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On the Mechanism of Cathodic Crystal Growth Processes

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ABSTRACT

An electron diffraction and electron microscopic study on thin films of copper electrodeposited on clean 1 mil foils of copper and platinum from acid-copper and complex copper-glycine baths maintained at 25°C has been conducted. The foils of copper and platinum consist of small grained structure. Results show that for a current density of 10 ma/cm² and high acidic conditions (pH 0.3 or 0.9), large crystal grains of copper (10-40μ) are developed, even when the deposit thickness is very small. A limited study on the effect of current density on the orientation of nickel, electrodeposited mainly on brass disks from some common plating solutions maintained at 25°C, has also been carried out. Results are discussed in light of existing mechanisms for the cathodic crystal growth process.

Studies on the mechanism of cathodic crystal growth processes have received considerable attention in recent years as a result of successful application of electron waves in determining the structure, orientation, and, hence, the mode of growth of cathodic deposits. Electron diffraction studies on the structure of electrodeposited metals of widely varying thickness on polycrystalline substrates suggest that these deposits are initially random and polycrystalline. They possess a fine grain structure which develops preferred orientations as the film grows thicker. These orientations which determine the mode of growth of electrodeposits were found to be profoundly influenced by bath conditions such as current density, temperature, pH, concentrations of anions and cations, presence of trace impurities and addition agents, and mechanical agitation of plating solutions (1-6). A systematic investigation of the structure of electrodeposited metals by electron diffraction and elucidation of a tentative mechanism of their growth process was first accomplished by Finch, Wilman, and Yang (1). According to their classical mechanism (1, 2), deposition conditions which favor either the plentiful supply or impoverishment of metal ions at the immediate vicinity of the cathode are the controlling factors in determining the preferred orientations developed by the deposits and hence their mode of growth. In a f.c.c. metal, the (110) orientation was supposed to be of outgrowth type whereas the (100) or (111) orienta-

tion, lateral type. Electrodeposits, however, often develop abnormal values of internal stresses (7, 8) which cannot be understood by the above mechanism. In working with nickel electrodeposited from solutions maintained at room temperature, one of the authors found recently that the outgrowth type of deposit, as characterized by the (110) orientation of nickel, is always favored at very low (0.5-1 ma/cm²) and very high (above 100 ma/cm² depending on the pH or bath temperature) current densities, whereas the lateral or transitional type of growth [i.e., (100) or (210) orientations, respectively] are favored at intermediate current densities. These results cannot be explained satisfactorily on the basis of the classical mechanism (1, 2).

These results on nickel prompted the study of the electrodeposition of copper which forms the main subject of the paper. In the present investigation, surface structure and morphology of copper, electrodeposited on thin foils of copper and platinum from three different baths were studied by electron diffraction and electron microscopy.

Experimental

The main experiments may be divided into three parts: (a) electrodeposition of copper at a current density of 10 ma/cm² from plating solutions maintained at room temperature on clean 1 mil foils of copper and platinum, (b) electron diffraction studies of these surfaces, and (c) electron microscopic

studies of the replicas of the surfaces of these electrodeposits.

Electrodeposition of copper on thin foils cleansed in suitable etching solutions was carried out from the following solutions:

[1] $CuSO_4 \cdot 5H_2O$, 120 g/l + H_2SO_4, 74 g/l, pH = 0.3

[2] $CuSO_4 \cdot 5H_2O$, 120 g/l + glycine, 25 g/l + H_2SO_4 added to give a pH of 0.9

[3] $CuSO_4 \cdot 5H_2O$, 120 g/l + glycine, 25 g/l, pH = 2.5

Bath [1] will be called an acid-copper bath and baths [2] and [3] will be called complex copper baths in the following discussions. All the chemicals used in the preparation of the solutions were of A. R. grade and the solutions were further purified by electrolyzing them at a low current density as described elsewhere (3). A foil area of *ca.* 4 cm² for deposition was available.

