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The effect of foreign atoms on the properties of electrolytic zinc powders[*]

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Kinetic and morphological studies have been made of the deposition of zinc powder on steel substrate, from pure alkaline zincate electrolytes and with small amounts of lead and tin ions in the electrolyte. The rate of co-deposition of hydrogen has been followed volumetrically and the current efficiency of zinc deposition calculated as a function of potential.

The addition of lead and tin was found to have a profound effect on the properties of the powder. The dendritic powder, obtained from pure zincate solutions, changes with the addition of lead into a mossy deposit consisting of very small crystallites. Both additives increase the specific surface area of the powder and the average lattice parameters. Hydrogen evolution per unit real surface area and hence the corrosion of the powder are somewhat inhibited by both additives.

1. Introduction

Modern technology places complex requirements on the properties of metal powders. An example is zinc powder for zinc-based batteries, which must have as large a surface area as possible in order to provide large currents without passivation (low true current density). On the other hand, in order to minimize the rate of corrosion, the hydrogen evolution reaction must be inhibited as much as possible. Also dendritic growth during redeposition (secondary batteries) should be prevented.

The large literature on the problem of the electrochemical deposition of metal powders (for a review see [1]), shows that our knowledge of these processes is largely empirical. Little has been done on the elucidation of the fundamental phenomena involved [2]. This is particularly true of the effects of electrolyte additives which are known to modify the reactivity of zinc powders (e.g. Pb, Sn, Cd, Al, as shown in [3]).

The definition of metal powder deposition is itself not clear. In some processes (e.g. copper refining), only the material which falls off the cathode is considered as powdered metal. In many processes of electrolytic powder production, however, powder is obtained by shaving the disperse metal deposit off the cathode. Hence, such deposits are powder precursors and a study of their deposition must be the starting point for a better understanding of the electrolytic formation of metal powders. Some recent papers on the electrolytic deposition of zinc from zincate solutions should then be considered relevant.

The deposition of zinc from zincate solutions shows a dependence of the type of deposit on the current density or overpotential of deposition. Mossy, compact and dendritic zinc have been known for a long time [4, 5] although conflicting reports are found in the literature concerning the conditions and causes of appearance of the first of the three types. The results of Sebborn [6] best show that the question is a complex one, since the appearance of mossy zinc was found to depend even on the position

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of the cathode (vertical yes, horizontal no).

Naybour [7] was the first to use scanning electron microscopy for the elucidation of this problem. He established that the mossy deposit appears in isolated spots in the low current density region (4 mA cm^{-2}) and that it is microcrystalline and not amorphous, as was believed by early investigators. At 20 mA cm^{-2} he found layer deposition with some formation of granulae on the compact surface, while dendrites appeared at 100 mA cm^{-2}. Mansfeld and Gillman [8] also found the appearance of mossy zinc, but in the high overpotential region (100 mV) and parallel to the pyramidal growth, characteristic of that potential. It appears that the spots of mossy zinc, formed at the bases of pyramids, later develop into typical dendrites and, hence, that they are different in origin from the moss obtained by Naybour [7].

Bockris, Nagy and Dražić [9] made a thorough study of the problem, which proved that the overpotential is the variable which determines the limits of appearance of different types of deposit. No mossy zinc appeared in their experiments; compact deposits were obtained up to overpotentials of 50 mV. In the category of disperse deposits they made a distinction between boulders, which were the main form at 100 mV, and dendrites, which prevailed at 200 mV. They considered boulders to be dendrite precursors, but not all boulders developed into dendrites (cf. [7] for a similar observation). As far as the value of the overpotential of the morphological transition is concerned, one of us (A. R. Despić, [10]) has shown that the time of observation is an important factor in defining the overpotential limits above which dendrites are grown and that in approaching steady-state conditions, any overpotential above 80 mV can be dendrite-producing in the deposition of zinc from zincate solutions. The finding that not all boulders develop into dendrites is understandable in terms of the conclusion reached by Justinijanović and Despić [11] that dendrites develop only if their precursor has a $\langle 10\bar{1}0\rangle$ or $\langle 11\bar{2}0\rangle$ axis oriented at right angles to the substrate.

