, but in general, the ionic *vs*.



Fig. 3. Peak height as a function of the square root of scan rate

Table	. Deposition	parameters
Table	. Deposition	parameter

Metal	Work function Φ, eV	E° V vs. SCE	<i>E</i> ° <sub>R</sub>	Electrode Reaction	$\Delta\Phi$	$\Delta U_{ m p}$	$E^{\circ}_{ m R}-\Delta U_{ m p}$
Pb Tl Ni Co	4.24 3.7 4.8 4.7	-0.37 -0.58 -0.50 -0.52	-0.507 -0.838 -0.613 -0.633	$\begin{array}{c} Pb^{2+}+2e^-\rightleftarrows Pb\\ Tl^++e^-\rightleftarrows Tl\\ Ni^{2+}+2e^-\rightleftarrows Ni\\ Co^{2+}+2e^-\rightleftarrows Co \end{array}$	+0.56 +1.10 0 +0.1	0.28 0.55	$-0.227 \\ -0.288$

metal-like character is a function of the interaction of the UPD species with the solvent as well as the substrate and the electrode potential. The work functions of Pb, Tl, Ni, and Co are collected in Table I. Also listed are the standard potentials,  $E^{\circ}$ , at pH = 6.5 and the reversible potential,  $E^{\circ}_{R}$ , at base metal ion concentration of 10 ppm.

The theoretical  $\Delta U_p$  values and the estimated potential  $(E^{\circ}_{\rm R} - \Delta U_p)$  at which UPD may be observed have also been included in Table I. The assumption is made that these theoretical values are a guide to UPD in neutral gold plating solutions. This assumption is partially valid, provided the substrate is not covered by an anodic oxide or cyanide film and the interaction of  $\rm CN^-$  with the surface is relatively weak compared to the interaction of the UPD layer with the substrate. When  $\Delta\Phi$  is close to zero, no UPD is normally expected. Alloy formation, however, may still occur.

Lead-gold system.-Table I predicts UPD of Pb and Tl on gold in the buffer solution at pH = 6.5. Figure 4 shows cyclic voltammetry curves, obtained on a gold electrode in the buffer solution to which has been added 0.87M K<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and increasing amounts of  $Pb^{2+}$ . The anodic stripping peak at -0.67V vs. SCE is ascribed to the dissolution of bulk lead. This was verified by holding the electrode at -0.8V vs. SCE for increasing amounts of time to deposit bulk metallic lead prior to the anodic scan. The stripping peak current increased as a function of the electrode holding time. I' is therefore complimentary to the stripping peak I, indicating that in this gold plating solution bulk lead deposition occurs at a potential of  $\approx -0.75$  V vs. SCE. This is negative to the reversible potential,  $E^{\circ}_{R}$ , for the Pb deposition reaction given in Table I, probably because of the tendency of  $Pb^{2+}$  to complex with phosphate or oxalate ions (21). The lead UPD peaks occur in the potential range -0.2V to -0.5V vs. SCE. These peaks cannot be resolved completely at the high potential scan rate (20 mV/s) at which the curves in Fig. 4 were taken.



Fig. 4. Cyclic voltammogram for gold in buffered solution containing potassium oxalate in the presence of Pb<sup>2+</sup>. Scan rate 20 mV/s, pH = 6.5,  $T = 65^{\circ}$ C, argon-saturated.

Thallium-gold system.-In the presence of Tl<sup>+</sup>, gold oxide or hydroxide formation is suppressed and gold dissolution enhanced. This has been postulated (22) as being due to the inhibition of the formation of the passivating anodic films by adsorbed thallium atoms. To determine if this phenomenon occurs in phosphate buffered solution at 65°C, the cyclic voltammetry curve on a gold electrode was first obtained in the absence of oxalate anions. This curve is represented in Fig. 5(a). The voltammogram for thallium-free electrolyte is also shown for reference. It is clear from Fig. 5(a) that the formation of the anodic film on gold is only slightly inhibited by the presence of Tl<sup>+</sup> in the electrolyte. Further, in view of the potentials where this occurs, the inhibiting species is more likely to be a thallium hydroxide, probably Tl(OH)<sub>3</sub> (23). This is also evident from the current peaks which appear during the cathodic potential scan. The cathodic peak for the reduction of gold oxide is shifted to a more negative potential and broadened. In addition, a new reduction peak appears at +0.35V vs. SCE. This peak is attributed to the reduction of Tl(OH)<sub>3</sub> formed





Fig. 5. Cyclic voltammogram for gold in solution at scan rate of 100 mV/s, pH = 6.5,  $T = 65^{\circ}$ C, argon-saturated. Top, in phosphate buffer solution. Bottom, in phosphate buffer and oxalate +40 ppm TI<sup>+</sup>.

during the anodic scan. A broad cathodic peak at -0.15V vs. SCE and its anodic conjugate at the same potential are attributed to the UPD of thallium and the anodic dissolution of these UPD species. The voltammetry in the UPD region was repeated at a slower scan rate and higher sensitivity for better resolution of the UPD peaks. The curve obtained in the presence of oxalate anions is shown in Fig. 5(b). It is obvious that more than one thallium UPD species is involved, but the voltammetry curve is quite complex and a more detailed interpretation will be given elsewhere. For this investigation it is only necessary to establish that the UPD of thallium on gold in the gold plating solution does occur and the potential range for this monolayer deposition is 0 to -0.2V vs. SCE.

