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# The structures of zinc electrodeposits formed at low current densities

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An examination of zinc electrodeposits formed at low current densities, mainly from alkaline zincate electrolytes but also from pyrophosphate, cyanide and acid sulphate baths, showed that the structures depend more on the cathode potentials than on current densities. Similar structures were formed at the same potentials but at different current densities, varied by changing temperature and making organic additions to the baths. The forms of the deposits are consistent with mechanisms which change from growth along close-packed crystal directions at low overpotentials to random growth at large overpotentials.

## 1. Introduction

Interest in zinc plating from alkaline zincate solutions is not new [1]. Pure electrolytes, consisting only of zinc metal and caustic soda, give black powdery deposits over almost the entire range of acceptable operating current densities [2, 3]. Semi-bright or bright deposits can be obtained from alkaline baths with current densities of $10^2$ to $10^3$ A m$^{-2}$, but only with the aid of organic additives to the electrolytes [4].

This paper describes an investigation into the variations with current density of electrodeposit structure, particularly at low current densities.

## 2. Experimental details

Most work was done using an electrolyte containing ZnO and NaOH. Organic additives used were polyethyleneimine (PEI) of molecular weight 5000 and triethanolamine (TEA). Other electrolytes were also used. The solutions were

(a) 10 g litre$^{-1}$ ZnO, 100 g litre$^{-1}$ NaOH

(b) 40 g litre$^{-1}$ $ZnSO_4 \cdot H_2O$, 200 g litre$^{-1}$ $K_4P_2O_7$

(c) 32 g litre$^{-1}$ Zn, 80 g litre$^{-1}$ NaOH, 72 g litre$^{-1}$ NaCN

(d) 180 g litre$^{-1}$ $ZnSO_4 \cdot H_2O$, 14 g litre$^{-1}$ $ZnCl_2$, 12 g litre$^{-1}$ $H_3BO_3$.

Electrodeposits were obtained under constant current or constant potential conditions. In all cases, a mild steel substrate was used and electrodeposition continued until a deposit weighing about 70 g m$^{-2}$ was obtained, as estimated from the current densities and current efficiencies.

The electrodeposits were examined visually, by scanning electron microscopy and by X-ray diffraction.

## 3. Results

Both temperature changes and the presence or absence of additives influenced the polarization curves for alkaline electrolytes as shown in Fig. 1. The limiting current densities for pure electrolytes at 20 and 50° C were ~120 and ~250 A m$^{-2}$, respectively. Examples of the surface morphologies of the zinc electrodeposits are shown in Figs. 2 and 3.

In the absence of additives, the deposits formed when the potential was more positive than about −1.35 V either had a spongy appearance, as in Fig. 2a, and were pyrophoric when dry, or had a leaf-like structure, as in Fig. 2b. When the potential was more negative, a flatter surface was obtained with many crystalline shapes clearly evident (Fig. 2c). At 20° C and at potentials more negative than ~ −1.5 V, where the measured current density of ~200 A m$^{-2}$ exceeded the limiting current density for zinc deposition,

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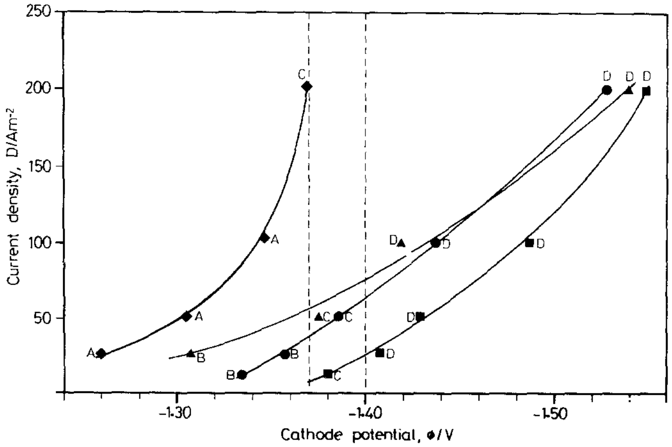


