Morphology of High Rate Electrozinc

By T.R. Roberts, F.H. Guzzetta and R.Y. Lin

High plating temperatures (60 to 70° C) and low current densities (50 to 100 A/din') tended to produce smooth zinc deposits during a bench-scale study simulating continuous strip plating. Microrough coatings were obtained when the applied current density exceeded 25 percent of the limiting current density.

Electrogalvanized sheet steel produced by zinc plating is currently used in the manufacture of automobile bodies, appliances, and construction materials. The electrogalvanizing process is often a batch operation, such as in rack and barrel plating,' but strip plating is continuous.? To produce sufficiently thick coatings at production strip speeds, high current densities are employed. At high current densities (>100 A/dm^2), however, spongy, powdery, dendritic coatings are formed, a result of Insufficient diffusion of zinc ions at the boundary layer.' Rough coatings on steel panels may affect the consistency and quality of the finished automobile body. For example, Keeler and Dwyer[4] have shown that rough electroplates exhibit higher coefficients of friction during forming operations than do smooth coatings, resulting in die pickup and in extreme cases, breakage. Roughness has also been found to affect the quality of the material when painted.'

Process parameters that may affect the properties of the zinc coating include plating temperature, zinc ion concentration, electrolyte flow rate, and current density. High flow rates have been used to achieve smooth coating surfaces. For example, by employing a turbulent solution flow rate of about 1.25 m/see Safranek and Layer[6] reduced coating roughness in a laboratory study while plating at high current densities. Successful commercial production of smooth coatings at high current densities has been accomplished utilizing a flow rate of 1 to 2 m/sec.[7] Substantial research has been devoted to developing and refining high-speed plating processes.[8-10] Other efforts in this area have resulted in the development of various types of high-flow-rate plating cells.''-" Most of these processes employ high-volume pumps and specially designed nozzles to induce high electrolyte flow.

The purpose of this investigation was to study the effect of plating temperature and current density on the surface roughness of zinc coatings using a bench-scale gravity flow cell, with an electrolyte flow rate of approximately 1.7 m/see. A new method of characterizing the surface roughness of the coating by measuring the cross-sectional surface length has also been suggested.

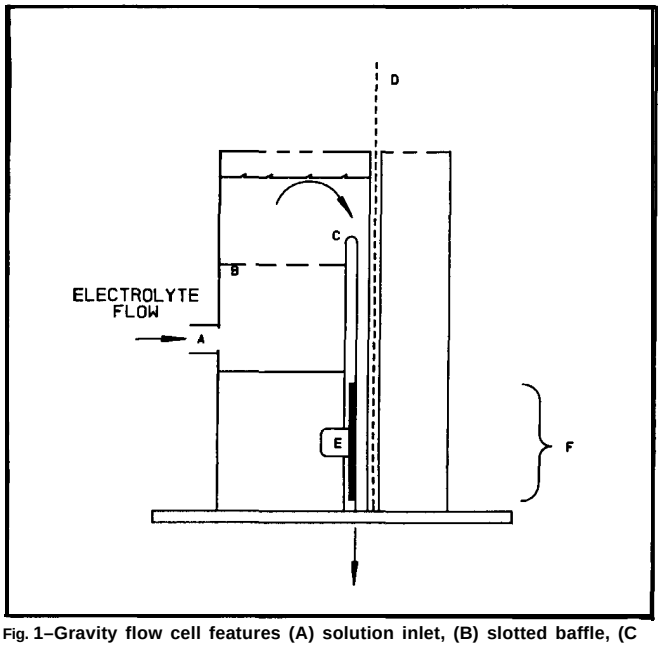

Fig. 1–Gravity flow cell features (A) solution inlet, (B) slotted baffle, (C overflow weir, (D) steel cathode, (E) anode, and (F) plating area.

Experimental Procedure

A small bench plating cell was constructed to simulate the ARUS-Andritz-Ruthner Gravitel Process.[16,17] The unit included a 300-A (24-V) rectifier, a 70-L electrolyte storage tank with a thermostatically controlled heater and cooling coil, a magnetically coupled (50 gal/rein) polypropylene pump, and a polyacrylate gravity flow cell. Details of the flow cell are shown in Fig. 1.