Nickel-gold system.—The work function of nickel is the same as the work function of gold (24) (Table I). Therefore, nickel is not expected to UPD on gold. The cyclic voltammetry curve for gold in the phosphate buffer solution containing 15 ppm of Ni<sup>2+</sup> (Fig. 6) shows that this is indeed the case. The current peak during the cathodic scan at -0.70V vs. SCE is due to the deposition of bulk metallic nickel. The onset of further cathodic current at the trailing edge of this peak is due to a combination of nickel deposition and hydrogen evolution. The hydrogen overpotential on nickel is much lower than that on gold, and consequently the hydrogen evolution current in the presence of plated nickel on the gold is much greater than on bare gold. During the anodic scan, the peak at -0.65V vs. SCE is attributed to the anodic stripping of the nickel electrodeposit, and to the oxidation of adsorbed hydrogen.

At the anodic end of the voltammetric curves shown in Fig. 6, there is clear evidence for alloy formation in the presence of nickel ions in solution. Alloy formation is quite possible because gold and nickel form a continuous series of solid solutions at temperatures somewhat below the solidus, but at lower temperatures separation into two phases can occur: an  $\alpha_1$  phase rich in gold, and an  $\alpha_2$  phase rich in nickel (25). In general, metals that can form homogeneous alloys display chemisorption properties that are an average of those of the components, while those that have a wide miscibility gap in their constitutional diagram give voltammetry curves that are simply the superimposition of those for the pure component metals (12). Figure 6 shows that oxide formation on gold in the presence of nickel is suppressed, while the oxide reduction peak is shifted to a more cathodic potential and slightly broadened, indicating that it is a composite of the oxide reduction characteristics of pure gold and pure nickel. This behavior is clearly the result of Ni atoms having sufficient mobility for alloying to occur during electrodeposition. The cyclic voltammetry curves in the potential region of nickel deposition were repeated in the presence of 0.87M  $K_2C_2O_4$ . Curves obtained at greater vertical sensitivity



----- NO NICKEL

Fig. 6. Cyclic voltammograms for gold in buffered solution in the presence and absence of nickel. Scan rate = 100 mV/s, pH = 6.5,  $T = 65^{\circ}$ C, argon-saturated.



Fig. 7. Cyclic voltammograms for gold in buffered solution in the presence and absence of  $Co^{2+}$ . Scan rate = 100 mV/s, pH = 6.44,  $T = 65^{\circ}$ C, argon-saturated.

clearly showed the deposition of nickel in the presence of oxalate anions.

Cobalt-gold system.—The cyclic voltammetry curves obtained on a stationary gold electrode in the absence and in the presence of 15 ppm of  $Co^{2+}$  in the buffer solution are given in Fig. 7. The voltammogram obtained in the presence of  $Co^{2+}$  ions in the electrolyte is similar to that obtained when Ni<sup>2+</sup> ions are present, in that there is no evidence of UPD in either case. This is predicted by Table II. Furthermore, the oxide formation and reduction regions in Fig. 6 and 7 indicate homogeneous alloy formation during the electrodeposition of bulk phases of the base metals. This too is consistent, as both the gold-nickel and the gold-cobalt systems form a continuous series of solid solutions (25).

The deposition of bulk phase metallic cobalt occurs at around -0.8V vs. SCE, which is negative to the reversible thermodynamic potential given in Table I. This is almost certainly due to complexation of Co<sup>2+</sup> with the phosphate anions (21). The anodic peak at -0.6V vs. SCE is attributed to the formation of Co(OH)<sub>2</sub> (23). At more anodic potentials (>0.7V vs. SCE), cobaltous oxide restructures to form mixed oxides of the type  $\text{Co}_3\text{O}_4$  (23). Mixed oxides of cobalt show good catalytic activity for  $O_2$  evolution (26). Therefore, the anodic current spike that occurs at +0.9V vs. SCE is ascribed to O<sub>2</sub> evolution. The thermodynamic reversible potential for O<sub>2</sub> evolution at 65°C and a pH of 6.5 is  $\sim +0.6V$ vs. SCE. During the cathodic scan the oxide reduction peak is a composite of the oxide reduction peaks for pure Au and pure Co, thus corroborating the proposal of the formation of a homogeneous Au-Co alloy during Co electrodeposition.

