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Measurement of polarization parameters impacting on electrodeposit morphology I: Theory and development of technique

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Abstract

A newly extended theory is presented on the role of polarization characteristics in determining the morphology of thick, polycrystalline metal electrodeposits. The theory is applicable to any system in which a single metal deposits. A simple galvanodynamic scanning procedure is more favourable than cyclic voltammetry, for predicting deposit morphology. The galvanodynamic technique represents an improved way of measuring accurately the nucleation potential and plating potential. According to the extended theory, these potentials can be readily related to the major metallographic structures of polycrystalline electrodeposits.

1. Introduction

In the electrodeposition of several metals of commercial value, there is often a need for a rapid indication of active amounts of additives used to optimize deposit morphology. The use of polarization measurements has been widely considered for this purpose [1–5]. These measurements have been applied to the control of additives in the electrodeposition of metals such as copper, zinc, and lead [2–7]. A review covering the history of polarization techniques in the study of zinc and lead electrodeposition was published by Gonzalez [8]. For laboratory studies, often the basic technique has been cyclic voltammetry [3, 9, 10].

In this paper, the term 'overpotential' has its usual electrochemical meaning, and will refer to the magnitude of the cathodic displacement from the equilibrium potential. For some measurements against a reference electrode, it will be more convenient to discuss the value or behaviour of the potential rather than the overpotential.

The effects of individual reagents on cyclic voltammograms, especially the hysteresis loop which is characteristic of electrochemical formation of a new solid phase [11], have been studied extensively [3, 4, 9, 10, 12, 13]. However, information on synergistic effects with other additives is scarce. For example, not much is known about synergistic effects involving surfactants [13–15], which are often added for acid mist suppression in electrowinning operations.

Kerby et al. [12, 16] invented a moving wire (or foil strip) sensor for one feature of the polarization curve, originally called the 'activation overpotential' [12, 14, 16] but, from about 1985, generally referred to as the 'nucleation overpotential'. This feature of the curve was shown to give a sensitive response to glue and antimony [9, 12], the reagents used to control deposit morphology and to optimize current efficiency. The instrument became known as a 'continuous electrolyte quality monitor' (CEQM).

Another technique, which will be referred to as the dual channel CEQM technique was developed by Kerby [6], for controlling lead electrodeposition [2, 17]. This process uses two types of addition agents, a levelling agent, and a grain refining agent [4]. The device, which uses two moving wire cathodes, provides continuous measurements of both a nucleation potential and a plating potential, the latter being an estimate of the cathode potential of an operating, commercial cell. This particular method has since been applied to a number of other metals [7], such as electrorefined copper and electrowon nickel. It has been more successful than instruments which estimate only one of these potentials [4, 5, 7].

Hydrodynamics and additive degradation can also be important in the control of deposit morphology [18]. These issues were addressed by Winand [5] in the development of a device, which monitors the plating potential under well-defined conditions of bulk metal deposition. Several dimensionless groups for the test cell were engineered to mirror the conditions of the industrial cells. However, only a single parameter was measured, (the plating potential in this case), and the results were most useful only when many process variables were kept constant.

In contrast to cyclic voltammetry, which is a controlled potential method, controlled current methods, such as galvanostatic and galvanodynamic techniques, could also be employed. Galvanostatic polarization curves for zinc deposition have been reported by Maja et al. [19], Ohyama and Morioka [20], and Noguchi et al. [21]. Based on the work of Krauss [1], the Cominco plant at Trail (BC, Canada) has also used a galvanodynamic scanning technique on a lead foil working electrode for many years to monitor its lead electrorefining electrolytes [8]. By using a foreign substrate, the two-wire CEQM and the galvanodynamic scanning technique could both provide data which can be interpreted in terms of two, essentially independent effects on deposit morphology, as explained below. However, neither of these techniques appears to have been applied to zinc electrolytes, the initial subject of further papers in this series.

