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Nucleation and growth of zinc electrodeposited from acidic zinc solutions

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The nucleation and initial crystal growth kinetics by electrodeposition from acidic zinc solutions was studied in the absence and presence of antimony and glue on a glassy carbon electrode. Zinc exhibits instantaneous nucleation under the experimental conditions employed in the potential region from −1600 to −2000 mV (mercurous sulphate reference). At low overpotentials antimony and glue increase the number of nuclei.

Nomenclature

A	nucleation rate constant
h	height of two-dimensionally growing cylinder
I	current
k	electrochemical rate constant of initial crystal growth
M	atomic weight
N_0	number of nuclei after instantaneous nucleation
t	time
z	number of electrons
ϱ	density of deposited metal

1. Introduction

Over half of the world's zinc is won from acidic sulphate solutions by electrodeposition. The active nature of zinc metal causes the electrolytic process to be very sensitive to the processing parameters employed in its production. The presence of various cationic impurities has been shown to influence strongly the efficiency of deposition and the electrocrystallization and growth of the zinc, including the morphology and orientation of the metal film. Hydrogen evolution can account for 10–20% of the current usage at the cathode under ordinary operating circumstances, but this value can increase dramatically when small concentrations (p.p.m. or p.p.b.) of certain impurities, such as antimony or germanium, are present. In turn, organics are commonly added to the electrolyte to counteract the adverse effects of these impurities. A very delicate balance exists among a number of chemical species in the solution whose presence can alter the zinc nucleation and growth process.

There is considerable current interest [1] in extending the application of zinc electrodeposition to the direct plating of steel in order to improve corrosion resistance. The automotive industry is projected to be a major consumer of this product. In order to ensure that the electrogalvanized material is uniformly consistent, it is necessary to control carefully any conditions or situations that might cause variations in product quality.

The aim of this study is to investigate the nucleation and the kinetics of electrocrystallization of zinc with and without a selected impurity and additive. Antimony and animal glue were selected for the initial research and a glassy carbon electrode was chosen as the substrate. Results are evaluated with respect to research conducted on the electrodeposition of zinc from acidic solutions reported by several workers [1–5].

Fleischmann and Thirsk [6] and Thirsk and Harrison [7] have developed equations that describe the current transient during the very early stages of metal deposition for specific types of nucleation and crystal growth under kinetic control. Once the growing crystals begin to overlap, these equations become invalid. During the early stages of metal deposition, nuclei are formed at energetically favourable sites. Whether or not a particular site is favourable depends on its surface energy and on the magnitude of the applied cathodic potential.

Of the expressions derived the following were considered. For two-dimensional growth after instantaneous nucleation,

$$I = 2zF\pi MhN_0k^2t/\varrho \tag{1}$$

for two-dimensional growth after progressive nucleation,

$$I = zF\pi MhAN_0k^2t^2/\varrho \tag{2}$$

for three-dimensional growth after instantaneous nucleation,

$$I = 2zF\pi M^2N_0k^3t^2/\varrho^2 \tag{3}$$

and for three-dimensional growth after progressive nucleation,

$$I = 2zF\pi M^2AN_0k^3t^3/3\varrho^2. \tag{4}$$

The type of nucleation process occurring and the N_0 value can be determined by examining micrographs of the nuclei taken with a scanning electron microscope. By comparing the I vs t^n relationship the electrochemical rate constant is obtained for the initial stages of crystal growth.

2. Experimental details

2.1. *Cell and electrode*

A straight-walled beaker with a PE foam cover was used throughout this study. The counter electrode was contained in a glass-fritted compartment to keep it separated from the working electrode. The working electrode was a PINE Instrument Company RDE with a detachable tip so that the glassy carbon working electrode could be placed into the scanning electron microscope. A U-shaped Luggin capillary was placed close to the working electrode. The reference electrode was a Metrohm Hg/Hg_2SO_4. Potentials are reported with respect to this reference. The solutions were sparged with oxygen-free nitrogen prior to each experiment.