Rotating disk electrode measurements.—Having established the adsorption-desorption characteristics of base metal ions on gold in oxalate electrolyte, rotating disk electrode measurements were undertaken to determine the effect of these ions on the kinetics and mechanism of gold deposition. But first, the mechanism of gold deposition from an oxalate gold plating bath was determined.

Mechanism of gold deposition.—Cyclic voltammetric measurements have revealed [above and Ref. (9)] that the

Table II. Tafel slope and transfer coefficients in presence of additives

	$i_{d}$ (exp) (mA)	Tafel slope	Transfer coefficient (α)
Pb	5.40	-130	0.57
Tl	5.20	-170	0.44
Ni	5.37	-200	0.39
Co	5.15	-190	0.37
NA	5.25	-315, -110	0.23, 0.67



Fig. 8. Polarization curves for Au deposition in 0.04M KAu(CN)<sub>2</sub> in buffered solution containing organic reducing agent. Scan rate = 20 mV/s, pH = 6.4, electrode area = 0.458 cm<sup>2</sup>,  $T = 65^{\circ}$ C, argonsaturated.

mechanism of gold deposition is a function of the applied potential. In the potential range -0.8 to -0.4 V vs. SCE, gold deposition involves the absorbed species (AuCN)<sub>ads</sub>, while at more negative potentials, direct discharge of the solution phase anion Au(CN)2<sup>-</sup> takes place. To obtain further verification of this, RDE measurements have been performed. The Au(CN)2<sup>-</sup> reduction currents obtained at different rotation rates are shown in Fig. 8. The hysteresis observed at larger overvoltage is due to changes in surface area during gold deposition. At low overvoltages, the hysteresis is attributed to changes in the mechanism of gold deposition during the cathodic and anodic potential sweeps. When the potential is swept cathodically, the electrode surface is partially covered with AuCN, and the gold deposition occurs via a combination of the reduction of this anodic film and direct charge transfer to solution phase Au(CN)<sub>2</sub><sup>-</sup>. During the anodic scan, the metal deposition is entirely due to the reduction of  $Au(CN)_2$ . The current wave at around -1.3V is due to the simultaneous evolution of hydrogen. This is demonstrated more clearly in Fig. 9, which shows polarization curves for gold deposition at 625 rpm as a function of solution pH.

The rotating disk electrode data were analyzed according to the Levich equation (27). For first-order kinetics, with respect to dissolved  $Au(CN)_2^-$  ions



Fig. 9. Polarization curves for Au deposition as a function of 
$$pH$$
 in  
0.04M KAu(CN)<sub>2</sub> solution containing organic reducing agent. Scan rate  
= 20 mV/s, electrode area = 0.458 cm<sup>2</sup>.

$$\frac{1}{i} = \frac{1}{i_{t}} + \frac{1}{i_{d}} = \frac{1}{i_{t}} + \frac{1}{B\sqrt{\omega}}$$
[3]

where  $i_k$  = kinetic current,  $i_d$  = diffusion limited current,  $\omega$  = electrode rotation rate, and *B* is the diffusion parameter given by (28)

$$B = \sqrt{2} \frac{\pi}{60} n \mathbf{F} \nu^{1/2} C_o \left[ 0.621 \text{Se}^{-2/3} \left( 1 + 0.298 \text{Se}^{-1/3} + 0.145 \text{Se}^{-2/3} \right) \right]$$
(4)

where *n* is the number of electrons per Au(CN)<sub>2</sub><sup>-</sup> ion passing through the Nernst boundary layer, F is the Faraday constant,  $\nu$  is the kinematic viscosity,  $C_0$  is the bulk concentration of Au(CN)<sub>2</sub><sup>-</sup>, Sc is the Schmidt number ( $\nu/D$ ), and D is the diffusion coefficient for  $Au(CN)_2^-$  in the oxalate media. Thus a plot of  $1/i vs. 1/\sqrt{\omega}$  for various potentials should yield parallel straight lines, with the intercepts corresponding to  $1/i_k$  and the slopes yielding 1/B values. Figure 10 depicts such a plot for the data shown in Fig. 8. The straight lines in Fig. 10 are not parallel, indicating a decrease in the value of n with potential. This is quite reasonable, as at low overpotential gold deposition occurs simultaneously by the reduction of the AuCN film on the electrode and Au(CN)<sub>2</sub><sup>-</sup> ions in the solution. The plot of 1/ivs.  $1/\sqrt{\omega}$  at -1.15V is linear and goes through the origin, indicating that at this potential the metal deposition reaction is entirely diffusion-controlled and that the reaction is first order with respect to  $Au(CN)_2^-$  ions in solution.