The effect of lead on the morphology of zinc deposits has been noted first by Kudryavtsev [12]. Bockris, Diggle and Damjanović [13], as well as Diggle and Damjanović [14], noted that lead, when present in sufficiently high concentration ($>10^{-4}$ M), totally suppresses the appearance of dendrites in zinc deposition. Their conclusion was based on the observation that in the presence of lead salts there was no increase in current with time (at constant overpotential), which is characteristic of dendritic growth. Mansfeld and Gillman verified this conclusion by comparing electronmicrographs of deposits obtained in the presence of lead [15] and tin [16] with those obtained in pure zincate. They found that dendritic growth has indeed been suppressed by both additives. However, dendrites were replaced by a highly dispersed deposit consisting of very small crystallites resembling moss. It has also been observed [17] that the addition of Pb and Sn, as well as Cd, decreases the rate of hydrogen evolution, and that the presence of lead improves the adherence of zinc deposits to the electrode [18]. The present work represents an attempt to define more closely the effect of such additives on the properties of electrolytic zinc powder.

2. Experimental

The deposition of zinc was carried out onto steel sheet electrodes from concentrated alkali (6 M KOH), which was 0·5 M in ZnO. Lead and tin were added to the electrolyte in the form of PbO and $SnCl_2$ respectively. (Mansfeld and Gillman [15] have shown that anions (acetate ions) do not affect the morphology of the deposit, as indeed they could hardly be expected to do at the very negative potentials of deposition. We tested the possible effect of chloride ions by adding first KCl to the electrolyte. The addition had no effect on the quality of the deposit.) Analytical grade reagents were used. Since Diggle and Damjanović have shown [14] that the purity of the electrolyte has practically no effect on the morphology, no special care was taken to purify the electrolyte. It was then confirmed in our experiments as well, that the morphology of the deposit remains the same, whether it is obtained from a fresh electrolyte or from one which has been subjected to prolonged electrolysis.

Two cells were used. The kinetic measurements were made with a horizontal cathode of small surface area (~1 cm^2); steady-state currents could be recorded at different constant potentials. The average zinc deposition current was determined after some time of deposition by performing anodic stripping at a constant anodic potential and integrating current with time. The hydrogen evolution current was determined volumetrically by measuring the amount of hydrogen entering a gas burette above the electrode as a function of time. Hence the current efficiency of zinc deposition could be calculated.

The other cell had a large (56·52 cm^2) cylindrical steel cathode which could be shaved off manually at given time intervals (1 min) by a Teflon blade placed between the cathode and a cylindrical anode, made of the same material, and surrounding the cathode at a distance of about 2 cm. Hg/HgO reference electrodes were used in both cells.

Using water jackets, the temperature of both cells was maintained at $25 \pm 0{\cdot}1$°C.

Kinetic investigations were carried out by the potentiostatic method, using the Wenking potentiostat and pulsing the electrode from +100 mV versus the reversible zinc potential, to a given negative value and back.

To obtain zinc powder, a current source delivering 40 A was used and the electrode potential was maintained by regulating the current manually. The zinc powder collected at the bottom of the large cell was drained, then washed with distilled water and alcohol, dried quickly and sealed into ampules for further investigation.

The powder was examined under a scanning electron microscope and its replicas were photographed in an electron microscope. Specific surface areas were determined by nitrogen adsorption in a Sorbet apparatus.

The lattice parameters of the powder were determined on a Phillips Diffractometer PW 1050 X-ray apparatus and a UNICAM S-25 goniometer.

3. Results

3.1. *Current-potential relationships for zinc and hydrogen*

Fig. 1 represents steady-state (average) zinc deposition currents as functions of potential in pure zincate electrolyte and in the presence of 0·00143 moles lead ions or 0·00144 moles tin ions in the electrolyte.

Fig. 2 gives the same data for hydrogen evolution. The curves for the current density of hydro-