2.2. *Potentiostats and recorders*

The nucleation study was carried out with a Wenking potentiostat (Bank Elektronik model VSG 72) and the potential pulses were applied from a D/A interface controlled by a Radio Shack TRS 80-III using a pulse duration of 0.3 s. The current–time curves for the kinetic study were measured with a PAR 170 connected to a Hewlett–Packard 7090A transient plotter. Data were transferred via IEEE 488 to an IBM PC for further treatment.

2.3. *Experimental procedure*

Before each run the working electrode was polished with 0.05 μm alumina powder and then cleaned for 30 s in an ultrasonic bath. The experiments with glue required a contact period with the solution of 10 min for an even distribution of nuclei.

3. Results

3.1. *Nucleation*

Nucleation of zinc was studied by counting the number of nuclei as a function of pulse potential and in the presence of 50 p.p.b. Sb^{3+} (as potassium antimony tartrate) and 25 p.p.m. Pearl glue (Fig. 1). The diameter of the nuclei versus pulse potential was also measured (Fig. 2).

Fig. 1 displays the average zinc nuclei per μm^2 versus pulse height for the pure zinc sulphate solution. The lowest pulse at which crystals were found to deposit, − 1656 mV, gave less than 1 nucleus per μm^2. As the pulse height increased the number of centres increased at the rate of 2.1 nuclei per μm^2 per 100 mV. McBreen and Gannon [8] also found that the number of particles per unit area increased with the applied overvoltage. Fig. 3 shows zinc crystals from the pure 1.0 M $ZnSO_4$/1.5 M H_2SO_4 solution at various pulse heights.

Between − 1900 mV and − 2000 mV, a sharp discontinuity appeared in the number of crystals formed for the pure zinc solution. The number per unit area almost doubled, from about 6 to 12 nuclei per μm^2. The number continued to increase at a much slower rate at the higher potentials,

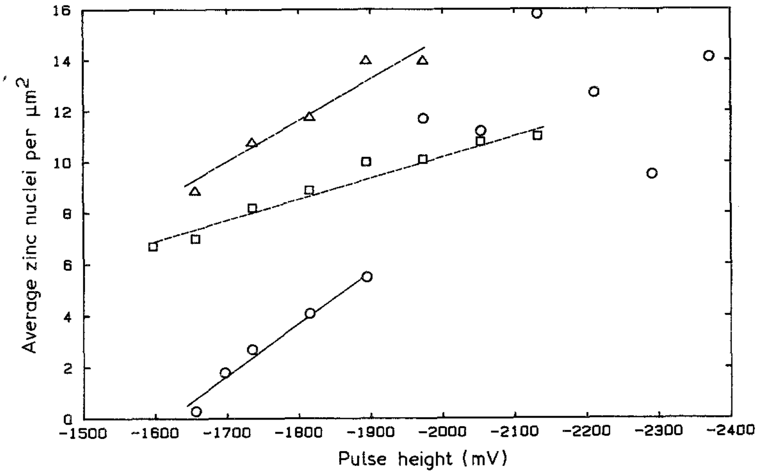

Fig. 1. Comparison of the average zinc nuclei per μm^2 versus pulse height for the three solutions indicated; RDE; 1000 r.p.m. ○, Pure zinc solution; □, 50 p.p.b. antimony impurity; △, 25 p.p.m. glue additive.

although a great deal of scatter is observed. The increase is probably due to the fact that the zinc deposit covers nearly the whole surface at about – 1900 mV, and any further nucleation starts to take place on top of the first layer of nuclei. It is easier for more zinc crystals to plate onto a surface which is partially or totally covered with zinc than onto a clean, polished substrate.

The initial size of the zinc crystals was between 0.4 and 0.5 μm, but this value decreased to an average diameter of 0.35 μm (Fig. 2). The zinc crystals maintained their hexagonal shape throughout this series.

Antimony is a common impurity found in industrial zinc electrowinning processes. Even in p.p.b. quantities it decreases the current efficiency of zinc deposits. It probably does this by lowering the hydrogen overpotential at the cathode, thus causing the evolution of more H_2 [9]. Therefore, the effect of antimony on the nucleation of zinc crystals was studied because of the influences that this impurity has on the bulk deposition process (Fig. 4).