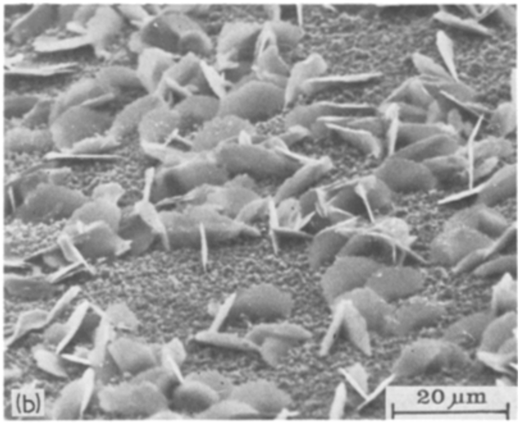
*Figure 1* The relationship between current density and cathode potential with respect to a normal hydrogen electrode for alkaline electrolyte (a). ▲ pure electrolyte, $T = 20°$ C, ◆ pure electrolyte, $T = 50°$ C, ■ electrolyte containing 5 g litre$^{-1}$ PEI, $T = 20°$ C, ● electrolyte containing 5 g litre$^{-1}$ PEI, $T = 50°$ C. A = spongy deposit, B = leaf-like deposit, C = crystalline deposit, D = smooth deposit.

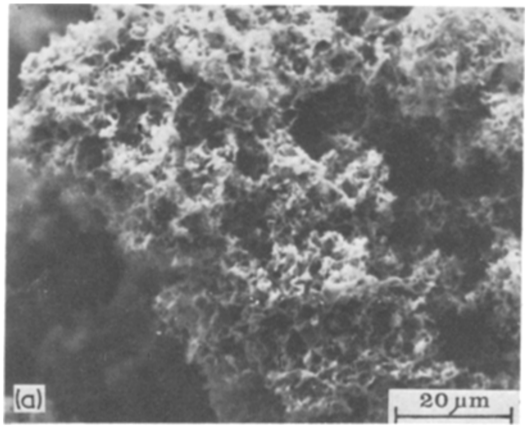
hydrogen was evolved and the deposit reverted to a powdery nature.

Altering the temperature changed the range of cathode potentials which could be obtained for the same range of current densities without involving other changes. The structures of the deposits appeared to depend on the potentials rather than on the current densities, i.e. deposits formed at the same cathode potential but at different temperatures and current densities had similar structures.

The presence of organic additives in the electrolyte affected the forms of the deposits produced at both high and low potentials, but had little effect on those formed at potentials between $\sim -1.37$ and $\sim -1.40$ V. Low current densities and potentials less negative than $\sim -1.37$ V always gave leaf-like deposits (Fig. 3a). Between $\sim -1.37$ and $\sim -1.40$ V, crystalline deposits were formed (Figs. 3b and c), whilst smooth deposits were obtained at potentials more negative than $-1.40$ V (Fig. 3d).

The general pattern of these results was identical for experiments carried out at constant cathode potential and at constant current,





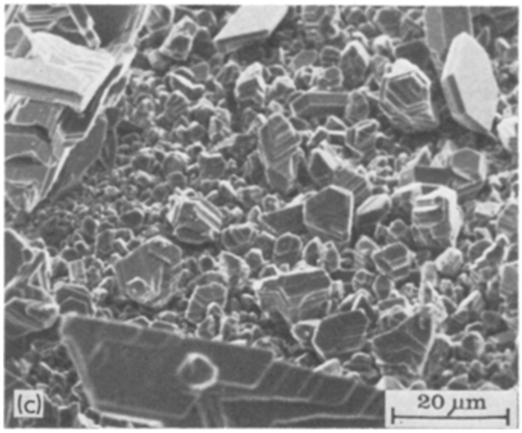


*Figure 2* Electrodeposits from pure alkaline electrolyte: (a) current control, $\phi = -1.30$ V, $D = 50$ A m$^{-2}$, $T = 50°$ C, (b) potential control, $\phi = -1.32$ V, $D = 17$ A m$^{-2}$, $T = 20°$ C; (c) current control, $\phi = -1.37$ V, $D = 200$ A m$^{-2}$, $T = 50°$ C.