The copper and platinum foils, of high-purity reagent grade, were obtained from Fisher Scientific Co. (Cat. No. C-428). Before electrodeposition, the copper foils were etched for a few seconds in moderately dilute HNO_3 followed by a dip in concentrated HCl and a rinse in distilled water. An electron diffraction study of the copper and platinum foil surfaces reveal ring patterns, characteristic of polycrystalline small grained structure. The pattern for the copper foil is shown in Fig. 1. The polycrystalline structure of the copper foil can also be seen from the platinum preshadowed carbon replica of the foil surface at a magnification of 1300X (before reduction for publication) in Fig. 2.

Following electrodeposition, the deposits of copper were washed with a jet of distilled water, dried with filter paper, and immediately removed for electron diffraction studies. They were examined with a 50 kv electron beam of 25μ width at grazing incidence by the reflection technique.

For replica studies, the freshly prepared surface was covered with a few drops of a dilute collodion solution. After evaporation of the solvent, a replica of the metal surface was obtained. The collodion
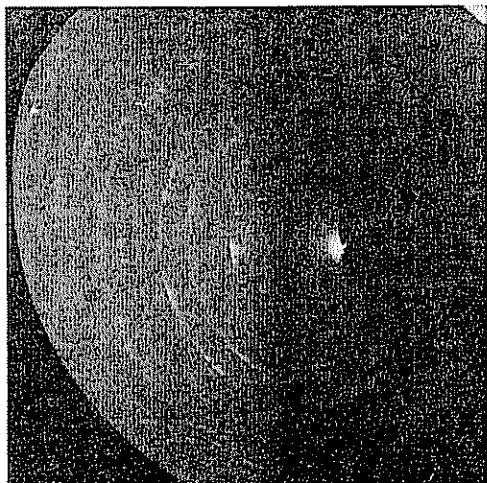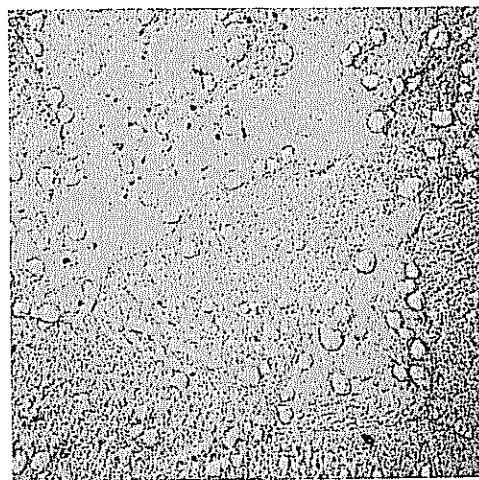

Fig. 2. Electron micrograph of the initial copper cathode, as obtained by platinum preshadowed carbon replica technique at a magnification of 1300X.

replica thus formed was removed from the metal surface (by attaching the collodion replica on to scotch tape), shadowed with platinum at angles varying from 15° to 35°, followed by deposition of a thin film of carbon in a vacuum evaporator. The collodion was then dissolved in amyl acetate and the carbon replica was collected on fine copper grids for an electron microscopic investigation.

In some limited preliminary studies, nickel was electrodeposited on mechanically polished thick brass disks and 1 mil thick foils of copper and platinum from sulfate-boric acid, chloride-boric acid, and sulfate-chloride-boric acid baths maintained at room temperature (25°C). The time of deposition was adjusted so as to have a thickness of about 3-5μ of electrodeposited nickel. Bath compositions are listed in Table II.

Results and Discussion

Results of electron diffraction studies of electrodeposited copper and nickel are presented in Tables I and II, respectively; and electron microscopic

Fig. 1. Electron diffraction pattern for clean copper substrate, revealing polycrystalline and small grained structure of initial cathode surface.