The antimony (50 p.p.b.) added to the 1.0 M $ZnSO_4$/1.5 M H_2SO_4 solution caused a large increase in the number of zinc crystals at low pulse heights (Fig. 1). Almost 7 nuclei per μm^2 were found at the pulse height of – 1597 mV. No crystals were found at this pulse height for the pure zinc system. The number of zinc centres increased by 0.9 nuclei per μm^2 per 100 mV, which is less than half of the number found for the pure solution. The crystal diameters increased from about 0.15 to 0.30 μm for the 500 mV potential range investigated (Fig. 2). Many crystals had an angular appearance.

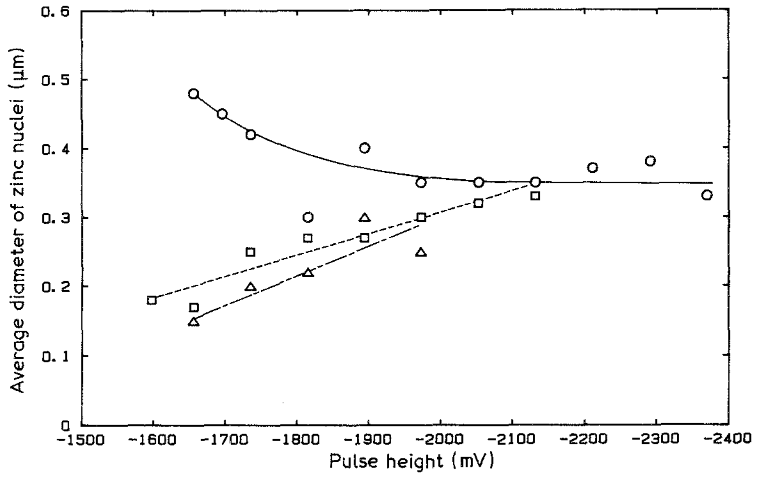

Fig. 2. Comparison of the average diameters of zinc nuclei versus pulse height for the three solutions indicated; RDE; 1000 r.p.m. ○, Pure zinc solution; □, 50 p.p.b. antimony impurity; △, 25 p.p.m. glue additive.

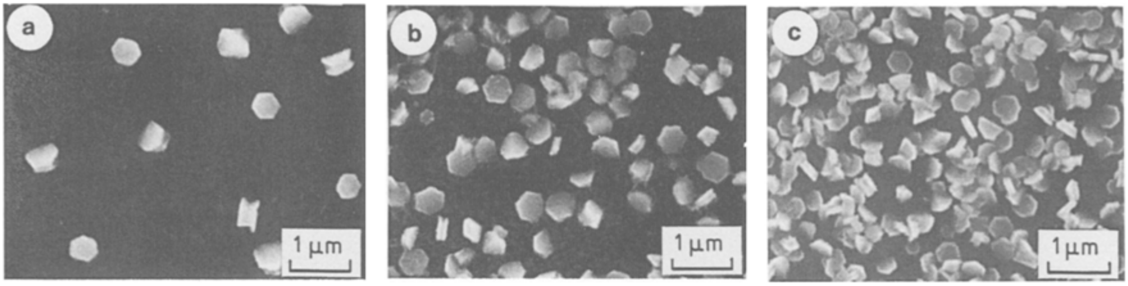

Fig. 3. Zinc crystals deposited from a 1.0 M $ZnSO_4$/1.5 M H_2SO_4 solution containing no additives at various pulse potentials: (a) − 1656 mV; (b) − 1735 mV; (c) − 1894 mV.

Organic additives such as glues are used to counteract the deleterious effects of antimony and other impurities. Glue also functions as a leveller to promote smooth deposits and is helpful in acid mist suppression.