In the present studies, the emphasis is on electrodeposition as applied to electrowinning or electrorefining of metals. However, in order to highlight the latent power of polarization measurements to predict the morphology of polycrystalline metal electrodeposits, various aspects of the underlying theory will first be considered here. It is important to note that these theoretical considerations may also be applicable to other processes which involve polycrystalline electrodeposition, such as electroplating and the operation of some rechargeable battery systems. Subsequent papers will focus on experimental results, initially results obtained for zinc electrowinning, which will demonstrate the proposed use of polarization parameters to assist in the prediction of long term deposit morphology.

2. Theoretical considerations

2.1. *Significance of independent measurements of nucleation potential and plating potential*

The techniques developed by Krauss and Kerby, and used at Trail by Cominco for controlling lead electrodeposition, using two types of organic morphology modifiers, (a levelling agent, and a grain refining agent) raise intriguing questions about what controls deposit morphology and how this happens. In the remainder of Part I, we hope to present some valid answers to these questions.

Building on pioneering work and a classification system developed by Fischer [22], Winand [5, 18, 23–25] has developed a pragmatic theory of electrocrystallization of polycrystalline metal deposits. This theory is summarized in the Winand diagram [25], which has five basic types of morphologies, as follows [18]:

(a) Field-oriented isolated crystals (FI)
(b) Base-oriented reproduction (BR)
(c) Twinning intermediate (Z)
(d) Field-oriented texture (FT)
(e) Unoriented dispersion (UD).

Type Z does not have a significant region of predominance, so it does not appear in the simplified Winand diagram. The Winand diagram represents the degree of inhibition versus availability of the reacting metal ion at the electrochemical interface.

Winand [18, 24] states that in pure solutions (without inhibitors), inhibition intensity is inversely proportional to exchange current density. When plating in or below the Tafel region, the main component of the total overpotential is the charge transfer overpotential, and, for a given operating current density, this has an approximately inverse relationship with exchange current density [26]. We suggest that the plating overpotential can be taken as the principal indicator of degree of inhibition and that this can be generalised to solutions containing inhibitors and activators, to describe their effects on inhibition intensity. For instance, levelling additives are easily adsorbed and generally increase the charge transfer overpotential [2, 4, 27, 28], probably by decreasing the exchange current density [29]. Oniciu and Muresan [30] have articulated the intuitive expectation that (a) additives which increase the plating overpotential at a given current density (for instance by altering the Tafel constants) can be considered 'deposit levelling additives' and also (b) additives which reduce primarily the nucleation overpotential can be considered (because of increased secondary nucleation events) to be 'grain refining additives'. It is well known that grain refinement is brought about by an increase in the nucleation rate [18, 31].

Under a particular set of conditions, Winand [18] correlated the transition from FT to UD deposits with a constant ratio of actual current density to the limiting current density. However, this result and those reported by other authors [32] are consistent with a relationship with the plating potential, which is usually a monotonic increasing function of current density. Based on consideration (b) of Oniciu and Muresan [30] as defined above, it is hypothesised that, for any given metal deposition system, there cannot exist a unique value of plating potential (or inhibition intensity) which corresponds to the transition from FT to UD deposits, because the nucleation potential also plays a crucial role.

The finest grained type (i.e., UD type deposits) require frequent 3D nucleation (on top of existing grains). This is sometimes referred to as 'secondary nucleation'. Our central hypothesis is that, for frequent 3D nucleation to occur *throughout plating*, a crucial factor is the relationship between the plating potential and the nucleation potential at very low current density, on a foreign substrate, as defined in Figure 1 for controlled current conditions. The foreign substrate is necessary (but not always sufficient) to observe tridimensional nucleation independently of crystal growth, in the time domain.

