Surface Roughness Effects in the Electrodeposition of Copper in the Limiting Current Range

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R. Piontelli, B. Mazza, and P. Pedeferri[36]: This paper gives very interesting information on some of the problems involved by the formation of powdery deposits.

The authors[37] consider the decisive condition to be that of reaching the limiting current of mass transport. As a matter of fact this is often a sufficient condition. It does not appear, however, to be a necessary one. Moreover, the mere statement that in the limiting current range, powdery deposits are often encountered, does not appear to throw sufficient light on the mechanism of the phenomena itself. Like the whole field of electrocrystallization this problem is still wanting a satisfactory solution.

Some suggestions arising from the systematic work carried out in this laboratory[38] on the powdery-deposits formation from sulfamate baths[39] may be recalled here. The incoherent deposits of the various classes (spongy, coarse-powdery, blacks) are formed in any case, starting from tridimensional nuclei, mutually independent and in respect to the basis metal.

The possibility of formation and the kind of the incoherent deposit depends on the relative formation rate of the nuclei themselves, which must be high enough, and on the distribution in space of their growth rate, which must be tendentially isotropic.[40]

In this sense a very essential role is played by the throwing power at the microscopic scale, largely decided by the rate of change of the overvoltages with current density, the contribution of the concentration polarization included. In this general frame the importance of the limiting current conditions, in view of the separation of powdery deposits, may find a reasonable interpretation, when one considers that everywhere the ratio: current density/activity of the metal ions attains high enough values; also the ensuing concentration polarization may be sufficient to deviate the cathodic metal separation, thus promoting a tendentially isotropic growth.

On the other hand also the intervention of factors, which appear to be rather underestimated by the "limiting current theory" of the powdery deposits formation, must be taken into account. This, especially in view of the study of the formation conditions of powdery deposits from complex-salt baths or from melts, and of explaining the transition from dendritic or spongy to powdery-deposits.

Among these factors one may recall: (A) the nature of the metal, as far as the exchange overvoltages, their dependence law on current density, the influence of the lattice forces on the properties and behavior of nuclei are concerned; (B) factors influencing the secondary inhibition effects by hydrogen, colloidal products, but also by anions, secondary constituents of the baths, etc.; and (C) the physical and mechanical conditions (also apart from their direct influence on the mass transfer).

As in many other fields of the theory of electrode processes, the models which do not explicitly acknowledge the direct influence of the nature of the metal and of the bath constituents, are at least incomplete.

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[37] See also N. Ibl, "Advances in Electrochemistry and Electrochemical Engineering," P. Delahay and C. W. Tobias, Editors, Vol. 2, pp. 49-143, Interscience Publishers, New York (1962).
[38] B. Mazza, P. Pedeferri, R. Piontelli, and F. Siniscalco, *Electrochimica Metallorum*, 1, 441 (1966); *ibid.*, 1, 449 (1966); see also "Proceedings of the Symposium on Sulfamic Acid and its Electrometallurgical Applications (Milan, May 1966); Associazione Italiana di Metallurgia, Editor; Milan (1967).
[39] Also in this field the sulfamate baths appear to be especially interesting in view of their versatility and capacity to give powders (of Cu, Ag, Zn, Cd, Ni, Co, Pb, Sn and others) free from inclusions and contamination.
[40] A predominating growth-rate parallel to the basis metal may lead to compact deposits, while one normal to the cathode enhances the dendritic or acicular growth.

N. Ibl[41]: The remarks of Piontelli *et al.*, are very pertinent. Reaching the limiting current is indeed in general a sufficient, but not always a necessary condition for the formation of a very rough or powdery deposit. We have discussed this question in more detail in a previous review paper[42]. Powdery or spongy deposits can be obtained well below the limiting current. A well-known case is the formation, at lower currents, of spongy Zn or Cd deposits from nonacidified sulfate solutions, a phenomenon which is very probably not due to mass transfer effects[42]. However, if no other causes of powder formation are operative at lower currents, the deposit, as a rule, becomes very rough or powdery when the limiting current is reached.

But the properties of the powders obtained at the limiting current are also affected by other factors[42] beside mass transport. For instance, we have found that copper powder deposited from a nonacidified copper sulfate solution containing gelatin is very finely divided and almost black, whereas the powder obtained without addition of gelatin is much coarser and reddish in color.[43] But in both cases powder formation starts at the limiting current. As pointed out by the authors, the structure of electrodeposits depends in general on a number of factors and their interaction. One of these factors is mass transport. Its role can be more or less important, depending on the circumstances. Sometimes it is negligible, but in certain cases it is predominant.