Table I. Electron diffraction studies on copper, electrodeposited at 10 ma/cm² and 25°C on 1 mil thick copper and platinum cathodes

| Bath	Time of depo-sition, min	Cathode substrate	Remarks on electron diffraction patterns	Figure
1	5-10	Cu	Spot pattern showing reflection, probably from (200) face of copper	3
1	5	Pt	Nearly spot pattern showing (110), preferred orientation	4
2	8-12	Cu	Spot pattern showing reflection from (111) face	5
3	10	Cu	Ring pattern showing (10$\bar{1}$0) + (211) preferred orientation	6
3	25	Cu	Dotted arc pattern showing (10$\bar{1}$0) + (211) preferred orientation	7
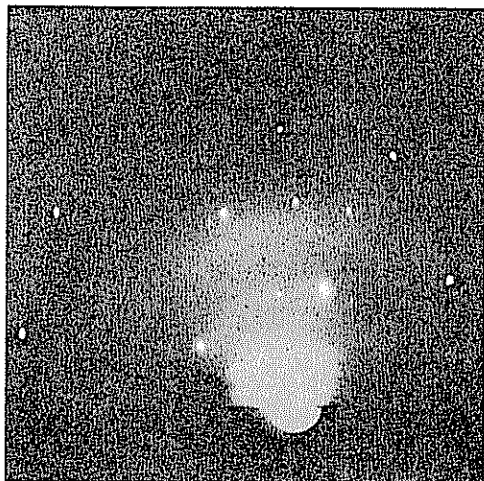
Fig. 3. Electron diffraction patterns of electrodeposited copper. See Table I for experimental details.
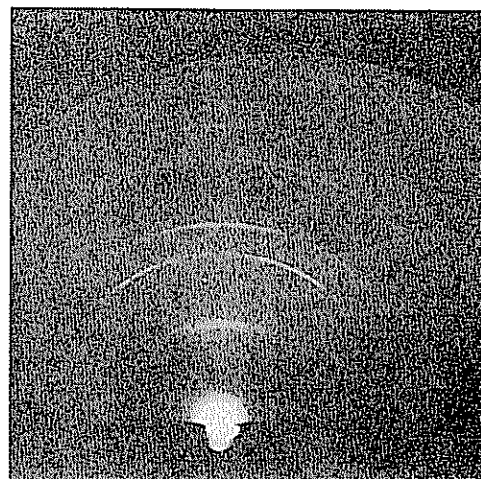

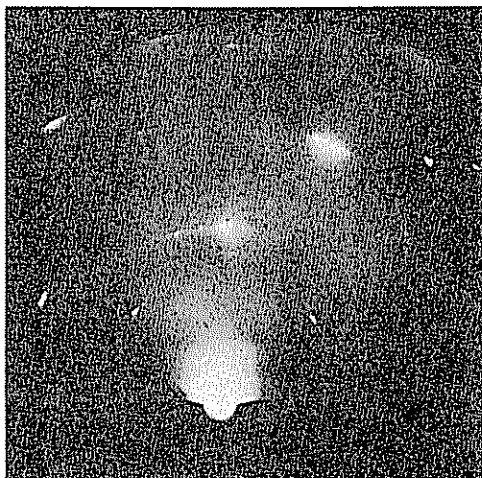Fig. 6. Electron diffraction patterns of electrodeposited copper. See Table I for experimental details.

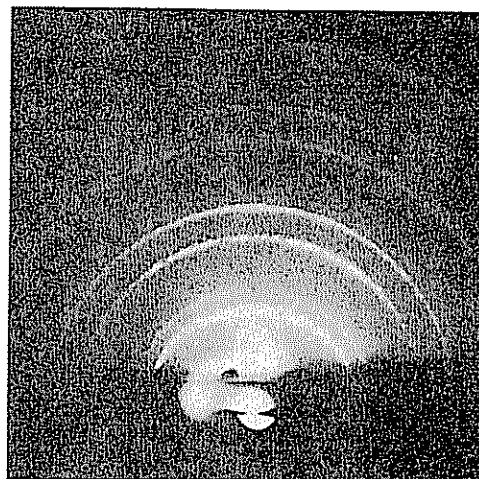Fig. 4. Electron diffraction patterns of electrodeposited copper. See Table I for experimental details.

Fig. 7. Electron diffraction patterns of electrodeposited copper. See Table I for experimental details.

figures listed in Table I. Bath [3] favors the development of a $(10\bar{1}0)$ + (211) preferred orientation of electrodeposited copper on 1 mil copper foils for short deposition times. Longer deposition times generally result in dotted arc patterns having larger grain sizes, as can be seen from Fig. 6 and 7.