Zinc crystals from the solution with a 25 p.p.m. glue addition also have a high number of nuclei at low pulse heights (Fig. 1). At a pulse of − 1656 mV there were already 9 nuclei per μm^2. The deposit increased by 1.7 nuclei per μm^2 per 100 mV. The diameters also grew from about 0.15 μm to almost 0.30 μm for a potential range of 350 mV (Fig. 2). The glue addition caused the zinc crystals to appear more rounded than angular. The morphologies of the zinc nuclei obtained at a pulse of − 1735 mV in the presence and absence of the additives are shown in Fig. 4.

The data compiled in Fig. 1 indicate that both glue and antimony produce a large increase in the number of nuclei deposited at low overpotentials. Both additives decrease the absolute diameter of the nuclei formed on glassy carbon, glue more than antimony. At high overpotentials the nuclei from all three solutions attain roughly the same diameter of 0.35 μm (Fig. 2). Fig. 1 also shows that the line for the solution containing antimony displays a regular, consistent increase in the number of zinc nuclei.

The diameters of the zinc crystals from the three solutions investigated have little scatter. This indicates instantaneous nucleation, because all the crystals produced at a given overpotential from the same solution are similarly sized.

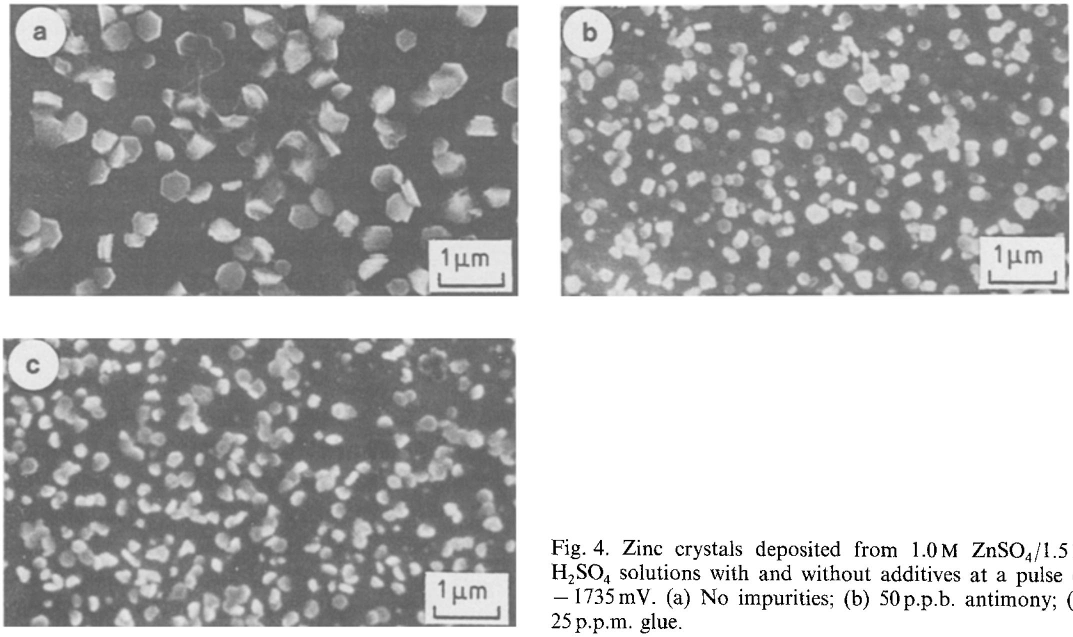

Fig. 4. Zinc crystals deposited from 1.0 M $ZnSO_4$/1.5 M H_2SO_4 solutions with and without additives at a pulse of − 1735 mV. (a) No impurities; (b) 50 p.p.b. antimony; (c) 25 p.p.m. glue.