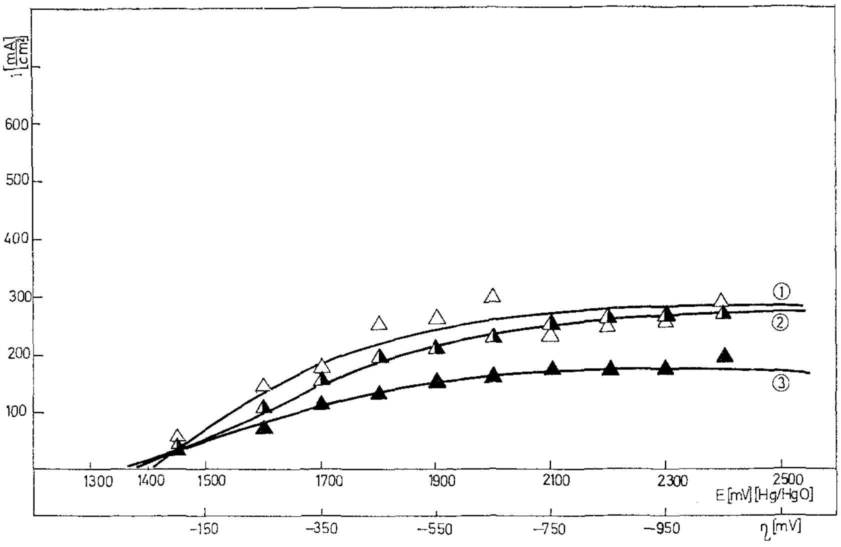


Fig. 1. Current density-potential relationship for the deposition of zinc from pure alkaline zincate solution (1) and from the same solution with the addition of tin (2) and lead ions (3).

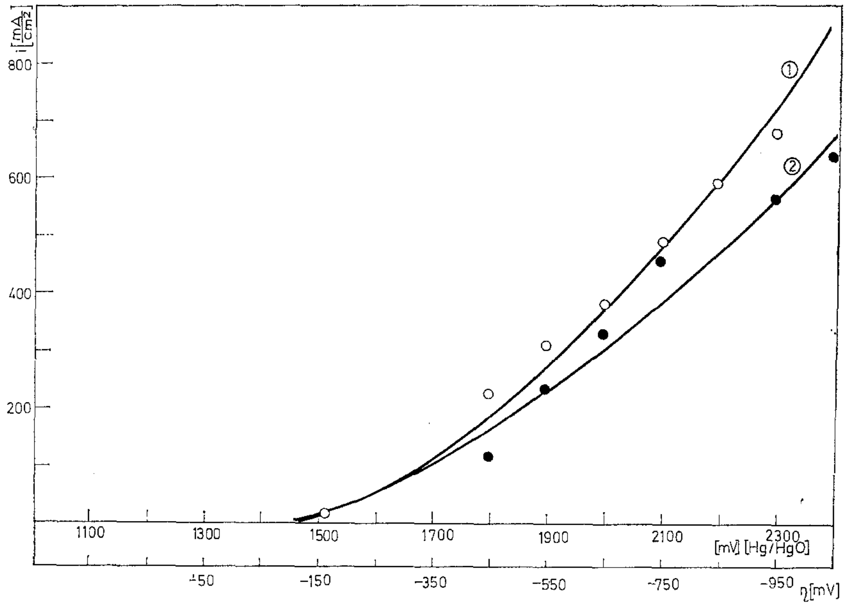


Fig. 2. Current density of hydrogen evolution as a function of potential in pure alkaline zincate solution (1), in the same solution with the addition of tin (1) and lead ions (2).

gen evolution calculated per unit geometric surface area of the electrode for pure zincate solution and those with the addition of tin practically coincide. The addition of lead causes some inhibition.

In the potential region between −1300 and −1450 mV, corresponding to the beginning of deposition of zinc, there is a hump in the low current density region (up to 10 mA cm^{-2}), i.e. an initial increase in the hydrogen evolution current and a subsequent decrease, due probably to the lower evolution rate on a zinc covered electrode than on the bare substrate.

3.2. *Current efficiency of zinc deposition*

This is shown in Fig. 3, as calculated from the determined zinc and hydrogen average partial currents. It is seen to exhibit a maximum in the overpotential region around 100 mV, reaching 90% for deposition from pure zincate and up to 95–96% in the presence of both additives. In

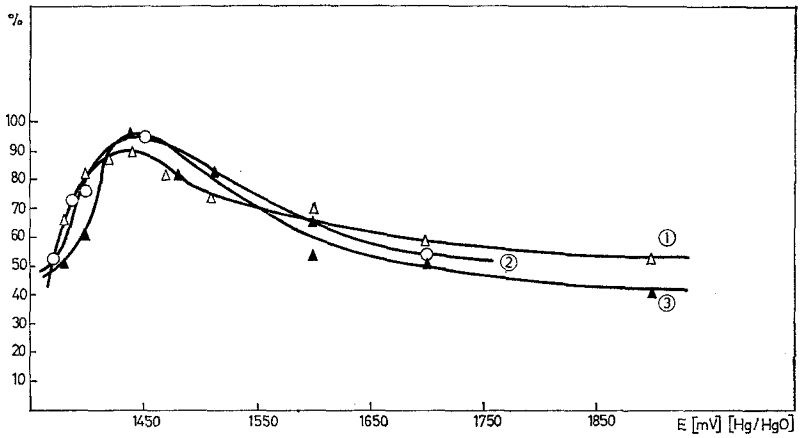


Fig. 3. Yield of zinc as a function of potential for the deposition from pure alkaline zincate solution (1) and from the same solution but with the addition of tin (2) and lead ions (3).

that overpotential region, the deposit is found to be predominantly dendritic [10]. At high overpotentials the efficiency of deposition seems to approach asymptotically a 50% limit.