Table II. Effect of current density on orientations of electrodeposited nickel at 25°C

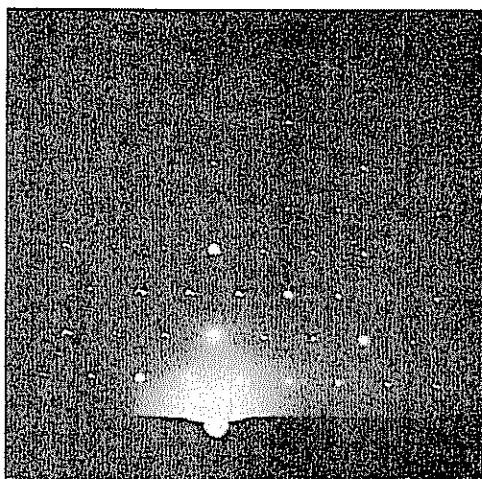| Bath	pH	Current density in ma/cm²	Orientations
$NiSO_4 \cdot 7H_2O$, 280 g/l	3.5	1	(110)
		10	(100)
+ H_3BO_3, 31 g/l		25	(210)
		45	(210) + (110)
		75, 100	(110)
$NiCl_2 \cdot 6H_2O$, 150 g/l	4.9	1	(110)
		10 to 50	$(10\bar{1}0)$ + (211)
+ H_3BO_3, 31 g/l		75, 100	(210)
		200	(110)
$NiSO_4 \cdot 7H_2O$, 280 g/l	3.6	1	(110)
		10	(100)
+ $NiCl_2 \cdot 6H_2O$, 48 g/l		20	(100) + (210)
		45	(210)
+ H_3BO_3, 31 g/l		75	(210) + (110)
		100, 200	(110)

Fig. 5. Electron diffraction patterns of electrodeposited copper. See Table I for experimental details.

studies of surfaces of electrodeposited copper are presented in Table III. Table I shows that under high acidic conditions, *i.e.*, baths [1] and [2], copper electrodeposited on 1 mil thick foils of copper and platinum (as cathodes) yields spot electron diffraction patterns, indicating a larger grain size. These results can be seen by studying the appropriate

Table III. Electron microscopic studies on copper surfaces, electrodeposited from different baths at 10 ma/cm² and 25°C (Magnification, 1300X before reduction for publication)

Deposition conditions	Time of deposition, min	Average grain size, μ	Figure
Bath [1], on 1 mil Cu foil	5	~35	8a
	10	>45	8b
Bath [1], on 1 mil Pt foil	5	Elongated grains more than 35μ in length and 10μ in breadth	8c
Bath [2], on 1 mil Cu foil	5	~10	9a
	10	~23	9b
Bath [3], on 1 mil Cu foil	5	<3	10a
	15	~7	10b

It is seen from Table II that very low and high current densities always favor the development of (110) preferred orientations of nickel, electrodeposited on mechanically polished brass disks as well as on thin foils of copper and platinum at 25°C from three commonly used nickel plating solutions. The trend of the results shown in Table II is maintained for all possible pH conditions for any of the baths used (9).

An estimate of the grain size of electrodeposited copper, as obtained under various conditions of deposition, was made possible by an electron microscopic study of the replicas of the surface.[1] The results are presented in Table III. It is noted that deposits with grains larger than 35μ separated by well-defined grain boundaries are obtained, even in very thin deposits, from bath [1] as compared with much smaller grains, even in comparatively thicker deposits, from bath [3] under otherwise identical conditions of deposition. This may be seen by comparing electron micrographs, Fig. 8a, 8b, and 8c with Fig. 10a and 10b. Relatively large grain deposits are also evident from bath [2], as seen in micrographs, Fig. 9a and 9b.