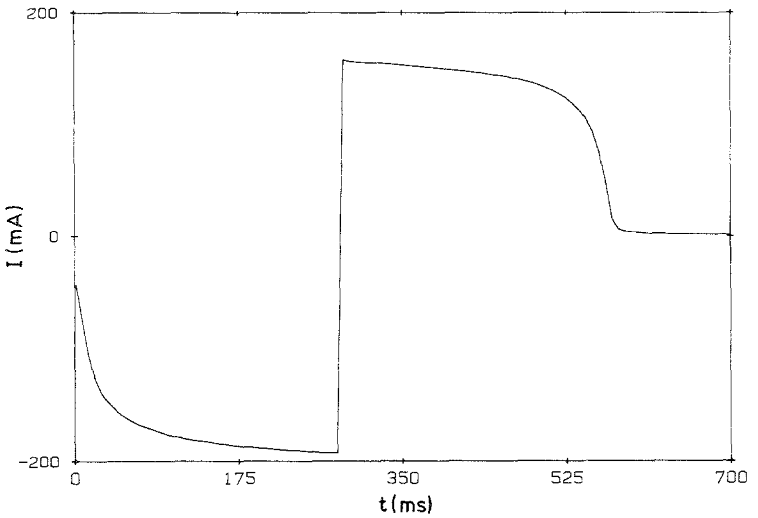

Fig. 5. Current transient obtained when a small amount of zinc was cathodically deposited from the zinc sulphate solution containing 50 p.p.b. antimony at − 1900 mV and then anodically dissolved at − 1300 mV.

3.2. *Current efficiency*

A sequence of a cathodic followed by an anodic pulse (similar to [3]) was used to determine the ratio of anodic to cathodic charges, the current efficiency with respect to zinc deposition and the partial zinc current. Fig. 5 shows the current response to the potentiostatic pulse used in this study. In all cases the initial and final potentials were the same. Curret efficiencies were checked in the nucleation and the kinetic experiments. The current efficiencies obtained by this method are given in Fig. 6. The duration of the pulse is adjusted so that the deposition current reaches a steady value. From these data, current efficiency and partial zinc currents are calculated.

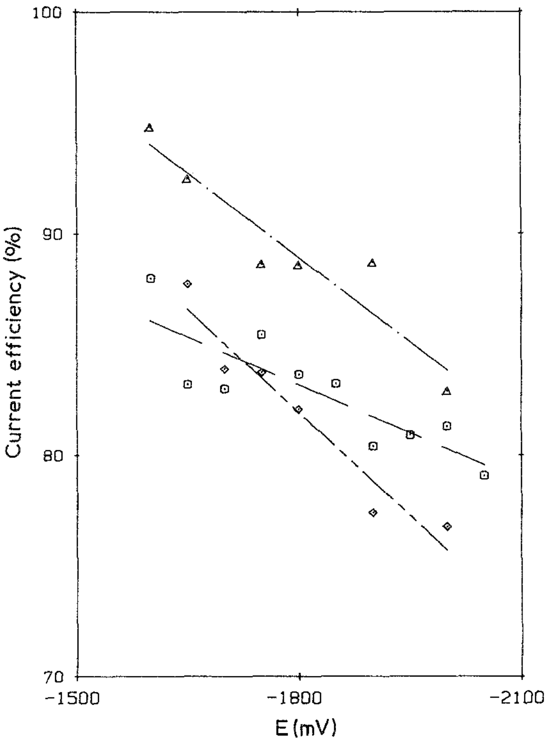

Fig. 6. Comparison of the current efficiency relationships obtained from the three solutions. □, Pure zinc sulphate solution; △, zinc sulphate solution containing 50 p.p.b. antimony; ◇, zinc sulphate solution containing 25 p.p.m. glue.

3.3. *Rate constant measurements*

Fig. 7 is a current–time curve for the deposition of zinc. The potential is stepped from − 1300 mV to the desired cathodic potential. The current density was plotted as a function of the t^2 and t^3 using the point of minimum current flow as the origin [7]. At more negative potentials the rise time of the cathodic current was very fast, and separate experiments were performed to increase the resolution and accuracy of the data by recording only the initial phase of crystal growth. The plots versus t^2 gave the best approximation to a straight line and were used to calculate the overall rate constant. A comparison between the fits can be made by inspecting Figs 8 and 9. No attempt was made to calculate separate lateral and vertical rate constants. Fig. 10 shows the log rate constants versus potential for pure acidic zinc solutions and with the additives antimony and glue. The log of the rate constants for the pure zinc solution