If faradaic charge transfer is rate-controlling with a uniform diffusion layer thickness and combined diffusion and kinetic control, the kinetic current density with negligible back reaction is related to potential by the relation

$$i_{\rm k} = \frac{ii_{\rm d}}{i_{\rm d} - i} = i_{\rm o} \exp \alpha n \mathbf{F} \frac{(E - E^{\rm o}_{\rm R})}{RT}$$
[5]

where n = 1 for Au(CN)<sub>2</sub><sup>-</sup> reduction and  $E^{\circ}_{R}$  is the thermodynamic reversible potential. Figure 11 shows a plot of log  $[ii_d/i_d - i]$  vs. *E* for the experimental data at 65°C. The value of  $i_d$  for this plot was calculated from the relation  $i_d = B\sqrt{\omega}$  and the *B* value obtained from Fig. 10.

Two linear regions are observed; the one at low overvoltages (anodic to -0.8V vs. SCE) yields a Tafel slope of -315 mV/decade. Such a high Tafel slope is difficult to interpret in terms of an "outer sphere"-type elementary charge transfer but may be explained if specific adsorption of charged reaction intermediates is assumed (29). Gnanamuthu and Petrocelli (29) have shown that the observed value of the charge transfer coefficient,  $\alpha$ , deviates substantially from 0.5 when the actual charge transfer occurs across only a fraction of the Helmholtz double layer. Under these circumstances the effective potential driving the charge transfer process is less than when the reacting species are in the OHP and the charge transfer occurs across the whole double layer. Therefore, in the anodic film reduction region the gold deposition reaction is compatible with the following sequence of steps

$$AuCN \rightarrow (AuCN)_{ads}$$
 [6]

$$(AuCN)_{ads} + e^- \rightarrow (AuCN^-)_{ads}$$
 [7]

$$(AuCN^{-})_{ads} + H^{+} \rightarrow Au + HCN$$
 [8]

At higher overpotentials (negative of -0.8V vs. SCE), the linear Tafel region in Fig. 11 yields a slope of -110 mV/ decade, which is in good agreement with the value of -101 mV/decade at 60°C in a phosphate buffer solution reported by Cheh and Sard (8). A Tafel slope of -110 mV/ decade at 65°C corresponds to an  $\alpha$  value of 0.62. This suggests a ligand-assisted (in this case CN<sup>-</sup>) charge transfer to a metal ion complex such as Au(CN)<sub>2</sub><sup>-</sup> (30). Under these circumstances gold deposition in this potential region occurs via direct electron transfer to Au(CN)<sub>2</sub><sup>-</sup>. Thus

$$Au(CN)_2^- + e^- + 2H^+ \rightarrow Au + 2HCN \qquad [9]$$

The effect of base metal ions on the two mechanisms of gold deposition will be examined next.

3621



Fig. 10. Current and rotation rate in the metal deposition reaction

Effect of base metal ions.-The base metal ions investigated are divided into two groups for the purpose of this discussion. Pb and Tl, which UPD on gold, are in one group, and Ni and Co, which do not UPD on gold but form a series of continuous solid solutions with gold, are in the other group. The other difference to note between these two groups of base metals, which is important from the point of view of gold deposition, is the catalytic activity for hydrogen evolution each group displays. Pb and Tl exhibit high hydrogen overpotential (higher than on gold), and therefore inhibit simultaneous hydrogen evolution during gold plating. Ni and Co, on the other hand, are better hydrogen catalysts than gold and thus enhance simultaneous hydrogen generation during gold plating. It will be shown that these properties of the two groups of metals have a profound effect on the microstructure and hardness of the gold deposits.

Lead and thallium.—Polarization curves for gold deposition from an oxalate plating solution containing 15 ppm of Tl<sup>+</sup> and Pb<sup>2+</sup> are shown as a function of rotation rate in Fig. 12A and B, respectively. Both sets of polarization curves show well defined limiting currents at low rotation rates. At higher agitation, the curves develop a slope in the diffusion-controlled region of the reaction. This is probably due partly to an increase in the macroscopic surface area of the electrode, and partly to a change in the crystal growth form with increasing deposition rate of the metal, resulting from decreasing diffusion layer thickness and increasing flux of Au(CN)<sub>2</sub><sup>-</sup> ions to the electrode.