Results on the formation of unusually large grains

[1] A longer time of deposition generally gives rise to larger grain size of deposits for identical conditions of deposition. The thickness of the deposits was found to depend mostly on the time of deposition for all three baths used for copper plating.
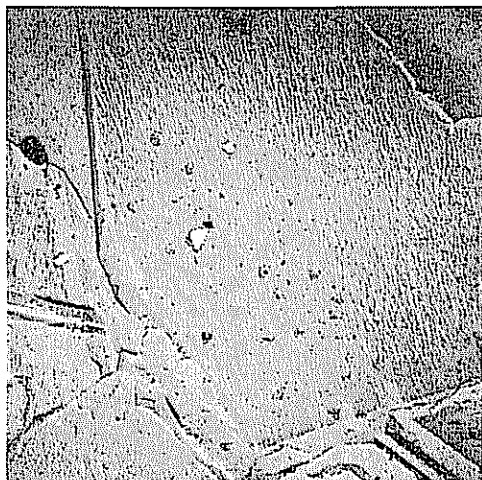
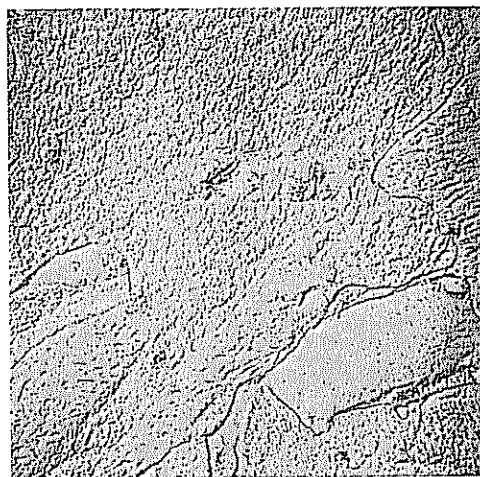Fig. 8a. Electron micrographs of electrodeposited copper surfaces. See Table III for experimental details.

Fig. 8b. Electron micrographs of electrodeposited copper surfaces. See Table III for experimental details.
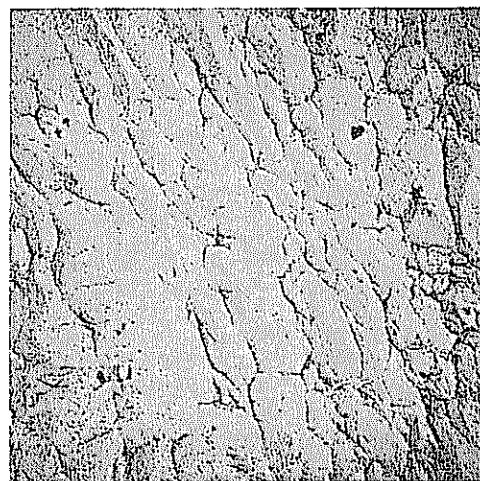
Fig. 8c. Electron micrographs of electrodeposited copper surfaces. See Table III for experimental details.
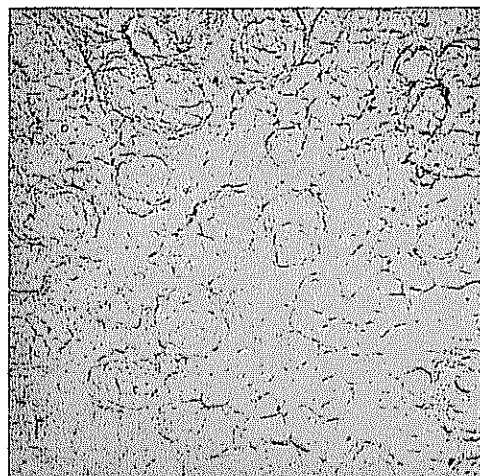
Fig. 9a. Electron micrographs of electrodeposited copper surfaces. See Table III for experimental details.