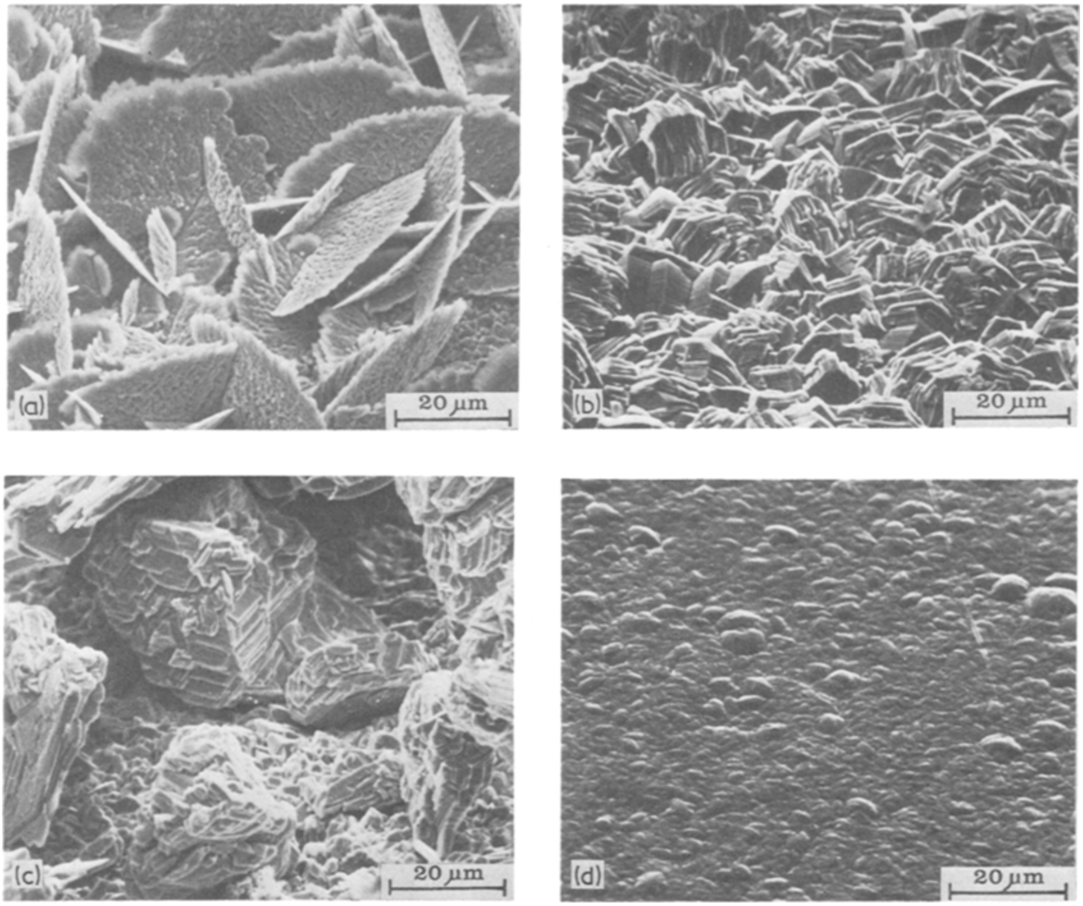


*Figure 3* Electrodeposits from alkaline electrolyte with organic additives: (a) 5 g litre$^{-1}$ PEI, current control, $\phi = -1.36$ V, $D = 25$ A m$^{-2}$, $T = 50°$ C; (b) 5 g litre$^{-1}$ PEI, current control, $\phi = -1.39$ V, $D = 50$ A m$^{-2}$, $T = 50°$ C; (c) 15 g litre$^{-1}$ TEA, potential control, $\phi = -1.40$ V, $D = 70$ A m$^{-2}$, $T = 35°$ C; (d) 5 g litre$^{-1}$ PEI, current control, $\phi = -1.53$ V, $D = 200$ A m$^{-2}$, $T = 20°$ C.

provided in this latter case that the potential did not alter much during the experiment. At low overpotentials, leaf-like structures appear to be encouraged by constant potential conditions.

For the other electrolytes studied, the results followed a broadly similar pattern. Deposits from pure acid-sulphate (solution d) with a small overpotential were spongy (Fig. 4a) and similar to those from alkaline solution at the lower range of overpotentials. Additions of dextrine resulted in the formation of leaf-like structures (Fig. 4b). Greater overpotentials in cyanide solution produced smooth deposits similar to those from alkali at high overpotentials (e.g. Fig. 3d).