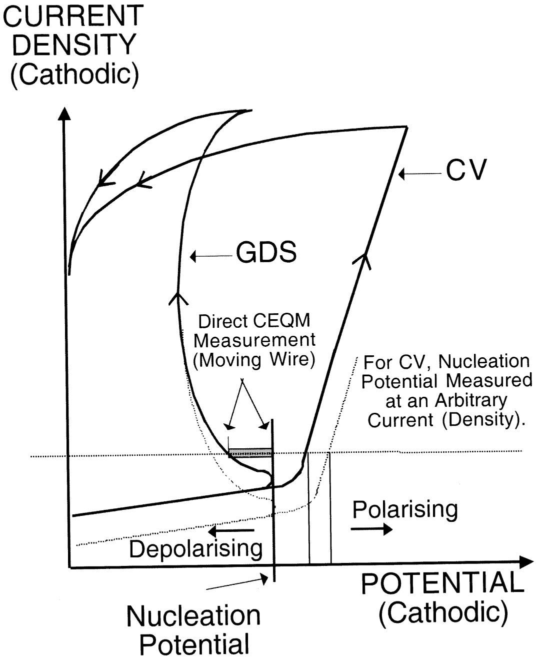

Fig. 1. Comparison of galvanodynamic scanning techniques (GDS) with cyclic voltammetry (CV). Note: GDS gives a value which is more fundamental and more repeatable than either CV or CEQM.

Tridimensional nucleation *during* deposit growth will only occur frequently if the overpotential for nucleation is low compared to the plating overpotential. In this case, with adequate inhibition, the deposit type should become UD. Conversely, if the electrode potential (plating potential) is considerably less cathodic than the nucleation potential, nucleation will not be favoured, and (at high inhibition and/or current density) it is likely that the deposit type will be FT. From this it can be seen that a simple change in nucleation potential may be sufficient to alter deposits between the FT and UD types.

Now consider the four schematic polarization curves (assuming a galvano-staircase cycle), shown in Figure 2. The various possible cases are denoted A, B, C and D. Each of these corresponds to one of the four zones shown in Figure 3. Zone A corresponds to high plating potential and a relatively low (cathodic) nucleation potential. Zone B corresponds to high plating potential, but high nucleation potential also. Zone C corresponds to a low nucleation potential, but also a low plating potential. Zone D corresponds to a low plating potential, but a relatively high nucleation potential. According to the reasoning given above, zone B should correspond to conditions favouring formation of FT deposits and zone A should correspond to conditions favouring formation of UD deposits. It can be inferred from the Winand diagram, that zones C and D should correspond (collectively) to low grade deposits, such as BR, FI or failure of the metal to deposit.

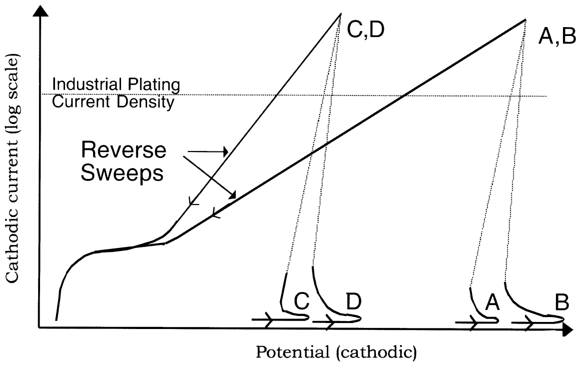

Fig. 2. Four basic dispositions possible for nucleation and plating potentials.

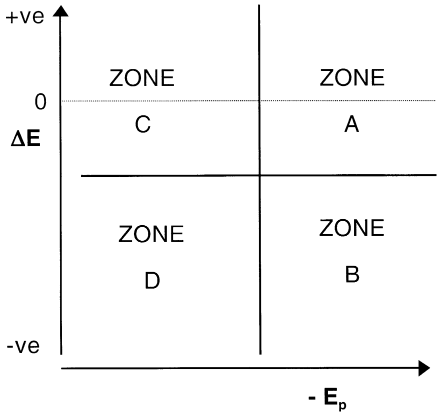

Fig. 3. Definition of four zones according to polarization properties.

It is well known [18, 33–35] that one of the major factors determining the overpotential (analogous to supersaturation in ordinary crystallization [35]) required to achieve nucleation above a critical rate is the surface energy. This is a microscopic analogue of surface tension, which affects the size of the critical nucleus [33, 35, 36]. As the *in situ* surface tension decreases, the energy or overpotential required for nucleation should fall rapidly. On a foreign substrate, the free energy of nucleation can be reduced [35], hence the nucleation potential can be lowered depending on the ability of the depositing metal to wet the substrate material. An ideal foreign substrate for this measurement would not cement or otherwise interact with the ions of the metal [37] nor become coated with underpotential monolayers or bulk phases [38]. It is expected that nonideal, conductive substrates will display a nucleation overpotential of lower magnitude than the value which would be observed on an ideal substrate. However, for a slightly nonideal substrate, it is anticipated that the observed gap between nucleation and plating potentials will be an industrially useful parameter, which can be calibrated with experience. Nucleation is affected by surface roughness–with step edges, grooves, and scratches acting as preferred nucleation sites [39–41]. Hence, a high degree of smoothness would be required.