of electrodeposited copper, resulting in spot electron diffraction patterns, or the development of much smaller grains, depending on the bath conditions used, cannot be understood fully on the basis of the classical mechanism for cathodic crystal growth processes proposed by Finch, Wilman, and Yang (1). Other possible explanations can be considered briefly.
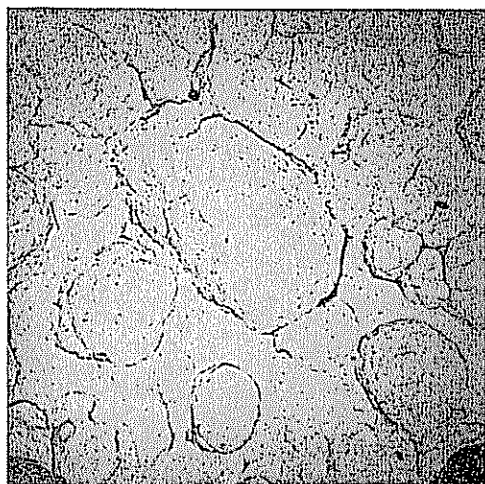
Fig. 9b. Electron micrographs of electrodeposited copper surfaces. See Table III for experimental details.
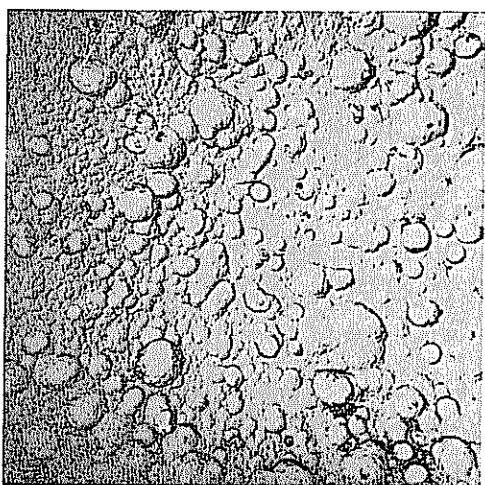

Fig. 10a. Electron micrographs of electrodeposited copper surfaces. See Table III for experimental details.
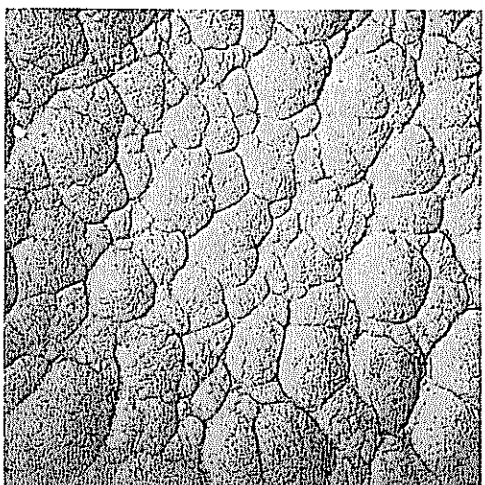

Fig. 10b. Electron micrographs of electrodeposited copper surfaces. See Table III for experimental details.

According to the dislocation theory of crystal growth, which was first proposed by Frank and his co-workers (10) and applied by Vermilyea (11), Cabrera and Vermilyea (12), and others (13) to explain various aspects of cathodic growth, a crystal can grow at a fast rate if there are present on the growing surface numerous imperfections in the form of kinks in steps of screw dislocations emerging at the surface. If atoms are deposited at kink sites or migrate there at a fast rate by a process of diffusion, a crystal grain may grow at a rapid rate resulting in large grained deposits. It is believed (12, 13) on the basis of dislocation theory that crystal growth occurs by movement of steps over close packed surfaces. When a crystal is exposed to a supersaturated medium, only those steps can advance which have a radius of curvature greater than a critical value, depending on the edge energy of a step per unit area and free energy decrease per unit volume accompanying deposition (the latter being proportional to supersaturation or overvoltage). Strongly adsorbed impurity particles such as atoms, ions, or molecules can prevent the movement of steps with which they are in contact. The larger particles by virtue of having smaller vibrational frequencies than metal atoms are likely to be embedded into the growing crystals. Dissolved oxygen from an acid-copper bath or glycine and codeposited hydrogen from a complex copper-glycine bath may thus radically alter the growth velocity at a given supersaturation of the species in the catholyte layer.[2] Since immobile, adsorbed impurities are more effective than mobile impurities in retarding and ultimately stopping the flow of growth steps and consequently growth of large crystals, we have reason to believe that dissolved oxygen is much more mobile than glycine or codeposited hydrogen so far as the advance of steps on growing cathode surfaces are concerned. The fact that abnormally large crystals showing spot electron diffraction patterns result during electrodeposition from an acid-copper bath which contains no impurity other than dissolved oxygen strongly suggests the above contention. This point has recently been thoroughly discussed by van der Meulen and Lindstrom (14). However, such impurities as H^+, OH^-, H_2O, or Cu^+ which are inherent with the bath may also be effective in producing dislocations and maintaining them on the growing surface.