Comparison of the polarization curves obtained for gold deposition in the absence of base metal ions in the plating solution (Fig. 8) with the polarization data shown in Fig. 12 reveals two major differences. In the potential region where the gold deposition reaction is under kinetic control, there is a marked shift in the current waves towards



Fig. 11. Tafel plot for Au deposition in 0.04M KAu(CN)<sub>2</sub> in buffered solution containing organic reducing agent. Electrode area = 0.458 cm<sup>2</sup>,  $T = 65^{\circ}$ C.

less negative potentials in the presence of base metal ions. This is due to the depolarization effect induced by the base metal ions (10). Further, the deposition currents in the potential region of kinetic control exhibit dependence on agitation in the presence of Pb<sup>2+</sup> and Tl<sup>+</sup>, while in the absence of these ions in the electrolyte, the deposition currents are independent of agitation. This is because in the potential region where gold deposition is kinetically controlled, Pb<sup>2+</sup> and Tl<sup>+</sup> undergo bulk metal deposition (see Table I). The diffusion-limited deposition currents for these metals, which are rotation rate-dependent, are superimposed on the gold deposition currents, thus resulting in the agitation-dependent currents exhibited in Fig. 12. In order to construct Tafel plots and plots of 1/i vs.  $1/\sqrt{\omega}$  from the data shown in Fig. 12A and B, the partial currents for the bulk metal deposition of the base metals were subtracted from the overall currents observed. The plots of  $1/i vs. 1/\sqrt{\omega}$  are not presented here, but these plots were constructed and found to indicate that even in the presence of Pb<sup>2+</sup> and Tl<sup>+</sup> in the plating solution, the deposition of gold is first-order with respect to Au(CN)2<sup>-</sup> concentration.



Fig. 12. Au deposition: 0.04M  $KAu(CN)_2$  in buffered solution, pH = 6.5, containing oxalate 0.87M. Electrode area = 0.20 cm<sup>2</sup>, T = 65°C.



Fig. 13. Tafel plot for Au deposition in the presence of 15 ppm Pb<sup>2+</sup>. dV/dt = 20 mV/s, pH = 6.5, electrode area = 0.2 cm<sup>2</sup>,  $T = 65^{\circ}$ C.

The mass transfer-corrected Tafel plot for gold deposition in the presence of  $Pb^{2+}$  is indicated in Fig. 13. The value of the diffusion-limited current  $i_d$ , for estimating the mass transfer factor  $i_d(i_d - i)$  (Eq. [5]), was obtained from the experimental curve at 400 rpm. A Tafel slope of -130 mV per decade is obtained for gold deposition in the presence of  $Pb^{2+}$  ions. This slope corresponds to a transfer coefficient of 0.57 for a one-electron transfer at 65°C. A Tafel plot for gold deposition in the presence of Tl<sup>+</sup> was constructed and yielded a Tafel slope of -170 mV/decade, corresponding to an  $\alpha$  value of 0.44. This is strong evidence that gold deposition in the presence of Pb<sup>2+</sup> and Tl<sup>+</sup> ions in the plating solution occurs via the direct discharge of the solution phase species  $Au(CN)_2^-$ , in accordance with Eq. [9]. In the same potential range, in the absence of these base metal ions, the Tafel slope has a value of -315 mV/decade, indicating the involvement of the adsorbed AuCN in the mechanism of the gold deposition reaction. The potential range over which the Tafel plots for gold deposition in the presence of lead and thallium were constructed also happens to be the potential range in which lead and thallium UPD on gold in the oxalate gold plating solution under investigation (Fig. 4 and 5). Therefore, it appears that the adsorption of  $Pb^{2+}$  and  $Tl^+$  on gold inhibits AuCN formation, leaving the surface available for the direct discharge of Au(CN)2<sup>-</sup>. The suppression of anodic oxide formation on gold in the presence of base metal ions such as  $Tl^+$  in the electrolyte has been described earlier (22), although this was in connection with the anodic dissolution of gold.

Nickel and cobalt.—The polarization curves for gold deposition from an oxalate gold plating solution containing  $Co^{2+}$  are presented in Fig. 14. Similar curves also were obtained for solutions containing nickel. These polarization curves are different from those obtained in the presence of  $Pb^{2+}$  or  $Tl^+$  (Fig. 12) in many respects. First of all, the depolarization effect encountered in the presence of  $Pb^{2+}$  or  $Tl^+$  is not observed when  $Ni^{2+}$  or  $Co^{2+}$  are present in the plating solution. This is clearly due to the inability of  $Ni^{2+}$  or  $Co^{2+}$ 



Fig. 14. Polarization curves for Au deposition in 0.04M KAu(CN)<sub>2</sub> in buffered solution containing organic reducing agent in the presence of 15 ppm Co<sup>2+</sup>. Scan rate = 20 mV/s, pH = 6.5, electrode area = 0.2 cm<sup>2</sup>,  $T = 65^{\circ}$ C.

to UPD on gold. Second, in the presence of Ni<sup>2+</sup> or Co<sup>2+</sup> two waves are observed in the polarization curves. (This is evident at much larger magnifications than depicted in Fig. 14.) The first current wave shows a well-defined limiting current and is attributed to the diffusion-limited deposition of the base metal ion. The second current wave, which is due to gold deposition, does not show a well-defined, diffusion-limited current even at low rotation rates. This is in contrast to the behavior observed in Fig. 12, and is due to H<sub>2</sub> generation on the codeposited Ni or Co. Pb and Tl suppress H<sub>2</sub> generation, resulting in well-defined, diffusion-limited currents for gold deposition in this potential region. The diffusion-limited currents,  $i_d$ , for gold deposition in the presence of different base metal ions are presented in Table II.