Since surface energy will be affected also by transport and adsorption of surfactants, and by other factors, the exact relationship between nucleation potential and a parameter such as surface tension would not be entirely predictable. Therefore, in complex systems, the measurement of both nucleation and plating potentials is essentially a minimum requirement for prediction of changes in morphology due to an additional active species in solution or some other change.

It can be seen that lowering the macroscopic surface tension, with a surfactant which does not greatly alter the plating potential, should in some cases lead to grain refinement and (under the right conditions) it may cause the morphology to switch from FT to UD type. However, it is important to be aware of changes in behaviour, which occur around the critical micelle concentration (c.m.c.) [30, 42]. Up to the c.m.c., many organic polarizing agents reduce the surface tension markedly and therefore may decrease the magnitude of the nucleation overpotential. Once the c.m.c. is reached, the surface tension becomes relatively constant. By this stage, a polarizing effect may be manifested in both increased plating overpotential and an increase in the nucleation overpotential, counter to the initial effect. Therefore, there may be a limited range of concentrations for which a reduction in nucleation overpotential will be observed with increasing concentration.

2.2. *Comparison of methods for independent measurements of nucleation and plating potentials*

For the dual channel CEQM, Kerby [6] took measurements at the same current density as used for plating to represent the nucleation potential, provided the wire moved through the solution faster than a critical speed. It was argued that tridimensional (3D) nucleation of the depositing metal would occur. However, not all of the polarization curves displayed a nucleation hysteresis loop. This is not surprising, since a foreign substrate was not actually used. The measured differences between plating and nucleation potentials can be interpreted as being related to changes in the numbers of active sites between the initial and steady states.

Cyclic voltammetry [3, 7, 14, 16] has often been used instead of two cells with moving wires, to estimate nucleation potential on the forward sweep and plating potential on the reverse sweep. However, even for systems displaying a nucleation hysteresis loop, there are a number of problems with the use of potentiodynamic measurements for determining where nucleation occurs:

(i) A potentiodynamic programme normally forces the potential to continue to rise even after tridimensional nucleation occurs. Hence, an opportunity (Figure 1) to observe a peak potential [43, 44] is lost.

(ii) The potential measurement must be made at a current, considered to be close to that required to cause nucleation. This is not entirely predictable from test to test, and the choice of a standard current density at which to read off the value is arbitrary. Therefore measurements of nucleation overpotential by cyclic voltammetry differ from the point at which nucleation occurs [11]. This is explained diagrammatically in Figure 1. Furthermore, a major repeatability problem occurred, since various laboratories around the world reported values derived under different conditions of cathode composition and preparation technique.

(iii) As pointed out by Biegler [11] and Gonzalez [8], most published cyclic voltammograms are distorted by the effects of uncompensated resistance, R_U. Since plating potentials are measured at high current densities, they are always affected the most significantly. The drop, IR_U is dependent on cell geometry. Various laboratories have reported values derived under different conditions of electrode geometry, cell geometry, or scan parameters, and this contributes to a lack of comparability [8].

(iv) At high currents or high values of uncompensated resistance, even the linearity of a potentiodynamic waveform can be distorted [8], and this may downgrade the reproducibility of the measurement.

Galvanodynamic techniques have the potential to overcome these problems. The solution to problems (i) and (ii) is seen in Figure 1. In addition, by using galvanodynamic scanning, the excitation signal cannot be affected by IR distortion, as can occur for cyclic voltammetry (problem (iv) above).