The chemical compositions of the deposits from alkaline solution were determined by electron probe micro-analysis. In all cases, the zinc content was not less than 99.5%. Traces of oxygen were found and carbon was also present in deposits formed in the presence of organic additives.

The results of X-ray diffraction experiments are given in Table I. Crystalline deposits were obtained in all cases. Strong diffraction lines were obtained in many cases from $\{1\,1\,\bar{2}\,0\}$ planes, which indicated that a close-packed direction in the zinc crystals was perpendicular to the surface and was the probable growth direction of the crystals. Similar observations have been made for deposits from cyanide by Lindborg *et al.* [5]. Grain sizes were estimated from line broadening, although in many cases no perceptible broadening was found.

TABLE I Results of X-ray diffraction experiments

| Cathode potential NHE, $\phi$ (V) | Current density, $D$ (A m$^{-2}$) | $T$(° C) | $\phi$ or $I$ control | Additive | Grain size | Crystallographic texture | Surface appearance |
|---|---|---|---|---|---|---|---|
| −1.34 | – | 20 | $\phi$ | none | large | no data | spongy |
| −1.36 | 25 | 50 | $I$ | 5 g litre$^{-1}$ PEI | large | $\{10\bar{1}1\}\{11\bar{2}0\}$ | leaves |
| −1.37 | – | 20 | $\phi$ | none | large | no data | spongy |
| −1.37 | 200 | 50 | $I$ | none | large | $\{10\bar{1}1\}$ | crystals |
| −1.38 | – | 35 | $\phi$ | 6.3 g litre$^{-1}$ PEI | large | no data | crystals |
| −1.38 | 50 | 50 | $I$ | 5 g litre$^{-1}$ PEI | med ~ 80 nm | $\{10\bar{1}0\}\{11\bar{2}0\}$ | crystals |
| −1.43 | 50 | 20 | $I$ | 5 g litre$^{-1}$ PEI | small < 80 nm | random | smooth |
| −1.46 | – | 35 | $\phi$ | 6.3 g litre$^{-1}$ PEI | very small | $\{11\bar{2}0\}$ | smooth |
| −1.53 | 200 | 50 | $I$ | 5 g litre$^{-1}$ PEI | small | $\{11\bar{2}0\}$ | smooth |
| −1.53 | 200 | 50 | $I$ | 5 g litre$^{-1}$ PEI | small | $\{11\bar{2}0\}$ | smooth |

Absence of line broadening indicated grain sizes larger than about 0.5 $\mu$m and these are described as large in Table I.

In general, grain size decreased with larger overpotentials or larger current densities. Once again, variations in temperature or additive content of electrolytes had no apparent effect on the grain sizes of deposits formed at similar electrode potentials. These conclusions about grain sizes were reinforced by microhardness measurements which varied from ~50 kg mm$^{-2}$ for deposits formed at low overpotentials to ~200 kg mm$^{-2}$ for deposits formed at large overpotentials.

## 4. Discussion

At large overpotentials, the deposits obtained were relatively flat and moderate or good reflectors of light, giving grey or bright surfaces. On the other hand, small overpotentials gave very irregular surfaces which scatter light and, therefore, appear dark.

It is generally accepted that nucleation is infrequent during electrodeposition at low overpotential and this leads to large crystallites in the deposit. Increasing overpotential leads to a smaller crystallite size. This is found to be the case with zinc.

It is also generally accepted that the morphology of the electrodeposit changes with the overpotential. At low overpotentials the deposit grows in a close-packed crystallographic direction in close-packed planes. This leads to a dendritic structure which is seen with many metals deposited near the reversible potential. Increasing the overpotential should lead to growth in all directions in the close-packed planes. In face centred cubic metals with four close-packed planes and six close-packed directions, this effectively means growth in all directions and results in a reasonably flat electrodeposit. However, zinc has a hexagonal crystal structure with an expanded $c/a$ ratio and, therefore, only one close-packed