Undoubtedly, many factors finally contribute to shape the structure and the properties of an electrodeposit, but the main fact which I would like to point out here is that we can visualize a pure trans-
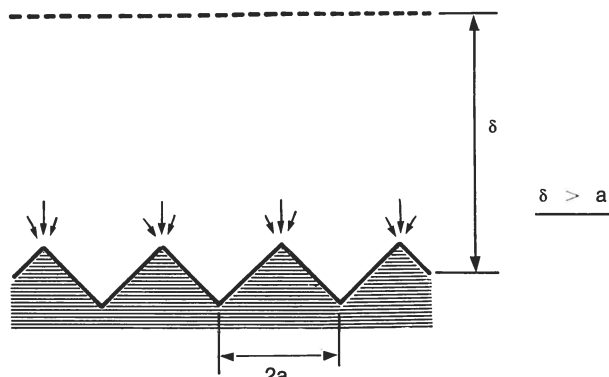
$\delta > a$

Fig. I.

port mechanism which should, in a very general way, cause the formation of a very rough deposit, at the limiting current as a rule, and, under certain circumstances, already below the limiting current. The leading ideas, which have been developed in more detail in a recent review paper[44], are as follows:

Let us consider a metal surface which has some initial roughness, with small crests and recesses, as shown schematically in Fig. 1. We will now discuss the question under which conditions certain factors tend to enhance the irregularities of the surface, and how they operate. This is a problem of current density distribution.

If the characteristic length a of such a profile is small as compared to the thickness of the diffusion layer δ (Fig. 1), the crests of the profile are priviledged from the viewpoint of mass transport, because the free cross section for diffusion increases with increasing distance from the crest: the crest

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[42] N. Ibl, "Advances in Electrochemistry and Electrochemical Engineering," P. Delahay and C. W. Tobias, Editors, Vol. 2, p. 49. Interscience Publishers, New York (1962).
[43] N. Ibl, *Helv. Chim. Acta.*, 37, 1149 (1954).
[44] N. Ibl, Proceedings of the International Conference, "Protection against Corrosion by Metal Finishing," Basle, Switzerland, November 1966, p. 48, Forster Verlag, Zurich, Switzerland.

is more accessible for mass transfer than a recess. However, this does not yet mean that the local current density is necessarily larger at the crest, because the current density distribution depends not only on the transport of mass but also on the transport of charges through the solution and through the electric double layer at the interface, i.e., it also depends on electric quantities (conductivity of the solution, overvoltage). Depending on the conditions, the current distribution is governed mainly by the transport of mass, or of charge, or by both simultaneously to a comparable degree.

Let us now consider the simple case that the current distribution is given solely by the geometry of the system and by the conductivity of the solution. We then have what is called in plating primary current distribution. Under these conditions, the local current density is larger at a crest than in a recess because the crest is privileged from the viewpoint of the transport of charges through the solution: the lines of electric flux converge toward the crest (Fig 1). Now, if we take into account overvoltage, the situation is changed: the overvoltage tends to make the current distribution more uniform (secondary current distribution). The decisive quantity is the polarization parameter P defined as the product of the specific conductivity of the solution κ and the slope of the current voltage curve, $d\eta/di$: $P = \kappa d\eta/di$. If P is large as compared to the characteristic length a of the profile, the current distribution is virtually uniform over the profile[45], in spite of the influence of the serrated geometry. This can be interpreted, at least qualitatively, in a simple manner. Along the interface, between crest and recess (Fig. 1), there is, in the solution, an ohmic potential drop ΔE_R, which must be compensated by the difference $\Delta\eta$ between the overvoltage at the crest and in the recess

$$\Delta E_R + \Delta\eta = 0 \qquad [1]$$

If the overvoltage η increases rapidly with increasing current density i ($d\eta/di$ large), a negligible increase in current at the crest will be enough to create an increase in overvoltage which is sufficient to compensate ΔE_R, and the current density is virtually the same at the crest and in the recess.