Galvanostatic measurements have been reported by various authors [19–21]. However, the literature on systematic galvanodynamic or galvano-staircase measurements is virtually limited to the work of Cominco researchers [6, 8] and associated companies [7] on lead electrolytes. A galvanodynamic ramp has been used successfully for many years by Cominco's Trail plant, to monitor lead electrodeposition processes [8]. For the corresponding electrolytes, Gonzalez [8] undertook an investigation of IR-compensated galvanodynamic techniques.

We postulated that the magnitude of the plating overpotential (after IR compensation) and the relative position of the nucleation potential will have general significance with respect to the determination of the morphological growth mode prevailing after the influence of the substrate is overcome. If this general applicability of the interpretation of galvano-staircase polarization curves in terms of the Winand diagram can be proved, it should simplify the requirements for characterization of a system and for process optimization and control. Specifically, a galvano-staircase waveform would represent an improved way of measuring both nucleation potential and plating potential, making it superior to the online sensors and other techniques described in the literature, including the dual channel CEQM [6]. The galvano-staircase technique takes small steps typically at intervals of a few tenths of a second. In practice, the potential is sampled and averaged near the end of the period at each step. This discriminates against nonfaradaic components, such as double layer charging current.

3. Development of experimental technique

From the foregoing considerations, it is expected that measurement of potential in response to a controlled current should allow determination of a number of parameters from a cyclic experiment commencing on a suitable foreign substrate, including: (i) nucleation potential, E_n (on the forward sweep), (ii) plating potential, E_p, as a function of current density (on the reverse sweep), and (iii) the gap, ΔE, defined as $E_n - E_p$. A preferred waveform developed in our work is represented diagrammatically in Figure 4 and the values of the parameters are given in Table 1. It can be seen that three different effective current scan rates were used. The intermediate rate was 5^2 times the slowest, and the fastest rate was 5^3 times the slowest. The scan was made up of very small steps, with the potential measured near the end of each step, as discussed at the end of Section 2.2. The total number of data points collected in a scan was 2798. Using this waveform, the nucleation potential was taken as the reading immediately after the most cathodic potential reached. Variations on this technique, which do not affect the essentials include: (i) the effective scan rate from the first change to the vertex, and (ii) the current densities for the first rate change and the vertex. Other effective scan rates should not be varied by more than an order of magnitude, unless the metal ion concentration or the activity of the electrode towards competing processes prior to nucleation changes significantly.

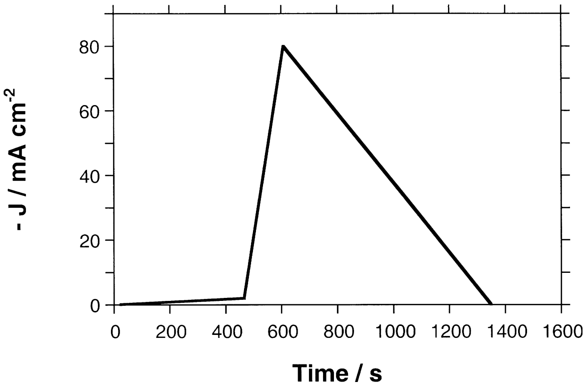

Fig. 4. Preferred galvano-staircase waveform, shown as a ramp.

Table 1. Definition of preferred galvano-staircase waveform

Element of waveform	Details	Value	Units
Instrument mode	galvanodynamic		
Initial J		0	mA cm^{-2}
Initial time delay	none*		
J for scan rate change	cathodic	2	mA cm^{-2}
J at vertex	cathodic	80	mA cm^{-2}
Final J		0	mA cm^{-2}
Scan rate I	cathodic	4.14	μA cm^{-2} s^{-1}
Scan rate II	cathodic	517	μA cm^{-2} s^{-1}
Scan rate III	anodic	103	μA cm^{-2} s^{-1}
Number of cycles		1	
Final state	cell off (open circuit)		

* Working electrode was placed in the cell at zero current 15 s prior to starting the scan.

With the method outlined here, there is an opportunity to compensate fully for differences in cell geometry, which may occur between different laboratories. This requires a knowledge of the uncompensated resistance, R_u, which affects mainly $-E_p$. Its effects on $-E_n$ are often negligible.