3.3. *Yield of disperse deposit as a function of overpotential*

Anodic stripping gave the total amount of electricity used in obtaining metallic zinc. Some anodic current versus time curves for deposition from pure zincate electrolyte are shown in Fig. 4.

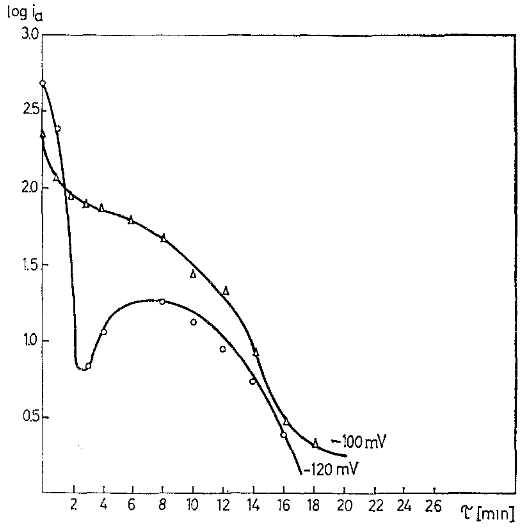


Fig. 4. Typical anodic stripping curves for the dissolution of zinc obtained from pure zincate solution (○) and from the same solution with the addition of tin (△) at the overpotentials of −120 and −100 mV, respectively.

Two regions are clearly seen: an initial high-current region and a low-current region at longer times with a broad-current maximum. On the basis of visual observations of the cathode, we ascribe the first part of the curve to the dissolution of the dispersed deposit and the second part to that of the compact deposit. For deposits obtained with additives, the two parts of the curve were not so clearly separated, suggesting a somewhat slower dissolution of the dispersed deposit.

From the amount of electricity corresponding to the first part of the curve and the total amount passed, the approximate yields of disperse deposit were calculated as a function of the deposition potential. They increase sharply to more than 90% at overpotentials around 40 mV.

3.4. *Shaving off and spontaneous shedding of the powder*

In all experiments the dispersed deposit could be shaven off the cathode only after some time. The longer this time, the more compact and adherent was the deposit. Fig. 5 shows the results obtained in depositions from pure zincate and from zincate with the addition of lead and tin. The two additives are seen to have a considerable effect on the structure of the deposit. In pure zincate solutions the powder did not fall off the cathode spontaneously within the time of the experiment. On the other hand, in the presence of both additives, spontaneous shedding occurred, and the quantity of electricity passed before this depended on the overpotential, as seen in Fig. 5. With lead as additive the quantity of electricity for spontaneous shedding was smaller than that needed for shaving off the powder in pure zincate solutions.

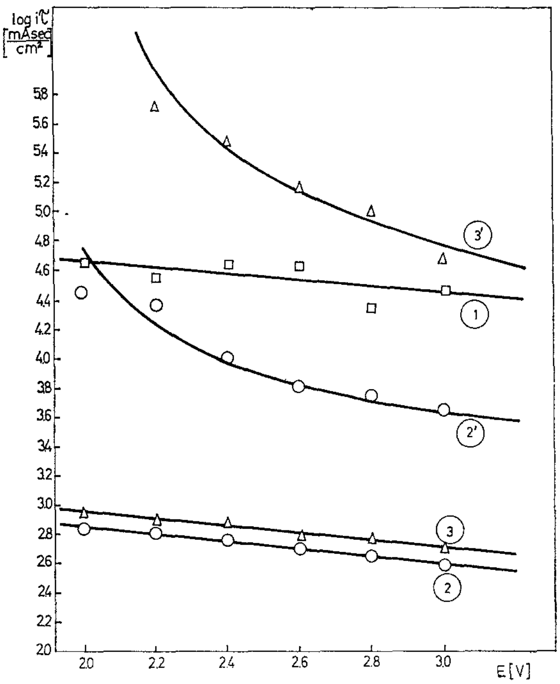


Fig. 5. Amount of electricity passed before the zinc deposit could be shaved off (1, 2 and 3) and before spontaneous falling of the powder (2′, 3′). Curve 1 pertains to deposition from pure alkaline zincate solution, curves 2 and 2′ to the same solution but with addition of lead ions, and 3 and 3′ with addition of tin ions.