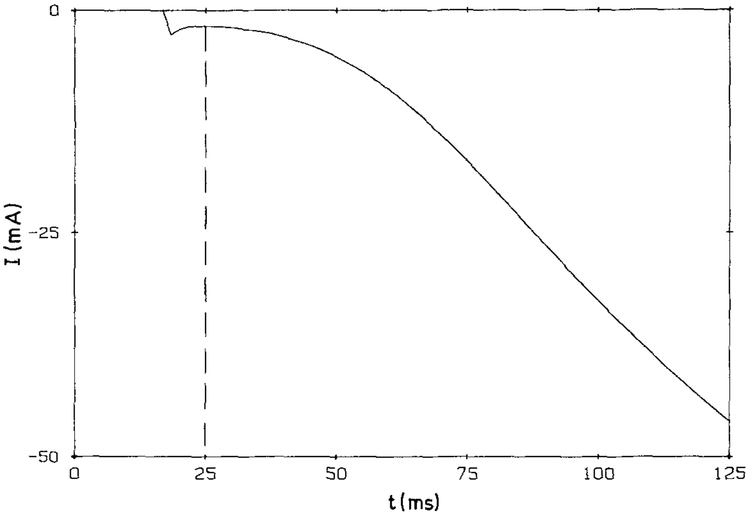

Fig. 7. Initial current transient obtained during the nucleation and early stages of zinc crystal growth from the pure zinc sulphate solution at an applied cathodic potential of − 1750 mV.

shows a change over two orders of magnitude in the potential interval studied. With the addition of antimony the apparent rate constant has a much higher value at the lower overpotentials, but changes over only one order of magnitude. The glue addition causes a decrease in the rate constant by almost an order of magnitude. The behaviour of these two additions is similar to that observed in the crystallization phase during cyclic voltammetric studies [10].

4. Summary and conclusions

In a few instances the results obtained when the impurity and additive were present did not follow the classical behaviour noted for these types of species. From previous work it might have been expected that antimony would decrease both the number of nuclei and current efficiency. A decrease in the number of nuclei due to inhibition of the nucleation by the adsorbed glue and a corresponding decrease in current efficiency would also be the more expected behaviour pattern. Of these, only the decreased current efficiency due to glue actually occurred. In retrospect, these results may not be as unusual as imagined upon first inspection.

First, the bulk of the information of zinc deposition from acid sulphate electrolytes has been generated using metal cathodes (often

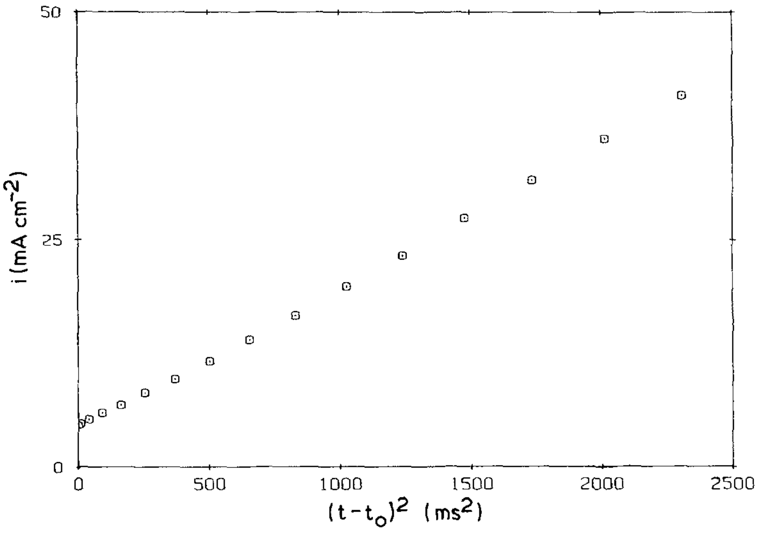

Fig. 8. Linear relationship between the current density and the offset-time squared obtained from the pure zinc sulphate solution at an applied cathodic potential of − 1750 mV.