Development of large grains may also take place as a result of coalescence of existing smaller grains if the temperature of the growing surface is sufficient to promote such a process. According to Wilman (7, 8) heat evolved as a result of neutralization of ions into atoms as well as metallic bond formation during electrodeposition may raise the temperature of a growing cathode surface well above its recrystallization temperature. Wilman suggests that such a temperature rise can, in part, be caused by the highly porous nature of some cathode deposits. This high porosity[3] results in a low thermal conductivity for the growing cathode and makes incorrect an estimate of rise in surface temperature if the growing cathode is assumed to have thermal conductivity values usually assigned to solid metals. Large

[2] The interference in crystal growth by colloidal copper hydroxide (or basic sulfate) present in the cathode film region, rendered more alkaline as a result of hydrogen discharge as compared with the bulk pH of the complex copper-glycine bath, is also a possibility.

[3] The porosity of electrodeposited metal generally decreases with increasing thickness (17). In fact, under certain conditions of deposit, as was observed by Ogburn and Benderly (18) in the case of nickel, an electrodeposited metal film as thin as 5μ can be formed essentially pore free. Our deposits, however, were much thinner than 5μ and may have contained considerable porosity.

amounts of internal stresses, which are developed in electrodeposits during the plating process (15), may deform surface layers of the original cathode to a considerable extent.⁴ This deformation may introduce lattice defects such as vacancies, interstitials, dislocations, and stacking faults on the cathode surface contributing to a lattice disturbance, which according to Broom and Barrett (16) is responsible for a large scattering of conduction electrons resulting in lower electrical conductivities for cathode-deposit interfacial layers. Development of large grains during electrodeposition can then possibly be explained by the combination of a rapid growth rate due to the presence of imperfections on the cathode surface and a predominantly stress-activated coalescence mechanism, where the recrystallization temperature will be appreciably lowered by deformation of the electrodeposited metal (19, 20). In this connection, Boudart (21) has shown by calculations that the heat evolved as a result of metallic bond formation is considerably lowered if the work function of the metal surface is raised due to chemisorption of hydrogen. The efficiency of the complex copper-glycine bath is reduced due to evolution of hydrogen at the cathode during electrodeposition. Whatever be the temperature of the growing cathode, it is possible that this evolved hydrogen may partly be chemisorbed on the growing surface and result in inhibition of grain growth by decreasing this temperature.

The transmission of heat through a porous material containing numerous defects is a complex phenomena, and little information is available on interaction of these defects not only with phonons but also with other adsorbed species from the catholyte layer. This we feel is partly responsible for the lack of a quantitative understanding of the crystal growth process at the present time. Hoffman and co-workers (22) calculated a temperature rise of about 700°C during the evaporation of nickel on mica under high vacuum at the instant at which the energy is shared by the first and second neighbors of a site. This temperature rise can be much larger in the case of electrodeposition of nickel or copper since the energy of neutralization is six times larger (7) than the energy required to incorporate neutral metal atoms into a crystal. The important question arises whether this idealized high-temperature pulse for a particular layer of deposited atoms would disappear by thermal conductivity with a relaxation

time of the order of 10^{-12} sec before the second layer of freshly deposited atoms appear on the surface. Also a full understanding of the properties of imperfections based on complete information on a variety of metal is necessary before one can arrive at a final conclusion as to the exact mechanism of the cathodic crystal growth process.

Acknowledgments

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⁴ We have recently observed with electron microscopy, using a platinum preshadowed carbon replica technique, the development of subgrain structure and facets on copper or aluminum cathode surfaces when a very thin film of nickel is electrodeposited at room temperature (25°C) from a Watts' type of bath of pH 3.2 and at a current density of 10 ma/cm². Since deformation of surface layers plays an important role in subgrain formation (19), although it is in general a thermally activated process (19), we believe that the cathode surface undergoes rearrangements during electrodeposition. This will be discussed in a later paper.