Scanning electron microscopy.—The surface morphology of gold deposits was characterized by scanning electron microscopy. The effects of base metal additives and varying cathodic potential were investigated. The surface roughness was found to vary systematically with both



Fig. 15. Tafel plot for Au deposition in the presence of 15 ppm  $\text{Co}^{2+}$ T = 65°C, electrode area = 0.458 cm<sup>2</sup>.





Fig. 18. Comparison of diffraction patterns for gold films shown in Fig. 17. Top left, 15 ppm Tl<sup>+</sup>. Top right, 15 ppm Pb<sup>2+</sup>. Center, 15 ppm Ni<sup>2+</sup>. Bottom left, 15 ppm Co<sup>2+</sup>. Bottom right, no additive.

these variables, and the trends are illustrated in Fig. 16. It is noteworthy that there is no simple correlation between the surface topography reported here and the grain sizes determined by transmission electron microscopy.

Transmission electron microscopy.—About a  $10 \,\mu\text{m}$  thickness of gold was deposited onto copper substrates from the same baths as were used in the kinetic studies. The gold foils were removed from the copper substrates using nitric acid, thinned to 1000Å by ion milling, and mounted on grids for transmission electron microscopy study.

Figure 17 shows representative areas of the microstructure of gold films deposited (a) without additives and (b-e) with 15 ppm Co, Ni, Tl and Pb, respectively. The corresponding diffraction patterns are shown in Fig. 18. Microstructural and orientational data are summarized in Tables III and IV, respectively. It is immediately clear that the additives have a profound effect on the grain size and the distribution of grain sizes. Grain sizes were observed to increase in the order: Co, Ni, no additive, Tl, and Pb. In the cases of Ni, Tl, and no additives, it was found that the grain size distribution was bimodal. This indicates that in these cases the grain growth during the deposition process is partially inhibited. By contrast, in the cases of Pb and Co, the grain structures were uniformly large and small, respectively, indicating the absence of inhibition of recrystallization in the case of Pb and almost total inhibition in the case of Co. The degree of grain growth during deposition of the films was observed to correlate with the hardness of the films deposited in the presence of Co and the softness of the films deposited in the presence of Pb. The defect densities (dislocation loops, dislocation lines, and

Table IV. Orientational data

Deposition potential (vs. SCE)	Plating charge (C)	Ratio 200/111 peak intensity*
-0.975V	5	1.43
-0.975	$4\overline{0}$	22.90
-1.050	5	0.65
-1.125	5	2.61
-0.975	5	0.91
-0.975	5	1.87
-0.975	5	0.94
-0.900	5	52.89
-0.900	5	140.45
	Deposition potential (vs. SCE) -0.975V -0.975 -1.050 -1.125 -0.975 -0.975 -0.975 -0.900 -0.900	$\begin{array}{c c} \text{Deposition} \\ \text{potential} \\ (vs. SCE) \end{array} \begin{array}{c} \text{Plating} \\ \text{charge}(C) \end{array} \\ \hline \\ \hline \\ -0.975 V 5 \\ -0.975 40 \\ -1.050 5 \\ -1.125 5 \\ -0.975 5 \\ -0.975 5 \\ -0.975 5 \\ -0.975 5 \\ -0.975 5 \\ -0.900 5 \\ -0.900 5 \\ -0.900 5 \end{array}$

\*The intensity rate of 200/111 is 0.52 in a randomly oriented film.

voids) decreased in the order: Co, Ni, no additive, Tl, and Pb.

The grain growth that occurs during the deposition process is accompanied by a change in the orientation distribution of the grains. This is suggested by the diffraction patterns in Fig. 18 and confirmed for large areas by x-ray diffraction. The curvature of grain boundaries, the presence of twins which do not completely traverse grains, and the texture change observed, all indicate that the grain growth processes play a key role in the evolution of the microstructure of electrodeposited gold.

In a polycrystalline deposit of a face-centered cubic (fcc) metal where the grains are randomly oriented, the ratio of the intensities of the 200 and 111 diffraction maxima is 0.52. Deviations from this value give an indication of the extent to which the grains are not randomly oriented. In a deposit with an ideal (100) fiber texture, the 111 maximum would be absent. X-ray investigations of the five goldbased deposits made in the present study indicate an extremely strong (100) texture for the Au-Tl and Au-Pb systems. In the Au-Ni and Au-Co systems, the number of (100)-oriented grains is only slightly above that which would be expected in a random distribution of grain orientations. In addition, the proportion of (100) grains increases in all cases for thicker films; this is because more extensive grain growth occurs during the time taken for growth of thicker films. It was also observed that increasing the concentration of the grain growth-inhibiting additives (Ni and Co) drives the orientation distribution toward a more random behavior. Higher deposition potentials were shown to increase the extent of grain growth.