3.5. *Specific surface area as a function of the deposition potential*

Specific surface areas differed markedly in deposits obtained with the addition of lead and tin from those obtained from pure zincate. At a given potential the largest surface area has been found in powders containing tin. The values are shown in Fig. 6 as functions of potential. A trend to larger surface area with increasingly negative potential has been maintained in all experiments. We have covered a considerably wider range of potentials than has been reported in the literature so far.

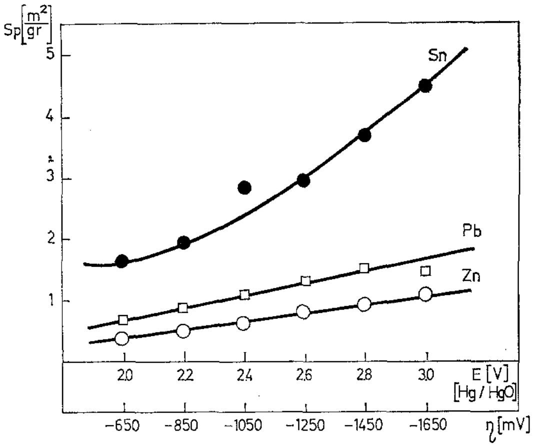


Fig. 6. Specific surface area of zinc powder obtained from pure alkaline zincate solution (Zn) and with the addition of lead (Pb) and tin (Sn) ions to the electrolyte.

3.6. *Crystal lattice parameters of different powders*

An interesting finding is that crystal lattice parameters are affected not only by the addition of lead and tin, but also by overpotential, as shown in Fig. 7. Thus, in zinc from pure zincate both lattice parameters of the hexagonal lattice increase by about 0·01 Å for the potential change between −1·5 and −1·9 V. The same change arises in the presence of lead within a change of potential of only 150 mV.

3.7. *Results of morphological studies*

Profound differences are found in the morphology of powders obtained from pure zincate and in the presence of lead and tin. The powder obtained from pure zincate consisted of particles having the shape of classical dendrites, as exemplified by Fig. 8a. Fig. 8b represents a closer view of the flat surface of a dendrite leaf from Fig. 8a, revealing development of triangular base pyramids in the process of further thickening of the dendritic stem. Most of the dendrites seem to develop in the $\langle 10\bar{1}0\rangle$ or $\langle 11\bar{2}0\rangle$ direction and could be considered as monocrystalline. Some, however, develop along

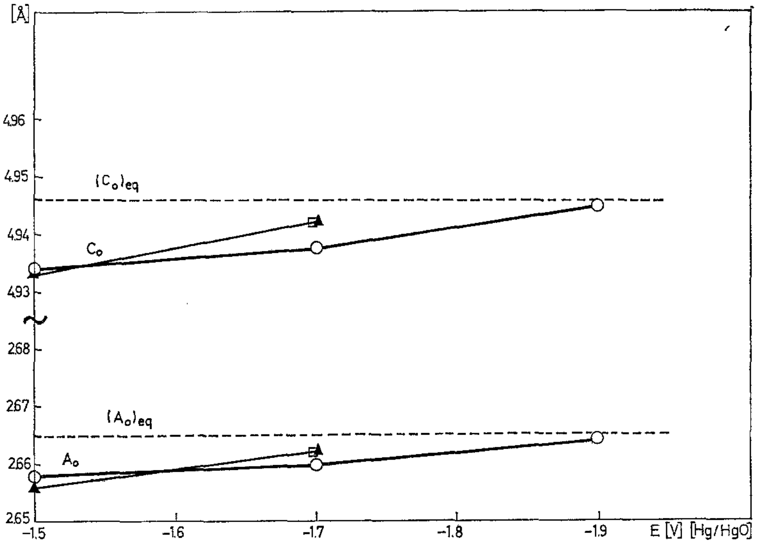
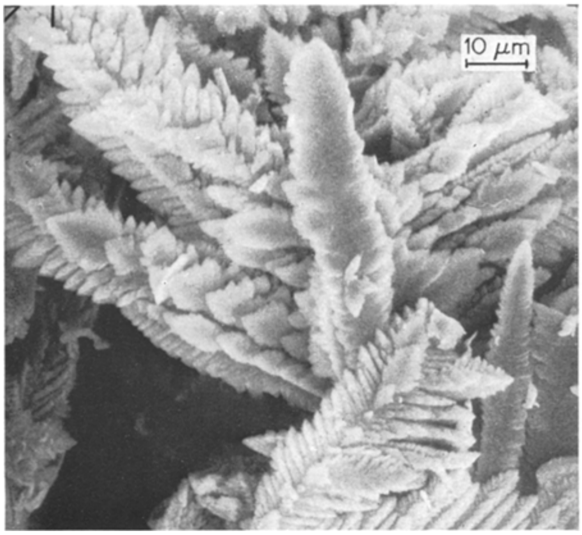
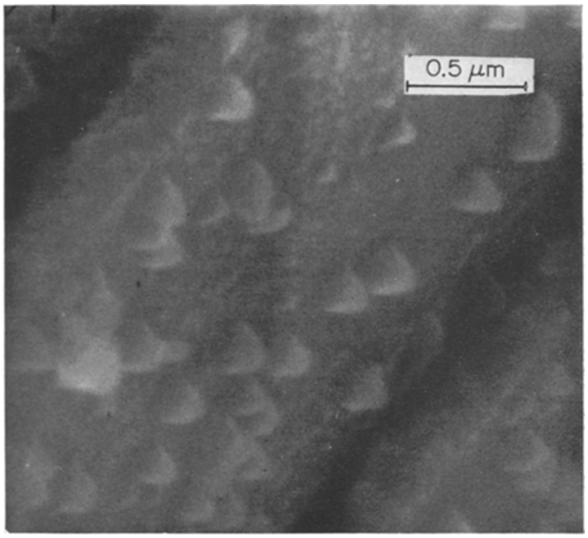