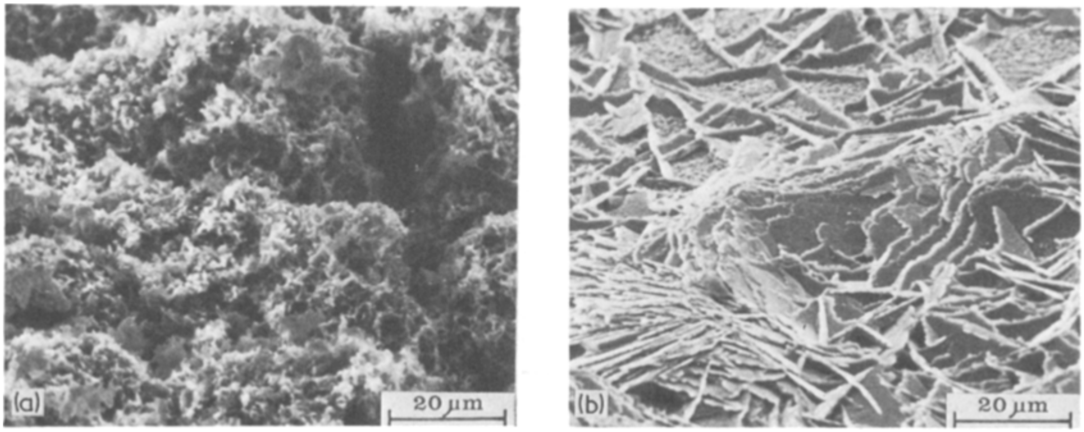


*Figure 4* Electrodeposits from acid-sulphate electrolyte (d): (a) pure electrolyte, current control, $\phi = -0.88$ V, $D = 50$ A m$^{-2}$, $T = 20°$ C; (b) electrolyte containing 0.5 g litre$^{-1}$ dextrine, current control, $\phi = -0.76$ V, $D = 50$ A m$^{-2}$, $T = 20°$ C.

plane and three close-packed directions. Thus, several intermediate stages can be observed between dendritic growth and a flat electrodeposit.

At low overpotential, the zinc electrodeposit grows in the close-packed directions in the close-packed planes, producing fine dendrites and a spongy deposit (Fig. 2a) in which the crystallite size is larger than the limit for X-ray line broadening (0.1 $\mu$m) and similar to the observed particle size of $\sim 0.3\,\mu$m.

At slightly increased overpotential, growth occurs in all directions in the close-packed plane, which in zinc is the basal plane, and we get leaves of the type shown in Figs. 2b and 3a growing approximately normal to the surface. These leaves, which have the crystallographic basal plane parallel to the plane of the leaves, contain many crystallites, the size of which is also larger than $\sim 0.1\,\mu$m.

Further increase in the overpotential gives crystalline deposits in which the crystals are approximately equiaxed, with clearly developed faces indicating significant growth normal to the close-packed planes. Under some circumstances, especially the use of additives (Fig. 3b) or under conditions of controlled potential (Fig. 3c) the crystals are very well developed but they are still composed of crystallites $\sim 80$ nm in size, which is smaller than the crystallite size in the leaf-like structures.

Finally, at the highest overpotential we get an almost smooth deposit (Fig. 3d) showing no crystallographic habit, which is composed of very small crystallites.

This work suggests that the method by which the overpotential is changed is not important. Thus increasing current density, changing temperature or making additions to the plating bath, may each change the overpotential. However, the morphology of the electrodeposit appears to be related to the overpotential irrespective of the way a particular value of overpotential is achieved.

The sequence of structures observed is not unexpected, but is an interesting example of the effect of increasing overpotential on the morphology and structure of electrodeposited metal. These steps would be expected in the development of the structure of deposits of metals such as copper and nickel but can only readily be shown by depositing a hexagonal metal like zinc.

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## References

1. N. T. KUDRYAVTSEV, A. I. LIPOVETSKAJA and K. N. KHARLAMOVA, *Zn. Prikl. Khim.* **22** (1949) 377; *Chem. Abstract* 43:6521.
2. H. G. TODT, *Trans. Inst. Met. Finish.* **51** (1973) 93.
3. H. GEDULD, *Plating* **62** (1973) 683.
4. H. G. CREUTZ and S. MARTIN, *ibid* **62** (1975) 681.
5. U. LINDBORG, S. RAMSIN, L. LIND and L. REVAY, *ibid* **61** (1974) 1111.

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