The microstructural observations provide an insight into the growth and mechanical properties of gold films. The final grain structure of a deposited film is governed by the interplay of nucleation, crystal growth, grain coarsening, and film thickening. Nucleation involves clusters of just a few atoms, and by the time a continuous film 1000Å thick has been formed, the microstructure is dominated by grain coarsening, *i.e.*, the density of nuclei far exceeds the density of grains, and the number of grains and their size distribution is the result of grain growth competition. This analysis is quite well established in the context of vapordeposited metal films (31) and is consistent with the observations made in this and related work concerning the elec-

Table	111.	Microstructura	data
-------	------	----------------	------

	15 ppm Co	30 ppm Co	15 ppm Ni	30 ppm Ni	No additive	15 ppm Tl	15 ppm Pb
Deposition potential	-0.975	-0.975	-0.975	-0.975	-0.975	0.975	-0.975
(VS. SCE) Smallest observed grain size	25 nm	20 nm	30 nm	25 nm	45 nm	700 nm	1100 nm
Largest observed	300 nm	150 nm	1500 nm	700 nm	2000 nm	>10000 nm	>10000 nm
Void size	1-15 nm	1.5-15 nm	5-10 nm	6-10 nm	6-15 nm		_

trochemical deposition processes. The key evidence from the present work is:

(i) The curvature of grain boundaries, which migrate toward their centers of curvature under capillarity.

(ii) The occurrence of occluded twins, which are interpreted as growth faults in an unstable grain structure formed earlier in the film growth and left behind by migrating boundaries.

(iii) The change in grain diameter from a few hundred Å to several µm with (Co, Ni) or (Tl, Pb) bath additives, respectively, which better fit a grain growth process than a varying nucleation hypothesis. Even the smallest observed grain sizes corresponding to the highest grain densities are too low to correlate with expected nucleation densities.

(iv) The change of texture from almost random to a very strong (100) fiber texture in the gold-plated from a bath with Tl or Pb additives, and the same texture change that occurs during film thickening beyond 100Å, can all be accomplished by grain boundary migrations.

(v) The broad range of grain diameter in the additive-free case shows that the grain structure of the electrodeposited Au in this study is on the verge of instability. Consequently the microstructure is extremely sensitive to perturbations in the deposition conditions.

(vi) The high density of voids and bubbles in Co and Ni additive cases impedes grain boundary motion and is thought to be responsible for the observed small grain diameter. Conversely, the virtual absence of voids and bubbles in the Tl and Pb cases permits extensive grain coarsening. Note that Co and Ni reduce the overpotential for the H<sub>2</sub> evolution, while Pb and Tl have the opposite effect.

Although the evidence for grain boundary migration during gold electrodeposition is overwhelming, the observation at such a low temperature as  $\approx 60^{\circ}$ C, *i.e.*, 0.25  $T_{\rm m}$ (where  $T_{\rm m}$  is the melting point in K) warrants further discussion. Normally (i.e., in bulk materials) the grain structure of metals is stable against coarsening and recrystalli zation below about 0.5  $T_{\rm m}$  (32). However, in growing thin films, the driving forces P<sub>i</sub> and grain boundary mobilities M can both be unusually high. The principal differences from the behavior of bulk materials stem from: the small grain sizes, which lead to a large capillarity force,  $2\nu/r$ ; the small thickness, which enhances the importance of surface energy differences,  $\Delta v/t$ ; the high yield stress,  $\sigma y = E/100$  (E is Young's modulus), which results in the possibility of large stored elastic energy  $(1/2 \sigma 2/y/E)$  per unit volume; and the excess concentration of point defects introduced during the growth process, which raises the grain boundary mobility (33).

Having established the reasons for the microstructural variations observed, it remains to correlate the structure and the hardness. The yield strength  $\sigma y$  of a polycrystalline body depends on the combination of the resistance of the individual grains to shear, which is expressed as a lattice friction  $\sigma_i$ , and the resistance offered by grain boundaries to the propagation of slip from one grain to the next, which is of the form  $kd^{-1/2}$  where k is a constant and d the grain diameter (34). The voids/bubbles in the Co/Ni films, plus the grain size effect, together result in hard gold, while the large grain size and absence of hardening from bubbles and voids in the Pb/Tl case give soft gold. Some of the very small proportions of the additives Pb and Tl in the baths may be incorporated by underpotential deposition into the gold deposit. However, the solid solution and boundary hardening effects are evidently negligible relative to the effect of additives on grain size. The grain boundary migration, which is so extensive in Pb/Tl material, can also eliminate excess dislocation and other defects that might otherwise increase  $\sigma y$ . As noted earlier, defect density decreased in the order: Co, Ni, no additive, Tl, and Pb.