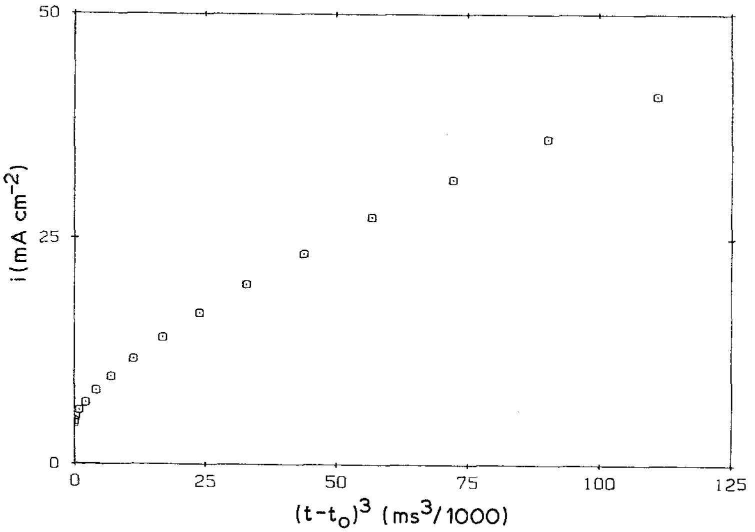

Fig. 9. Non-linear relationship between the current density and the offset-time cubed obtained from the pure zinc sulphate solution at an applied cathodic potential of −1750 mV.

aluminium) and at much lower current densities (by a factor of nearly ten). Most of the research is done galvanostatically rather than potentiostatically, and crystallization behaviour in these two modes would obviously vary. Also, the current efficiency as well as grain structure and orientation are usually determined for bulk deposits that are of significant thicknesses. The effect of time on these properties is well established, and it has been shown that current efficiency, in particular, often decreases as deposition time increases. Therefore, due to the very short deposition times and high current densities employed in this study, deviations in normal behaviour may not be unreasonable. One aspect which does seem to be magnified is the need to examine in more detail the nucleation and growth process, even for the more standard zinc deposition process, since the behaviour of impurities and organics may be very process-sensitive. It would probably be particularly beneficial to examine the influence of other substrates such as aluminium, and also their pretreatment, on the nucleation and growth mechanism for zinc from acid electrolyte.

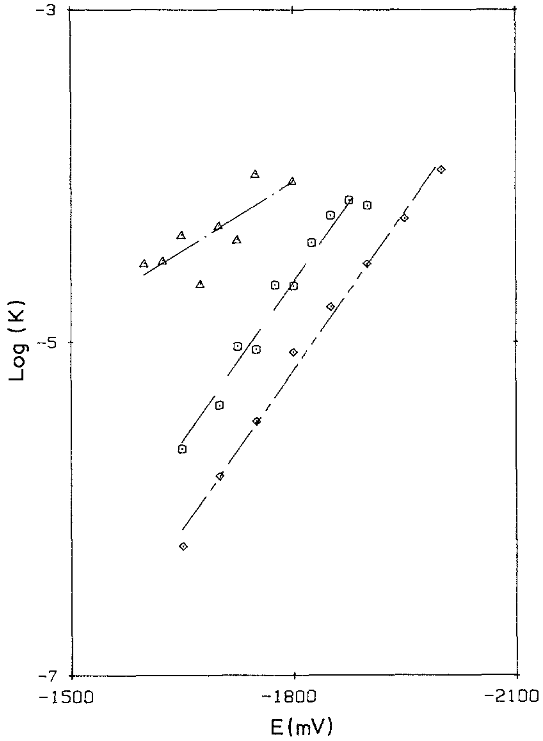

Fig. 10. Comparison of the relationships between the logarithm of the electrochemical rate constant and the applied cathodic potential obtained from the three solutions. □, Pure zinc sulphate solution; △, zinc sulphate solution containing 50 p.p.b. antimony; ◇, zinc sulphate solution containing 25 p.p.m. glue.

Acknowledgements

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