Details of the application of this method to studies of conventional and nonconventional zinc electrowinning solutions will be reported in Parts II and III of this work. An overview is already available [44]. As an example, Figure 5 shows the *IR*-compensated results from a scan on an additive-free solution of low acidity, doped with a high level of Fe^{2+} (similar to the Zn^{2+} content). Initially, the potential increases gradually as the current density increases, with the current mainly going into hydrogen evolution. At the nucleation potential, the movement of the potential is naturally reversed. Upon speeding up the scan rate, the potential increases again to a broad peak, and is relatively steady once the vertex (800 A m^{-2}) is reached. A near-steady state depolarization curve is then obtained.

For measurements in zinc sulfate solutions, aluminium protected by a thin film of alumina is a substrate, which has been used extensively for cyclic voltammetry studies [9, 12, 13, 15, 45, 46]. This system, beginning with >99.99% pure aluminium discs, was used for initial evaluation of the proposed technique. Other suitable substrates, for the deposition of a range of metals, may include glassy carbon, and titanium with a thin, protective oxide film. There is a strong dependence on the method of substrate preparation [39–41], as anticipated in Section 2.1.

After each use, the working electrodes must be polished to remove traces of the metal being plated. These would interfere with nucleation measurements, since, using zinc as an illustration, it could grow on existing zinc without tridimensional nucleation occurring. However, a polished, unoxidized aluminium electrode could cement solution impurities. Without sufficient time for the protective alumina layer to be restored, we have observed anomalous scans. To avoid this, our routine measurements were carried out on aluminium electrodes, which had been aged in air for at least 36 h since polishing.

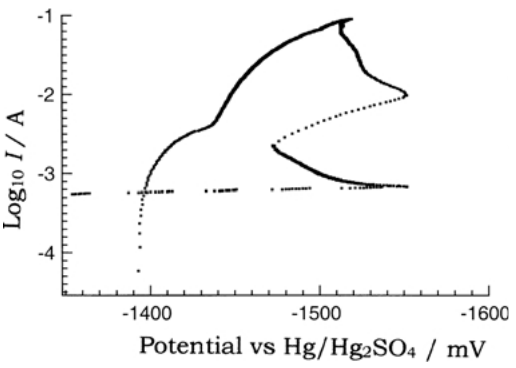

Fig. 5. Example of the result of a scan using the preferred waveform.

Table 2. Nucleation potentials measured on identical solutions with different electrode finishes

Details of polish	$-E_n$ on polished and oxidized Al /mV vs Hg/Hg_2SO_4	$-E_n$ on used, then pickled Al /mV vs Hg/Hg_2SO_4
SiC/P600/vertical	1510	1519
SiC/P1200/random	1531	1532
SiC/P1200/vertical	1536	1517
Diamond/3 μm/vertical	1545	1547
Diamond/0.25 μm/random	1558	1543

In Table 2, comparisons are made for $-E_n$ between a P600 and a P1200 vertical emery finish as well as with electrodes polished using diamond paste down to 3 μm or 0.25 μm. Electrodes, which were simply pickled and not repolished since their previous use, usually gave different results, as shown in Table 2. There is no simple trend in these differences. However, on electrodes which had been polished and air-oxidized, the clear trend is for higher nucleation potential observed on a surface with finer features. This is in accord with recent advances in the understanding of electrocrystallization theory [47], and could have ramifications for cathode preparation in industry, for the optimization of machine or hand stripping of deposits. For finer finishes, there are fewer sites energetically favourable for nucleation, as shown by the 48 mV spread of results in the first column of Table 2. Vertical alignment of the scratches seems to have a definite, small influence. It was observed to increase the magnitude of the nucleation potential by 5 mV compared to a circular polishing motion. For electrowinning, an optimally prepared surface finish would be expected to result in the most even distribution of attachment points.

Clearly, a standard surface polishing technique is required in order to compare different electrolyte solutions. From replicate measurements using a vertical P1200 finish, it is known that the standard deviation for nucleation potential is in the range 3–4 mV. Ultimately, following a review of data such as that shown in Table 2, the standard polish was taken through to P2400 (or, more recently at Pasminco, P4000) grade using SiC paper only. Either of these finishes gave excellent reproducibility. The smoothness is similar to that which would be achieved with about 1 μm diamond paste.