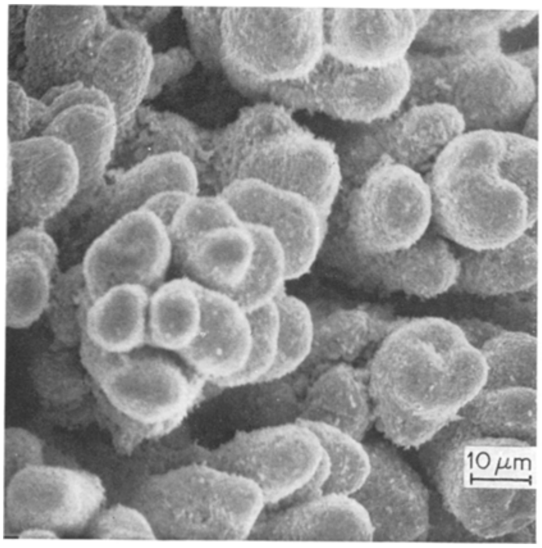
Fig. 7. Lattice parameters of zinc deposited from pure zincate solution (○) and with addition of lead (▲) and tin (□) ions to the electrolyte. Dashed lines represent equilibrium values of the lattice parameters.



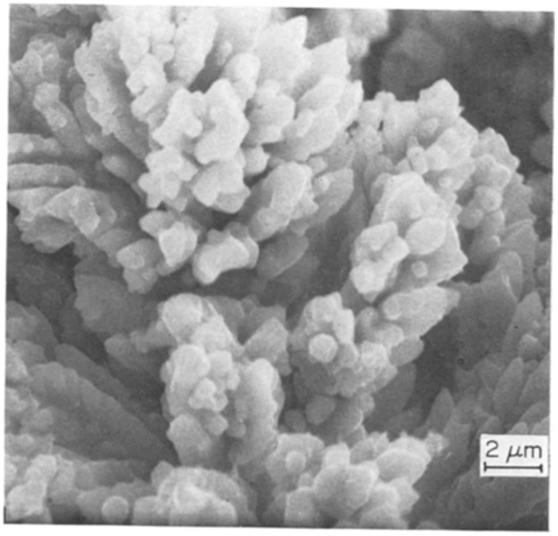
(a)



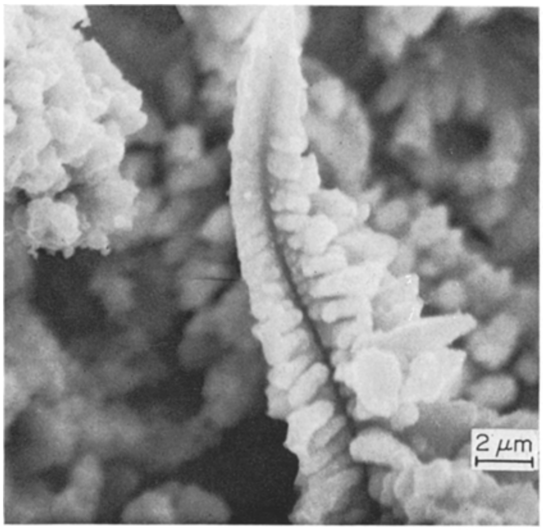
(b)