Let us now consider separately concentration and activation overvoltage, which we denote by η_c and η_a, respectively; we therefore split the total overvoltage difference $\Delta\eta$ in two parts, $\Delta\eta_c$ and $\Delta\eta_a$, which correspond to concentration and activation overvoltage, respectively. Equation [1] thus takes the form

$$\Delta E_R + \Delta\eta_c + \Delta\eta_a = 0 \qquad [2]$$

In this equation, $\Delta\eta_c$ and $\Delta\eta_a$ have not the same sign. This can be seen as follows. If the current distribution is virtually uniform, the lines of the electric flux and those of the flux of mass do not converge toward the crests as indicated in Fig. 1, but are essentially parallel, vertical lines. The concentration c_i of the metallic cations at the interface electrode-solution is then larger at the crest than in the recess; the difference Δc_i between the interfacial concentration at the crest ($_cc_i$) and in the recess ($_rc_i$) is given by

$$\Delta c_i = {_cc_i} - {_rc_i} = h\, dc/dy \qquad [3]$$

where h is the vertical distance between crest and recess and dc/dy the concentration gradient in the vertical direction[46]. We see that the concentration overvoltage is larger in the recess than at the crest; therefore, $\Delta\eta_c$ is of the same sign as ΔE_R but has the opposite sign of $\Delta\eta_a$. We thus come to the important conclusion that only activation overvoltage neces-

sarily tends to flatten the current distribution; in the case of a microprofile ($a < \delta$), concentration overvoltage cannot contribute to making the current distribution more uniform than would correspond to primary current distribution; to the contrary, it counteracts the equalizing action of activation overvoltage and tends to make the current distribution nonuniform. The extent of the departure from an even distribution depends on the relative values of ΔE_R, of $\Delta\eta_c$ and of $d\eta_a/di$, i.e., of the variation of the activation overvoltage with current density. If $\Delta\eta_c$ is large, the current distribution will be nonuniform even if the slope of the current voltage curve, $d\eta/di$, is large. An extreme case is that of the limiting current. It can be easily shown that $\Delta\eta_c$ is proportional to $\ln\,(_cc_i/_rc_i)$; at the limiting current, or close to it, $_rc_i$ tends to zero, whereas $_cc_i$ is still finite; the value of $\Delta\eta_c$ thus tends to be exceedingly large. Under these conditions, the influence of concentration overvoltage is overwhelming and the current distribution is controlled by mass transport. Since the crests of a microprofile are privileged from the viewpoint of diffusion, under mass transport control, the local current density is larger on a crest than in a recess. Geometric irregularities of the surface will then tend to grow.

The surface of a polycrystalline metal is usually heterogeneous. This causes local variations of the activation overvoltage, and therefore of the current density, which are, in general, randomly distributed, both in location and in time. There is thus a natural tendency for the formation of small, geometric irregularities in the deposit. Below the limiting current, the concentration overvoltage changes only slowly, and the influence of activation overvoltage on the current distribution at a microprofile is often predominant. If the polarization parameter P is sufficiently large, the small protuberances of the surface, randomly distributed in space and in time, are, on the average, not privileged; the local current density tends to be the same on the crests and in the recesses and, on the time average, peaks do not grow faster than the rest of the deposit. At the limiting current, however, the situation is very different. According to the above discussion, the current distribution is mass transport controlled and the current density is larger at the peaks, which thus grow faster; the irregularities of the surface are strongly amplified: there is, at the limiting current, a sort of instability with respect to small protuberances present by chance on the surface, and a very rough or dendritic deposit results.

Let us note that, under certain circumstances, a similar situation prevails even below the limiting current, or at least already when the limiting current is being approached. The essential condition is that the rate of change of activation overvoltage with current density, $d\eta_a/di$, is sufficiently small. If this is the case, the current distribution over a microprofile is nonuniform, and the deposit tends to become very irregular even at low currents. The activation overvoltage is usually very small in the deposition of metals from fused salts, because the high temperatures involved much accelerates the ion exchange at the interface. But it is sometimes also very low at room temperature in aqueous solutions, for instance, in the deposition of Ag from aqueous $AgNO_3$. It is well known that it is indeed very difficult to get even deposits in molten salt electrolysis, and that metals of an irregular, dendritic form are usually obtained. Similarly, in the deposition of silver from an aqueous $AgNO_3-$ solution there is a marked tendency for the formation of long dendrites and needles which grow outward into the solution. This is in qualitative agreement with the above discussion.

Generally speaking, the formation of very rough or dendritic deposits is necessarily linked with nonuniform current distribution. It is therefore to be expected that the factors which govern current den-

[45] C. Wagner, This Journal, 98, 116 (1951).
[46] A more quantitative treatment along these lines has been developed and compared with experiment (unpublished calculations of J. Levkov and N. Ibl). The results will be published later.

sity distribution (conductivity of the solution, overvoltage, and mass transport) have a very great influence on the structure of electrodeposits. It was the main purpose of the paper under discussion, and of some of our earlier articles, to stress these aspects which have been hitherto rather neglected in the literature. Undoubtedly, factors such as the formation of new nuclei and the rate of growth of already existing crystals play an eminent role in electrocrystallization. But they have been already studied by quite a number of authors.