Using such a preparation method and the scan parameters in Table 1, detailed characterization of polarizing effects of species in zinc electrowinning solutions has been accomplished [44]. Results for the conventional electrowinning system will be presented in Part II of this series.

4. Conclusions

1. A new method of measuring nucleation potential in a consistent manner has been developed. It is possible to measure plating potential in the same galvano-staircase routine. By knowing the uncompensated resistance, offline *IR*-compensation can correct these potentials, and the true gap between them can be calculated.
2. Morphology will be affected in different ways by the plating potential and the potential at which nucleation becomes favoured. The combination of (a) the gap between the nucleation potential and the plating potential and (b) the *IR*-compensated plating potential are proposed as parameters having fundamental significance in the development of polycrystalline electrodeposit morphology, once any substrate effect is overcome. Parameter (a) affects grain size, whereas parameter (b) affects deposit levelling. It is further asserted that in complex systems the absolute concentration of an individual additive is of less importance than these two parameters.
3. The galvano-staircase technique is a rapid means for acquiring data on the most important effects of morphology modifiers, both for existing operations or new processes. The basic principles should be applicable to electrodeposition of many different metals.
4. To establish the utility of the new galvano-staircase technique, coupled complementary studies (in deposition cells) are required. Such studies will be the subject of future papers in this series.

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References

1. C.J. Krauss, *J. Metals* **28**(11) (1976) 4.
2. C.J. Krauss and R.C. Kerby, *in* I.H. Warren (Ed), 'Application of Polarization Measurements in the Control of Metal Deposition' (Elsevier, Amsterdam, 1984), pp. 241–252.
3. T.J. O'Keefe, *in* I.H. Warren (Ed), *op. cit.* [2], pp. 15–41.
4. T.N. Andersen, R.C. Kerby and T.J. O'Keefe, *J. Metals* **37**(1) (1985) 36.
5. R. Winand, M. Degrex and V. Bastin, *in* W.C. Cooper, D.J. Kemp, G.E. Lagos and K.G. Tan (Eds), 'Copper 91 (Vol. III: Hydrometallurgy and Electrometallurgy of Copper)', (Pergamon, New York, 1992), pp. 341–354.
6. R.C. Kerby, *US Patent 4 443 301* (1984).
7. R.E. Alford, *in* P.L. Claessens and G.B. Harris (Eds), 'Electrometallurgical Plant Practice' (Pergamon, New York, 1990), pp. 309–313.
8. J.A. Gonzalez-Dominguez, *Minerals Eng.* **7** (1994) 87.
9. B.A. Lamping and T.J. O'Keefe, *Met. Trans. B.* **7** (1976) 551.
10. D.J. Mackinnon and J.M. Brannen, *J. Appl. Electrochem.* **7** (1977) 451.
11. T. Biegler, *in* I.H. Warren (Ed), *op. cit.* [2], pp. 32–46.
12. R.C. Kerby, H.E. Jackson, T.J. O'Keefe and Y-M. Wang, *Metall. Trans. B* **8** (1977) 661.