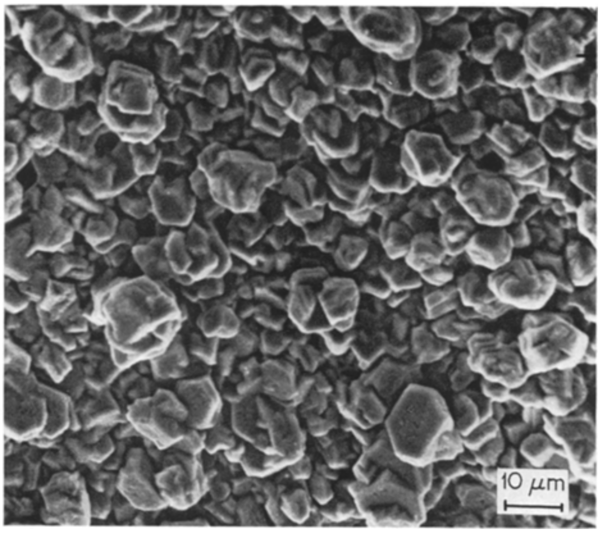
(c)



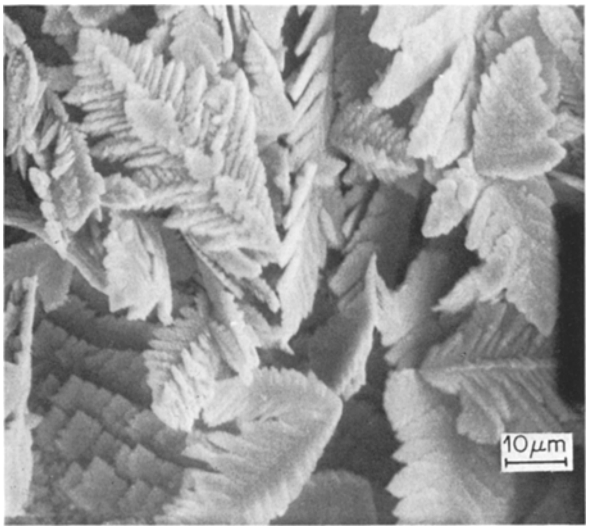
(d)



(e)

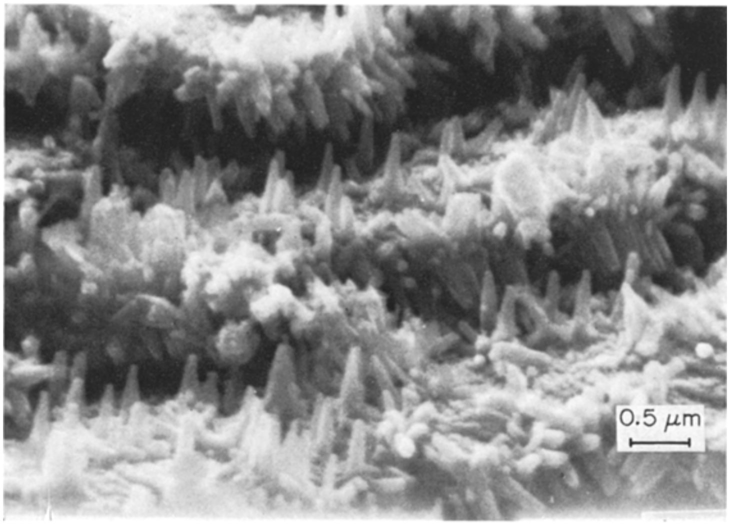


(f)



(g)

Fig. 8. Electron micrographs of zinc powder particles, (a), deposit from pure zincate solution obtained at the potential of −2·6 V (×1000); (b), detail of the surface of the dendrite leaf seen on (a) (×40300); (c), deposit from zincate solution containing lead ions obtained at −1·9 V (×1000); (d), same, obtained at −2·4 V (×5000); (e), same, obtained at −2·8 V (×5000); (f), deposit from zincate solution containing tin ions, obtained at the potential of −1·5 V (×1000); (g), same, obtained at −2·2 V (×1000); (h), detail of the surface of a dendrite leaf seen on (g) (×20000).