Manuscript submitted Sept. 30, 1988; revised manuscript received June 19, 1989.

International Business Machines Corporation assisted in, meeting the publication costs of this article.

#### REFERENCES

- 1. M. Antler, "Gold Plating Technology," F. H. Reid and W. Goldie, Editors, Electrochemistry Publications, Ayr, Scotland (1974).
- 2. Y. Okinaka and S. Nakahara, This Journal, 123, 1284 (1976).
- 3. G. B. Munier, Plating, 56, 1151 (1969).
- 4. C. J. Raub, A. Knoedler, and J. Lendvay, Plat. Surf. Fin., 63, 35 (1976).
- 5. R. L. Cohen, F. B. Koch, L. N. Schoenberg, and K. W. West, This Journal, 126, 1608 (1979).
- E. T. Eisenmann, *ibid.*, **124**, 1957 (1977).
   J. A. Augis, C. C. Lo, and M. R. Pinnel, J. Appl. Phys., 50, 6887 (1979).
- H. Y. Cheh and R. Sard, This Journal, 118, 1737 (1971).
   D. M. MacArthur, *ibid.*, 119, 672 (1972).
   J. D. E. McIntyre and W. F. Peck, *ibid.*, 123, 1800 (1976).

- 11. E. T. Eisenmann, ibid., 125, 717 (1978).
- 12. R. Woods, "Advances in Electroanalytical Chemistry," Vol. 9, A. J. Bard, Editor, Marcel Dekker, New York (1977).
- 13. R. Cordova, M. E. Martins, and A. J. Arvia, This Journal, 126, 1172 (1979).
- D. D. Bode, T. N. Andersen, and M. Eyning, J. Phys. Chem., 71, 792 (1972).
- I. Angerstein-Kozlowska, B. E. Conway, and J. Klinger, J. Electroanal. Chem. Interfacial Electro-15. M. chem., 87, 301 and 321 (1978).
- 16. "Organic Electrochemistry," M. Baizer, Editor, Marcel Dekker, New York (1973).
- A. Capon and R. Parsons, J. Electroanal. Chem. Inter-facial Electrochem., 44, 23 (1973) and 45, 205 (1973).
- 18. P. Bindra and J. Roldan, This Journal, 132, 2581 (1985).
- 19. D. M. Kolb, "Advances in Electrochemistry and Electrochemical Engineering," Vol. 11, H. Gerischer and C. Tobias, Editors, Interscience, New York (1977), and references therein.
- 20. H. Gerischer, D. M. Kolb, and M. Prasnyski, Surf. Sci., 43, 662 (1974).21. L. C. Sillen, "Stability Constants of Metal-Ion Com-
- plex," Section 1, Special Publication No. 17, The Chemical Society.
- 22. (a) K. J. Cathro and D. F. A. Koch, This Journal, 111, 1416 (1964); (b) K. J. Cathro, Proc. Australian Ins. Min. Metall., 207 180 (1963).
- 23. M. Pourbaix, "Atlas of Electrochemical Equilibria,"
- (Engl. Trans.), Pergamon Press, New York (1966).
   24. S. Trasatti, in "Advances in Electrochemistry and Electrochemical Engineering," Vol. 10, H. Gerischer and C. Tobias, Editors, Interscience, New York (1976).
- 25. M. Hansen, "Constitution of Binary Alloys," 2nd Ed.,
- McGraw-Hill, New York (1958). 26. V. S. Bagotsky, N. A. Shomilova, and E. I. Khruscheva,
- Electrochim. Acta, 21, 919 (1976). G. Levich, "Physicochemical Hydrodynamics," Prentice-Hall, Englewood Cliffs, NJ (1962). 27. V.
- 28. J. Newman, J. Phys. Chem., 70, 1327 (1966). 29. D. S. Gnanamuthu and J. V. Petrocelli, This Journal, 114, 1036 (1967).
- W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer," p. 144, The Ronald Press Co., New York (1966).
- 31. C. R. M. Grovenor, H. T. G. Hentzell, and D. A. Smith, Acta Metall., 32, 773 (1984).
- 32. "Recrystallization of Metallic Materials," F. Haessner, Editor, Dr. Reiderer-Verlag, Stuttgart FRG (1978).
- 33. H. G. Grewe, P. F. Schmidt, and K. Schur, Z. Metallkd., 64, 502 (1973).
- 34. N. J. Petch, J. Iron Steel Inst., 174, 25 (1953).