13. A.M. Alfantazi, D.B. Dreisinger, M. Boissoneault and J. Synnot, *in* D.B. Dreisinger (Ed), 'Aqueous Electrotechnologies: Progress in Theory and Practice', The Minerals, Metals & Materials Society (1997), pp. 139–161.
14. I.H. Warren, *in* K. Tozawa (Ed), 'Zinc '85: Proceedings of the International Symposium on Extractive Metallurgy of Zinc', (MMIJ, Tokyo, 1985), pp. 251–264.
15. D.J. Mackinnon, R.M. Morrison, J.E. Mouland and P.E. Warren, *J. Appl. Electrochem.* **20** (1990) 728.
16. R.C. Kerby and C.J. Krauss, *in* J.M. Cigan, T.S. Mackey and T.J. O'Keefe (Eds), 'Lead-Zinc-Tin '80', TMS-AIME, Warrendale, PA (1980), pp. 187–203.
17. R.C. Kerby and W.A. Jankola, *in* P.L. Claessens and G.B. Harris (Eds), *op. cit.* [7], pp. 323–330.
18. R. Winand, *Hydrometallurgy* **29** (1992) 567.
19. M. Maja, N. Penazzi, R. Fratesi and G. Roventi, *J. Electrochem. Soc.* **129** (1982) 2695.
20. S. Ohyama and S. Morioka, *in* K. Tozawa (Ed), *op. cit.* [14], p. 219.
21. F. Noguchi, T. Nakamura and M. Sakata, *in* T. Azakami, N. Masuko, J.E. Dutrizac and E. Ozberk, (Eds), 'Zinc & Lead '95', (MMIJ, Tokyo, 1995), pp. 404–413.
22. H. Fischer and H.F. Heiling, *Trans. Inst. Metal Finish.* **31** (1954) 90.
23. A. Weymeersch, L. Renard, J.J. Conreur, R. Winand, M. Jorda and C. Pellet, *Plat. Surf. Finish.* **73**(7) (1986) 68.
24. R. Winand, *J. Appl. Electrochem.* **21** (1991) 377.
25. R. Winand, *Electrochim. Acta* **39** (1994) 1091.
26. K.J. Vetter, 'Electrochemical Kinetics. Theoretical and Experimental Aspects', translated by S. Bruckenstein and B. Howard (Academic Press, New York, 1967), pp. 134–154.
27. K.J. Vetter, *op. cit.* [26], pp. 565–570.
28. H. Fischer, *Angew. Chem. Internat. Ed. Engl.* **8** (1969) 108.
29. E. Budevski, G. Staikov and W.J. Lorenz, 'Electrochemical Phase Formation and Growth' (VCH, Weinheim, 1996), pp. 20–39.
30. L. Oniciu and L. Muresan, *J. Appl. Electrochem.* **21** (1991) 565.
31. E. Budevski, G. Staikov and W.J. Lorenz, *op. cit.* [29], p. 273.
32. Y. Ogata, K. Yamakawa and S. Yoshizawa, *J. Appl. Electrochem.* **13** (1983) 611.
33. K.J. Vetter, *op. cit.* [26], pp. 326–327.
34. E. Budevski, G. Staikov and W.J. Lorenz, *op. cit.* [29], p. 163.
35. J.W. Mullin, 'Crystallisation' (Butterworths, London, 2nd edn, 1972), pp. 136–150.
36. J.C. Brice, 'The Growth of Crystals from Liquids' (North-Holland Publishing, Amsterdam, 1973), pp. 89–97.
37. T. Xue, W.C. Cooper, R. Pascual and S. Saimoto, *J. Appl. Electrochem.* **21** (1991) 238.
38. E. Budevski, G. Staikov and W.J. Lorenz, *op. cit.* [29], pp. 180–199.
39. S. Fletcher, *Electrochim. Acta* **28** (1983) 237.
40. S. Fletcher and D.B. Matthews, *J. Appl. Electrochem.* **11** (1981) 11.
41. E. Budevski, G. Staikov and W.J. Lorenz, *op. cit.* [29], p. 39.
42. A.W. Adamson, 'Physical Chemistry of Surfaces' (Wiley Interscience, New York, 5th edn, 1990), pp. 508–513.
43. K.J. Vetter, *op. cit.* [26], pp. 671–673.
44. P.A. Adcock, S.B. Adeloju, O.M.G. Newman, *in* J.A. Gonzalez, J.E. Dutrizac and G.H. Kelsall (Eds), 'Electrometallurgy 2001', (CIM, Montreal, 2001), pp. 401–414.
45. M.J. Howell, A.R. Ault, O.M.G. Newman, K.J. Cavell and B.V. O'Grady, *in* I.G. Matthew (Ed), 'World Zinc '93', (AusIMM, Melbourne, 1993), pp. 307–314.
46. T. Xue, W.C. Cooper, R. Pascual and S. Saimoto, *J. Appl. Electrochem.* **21** (1991) 231.
47. E. Budevski, G. Staikov and W.J. Lorenz, *op. cit.* [29], p. 179.