(h)

axes of higher indices and must involve twinning.

The addition of lead shifted the appearance of dendrites to much more negative potentials. Fig. 8c shows the type of powder particles obtained at −1·9 V, in the presence of lead. They could be placed into the category of boulders, built up as piles of very disordered layers. It is only at −2·4 V that crystals start extending into the solution (Fig. 8d) and at −2·8 V typical dendrites are formed (Fig. 8e).

The addition of tin also stimulates the growth of boulders at less negative potentials. However, as seen in Fig. 8f, these have a much less disordered structure than those containing lead. They also develop into dendrites at more negative potentials (Fig. 8g).

These dendrites, however, in many instances appeared not to be single crystals. Fig. 8h represents a very magnified section of a dendrite surface. Disordered outgrowths are seen. Hence, these particles would fall in the class of false dendrites of Wranglen [19].

4. Discussion

From the above results it is clear that the addition of lead and tin into zincate electrolytes affects the crystallization of zinc powders.

At overpotentials sufficiently high to cause concentration polarization and thus an increase in surface roughness [20] no smooth deposit is obtained in any of the cases studied. However, while dendrites developed from pure zincate, addition of lead caused the formation of hemispherical structures and addition of tin produced boulder-like single crystals. It was shown elsewhere [11] that fast unidirectional extension of the crystal to form a dendrite in pure zincate solutions could be explained by the large difference in the rates of incorporation of adatoms in $(10\bar{1}0)$ planes compared to the (0001) plane, which causes preferential growth along with $\langle 10\bar{1}0 \rangle$ axis. This was absent in the presence of additives.

The conclusion can be drawn that the adatoms of the additive co-deposited with zinc, block the growth on the fast incorporating planes, and make the growth more even within the spherical diffusion field, as predicted by the theory of transport controlled growth. Slower extension of the outgrowths in the direction perpendicular to the electrode and thus slower penetration into the diffusion field, account for the lack of increase in the deposition current with time. However, this does not mean that there is a reduction in the degree of dispersion of the deposit. On the contrary, both additives produce, at all overpotentials, deposits of a specific surface area considerably larger than that of deposits obtained from pure zincate.

Microscopic observations reveal that hemispherical outgrowths in deposits obtained from lead-containing electrolyte in the low overpotential region, are composed of innumerable needle-like crystallites of very small dimensions (of the order of 4000 Å in length). Obviously lead atoms block crystal growth and thus stimulate nucleation throughout the deposition.

Tin has a similar, but less pronounced effect. The increase in the specific surface area seems here to be due primarily to the number of boulders, as compared with the number of dendrites obtained from pure zincate. The boulders themselves seem to be of compact structure (monocrystalline). Hence, tin appears to block the early phase of growth and thus increases the number of nuclei at the very beginning of deposition. The overall effect on the specific surface area is larger than that of lead.

At high overpotentials, where typical dendrites are developed both in the absence and in the presence of additives, the differences in specific surface areas increase even further. In the case of the addition of lead, this seems to be due to a coral-like structure of the dendrites while tin seems to stimulate the outgrowth of small crystallites on the surface of the dendrite leaves (compare Fig. 8b and 8h). This may be due to the blockage of the layer growth on the leaves by adsorption of tin adatoms at the steps, which forces the incorporation of accumulating zinc adatoms into the closest spiral dislocation, where they form hexagonal towers and thus develop the surface area.

Both additives also cause an increase in the concentration of points or lines of growth, as demonstrated by the increase in average lattice parameters.

An important finding is that both additives have some inhibiting effect on hydrogen evolution. In the presence of tin, the overall rate of that reaction remains the same as on zinc from pure zincate, in spite of the increased surface area of the metal. The presence of lead even causes a decrease in the rate of hydrogen evolution.

The conclusion from these results is that addition of both lead and tin to the electrolyte for the deposition of zinc powder imparts properties to the powder, which are beneficial for its use in the chemical energy sources: it produces increased specific surface areas of the powders without increasing the hydrogen corrosion of zinc. The addition of tin is to be preferred, because it results in coarser crystals of even larger specific surface area, which may lead to better conductivity of the powder paste. The additives also have a beneficial effect on the production of the powder, because they cause spontaneous shedding of the powder from the cathode surface. With increasing overpotential, higher rates of codeposition of hydrogen foster this process further.

Acknowledgements

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