A steel sheet approximately 12 x 60 cm was inserted into the sample slot. Electrolyte flowed over the weir and down the gap between the anode and cathode (steel sheet). The anode was placed approximately 32 cm below the top of the weir, resulting in a restricted electrolyte flow of about 1.7 m/see across the anode. The gravity flow cell contained an IrO_2-coated titanium insoluble anode (about 9.5 x 15 cm). Plating occurred on the steel cathode only in the area directly across from the anode. The anode-to-cathode gap was set at 8 mm at the top and 5 mm at the bottom, simulating the geometry of the Gravitel cell.

Lightly oiled, cold-rolled steel sheets were spray alkaline cleaned, water rinsed, electrolytically alkaline cleaned, water rinsed, and then lightly activated in sulfuric acid prior to electroplating. Each 1.425-dm^2 sample was plated for 1.62 A-hr to obtain a coating weight of 140 g/m' (19.6 Pm). The electrolyte contained 125 g/L Zn, 5 g/L H_2SO_4 and 2.4 g/L Al. The temperature of the solution was increased in 10° increments from 30 to 70" C; the current density was approximately 50, 75, 100, 125 or 150 A/dm^2 for the various experiments.

Electroplated samples were cross sectioned and polished using metallographic procedures developed for electrogalvanized steel.[18] Five representative cross sections of each sample were photographed at 1000X. The surface length of each section was traced using point-to-point

contact and a digitizer." These data were then filed in a computer." Each trace was compared by the program to a flat surface with an assigned length of 1.0. The means and standard deviations were determined from the five contours of each sample. Surface morphologies were recorded by scanning electron microscopy after sample surfaces were coated with 2 to 3 nm of Au/Pal to enhance secondary electron imaging.

Results

The voltage required to adjust the current density to a preselected value declined as the temperature was increased. The plating efficiency, however, was not significantly affected by temperature changes. Dark, rough deposits were obtained at high current densities and low temperatures. Figure 2 shows representative cross sections; surface-contour data are given in Fig. 3; and Fig. 4 shows scanning electron micrographs (SEMs) of the deposits. When the temperature was >50° C, the crystals became smaller and more closely packed.

Figures 5 and 6 compare the crystal morphology (at a high magnification) of coatings produced at 30 and 70° C, respectively. The crystals of the deposits from the 30° C solution were much larger. At the higher temperature (70° C), the morphology was unchanged with shifts in current density.

Discussion

Seekely and Themelis[19] found that for turbulent fluid flow over a flat plate, the diffusion layer thickness, ð, is:

$$\delta = \frac{L^{0.1}}{U_b^{0.9}} \nu^{1.30} (D_{A-B})^{1.3} \qquad (1)$$

where L = the distance from the leading edge of the plate in the direction of the fluid flow; U_b = the velocity of bulk flow parallel to the surface of the plate = the kinematic viscosity of the fluid; and D_{A-B} = the diffusivity of Zn ion in the fluid (electrolyte).

The molar flux, N_a, of A between the bulk fluid and the surface is:

$$N_a = \frac{CD_{A-B}}{\delta(C_B)_{lm}} (C_{A,0} - C_{A,b}) \qquad (2)$$

where C = the molar density of fluid; $(C_B)lm$ = log mean concentration of the nondiffusing species B; $C_{A,0}$ = the concentration of A at the surface; and $C_{A,b}$ = the concentration of A in the bulk fluid.

Equation 1 indicates that the diffusion-layer thickness of the electrolyte is inversely proportional to the fluid viscosity to the 0.9 power, providing the other fluid properties (i.e., kinematic viscosity and diffusivity of Zn ion) remain constant. Equation 2 shows that with a reduced diffusion-layer thickness, the number of Zn ions arriving at the plating surface increases. On the other hand, previous studies demonstrated that at a constant current density, smooth coatings were obtained with an electrolyte flow rate of 1 to 2 m/see. These results may be attributed to a sufficient supply of zinc ions at the plating surface.

At low temperatures, current density had a pronounced effect on roughness. As the electrolyte temperature increased, the effect of current density on roughness

'Tektronix 4954, Tektronix, Beaverton, OR.
"Hewlett-Packard HP 3000, Hewlett-Packard, Sunnyvale, CA

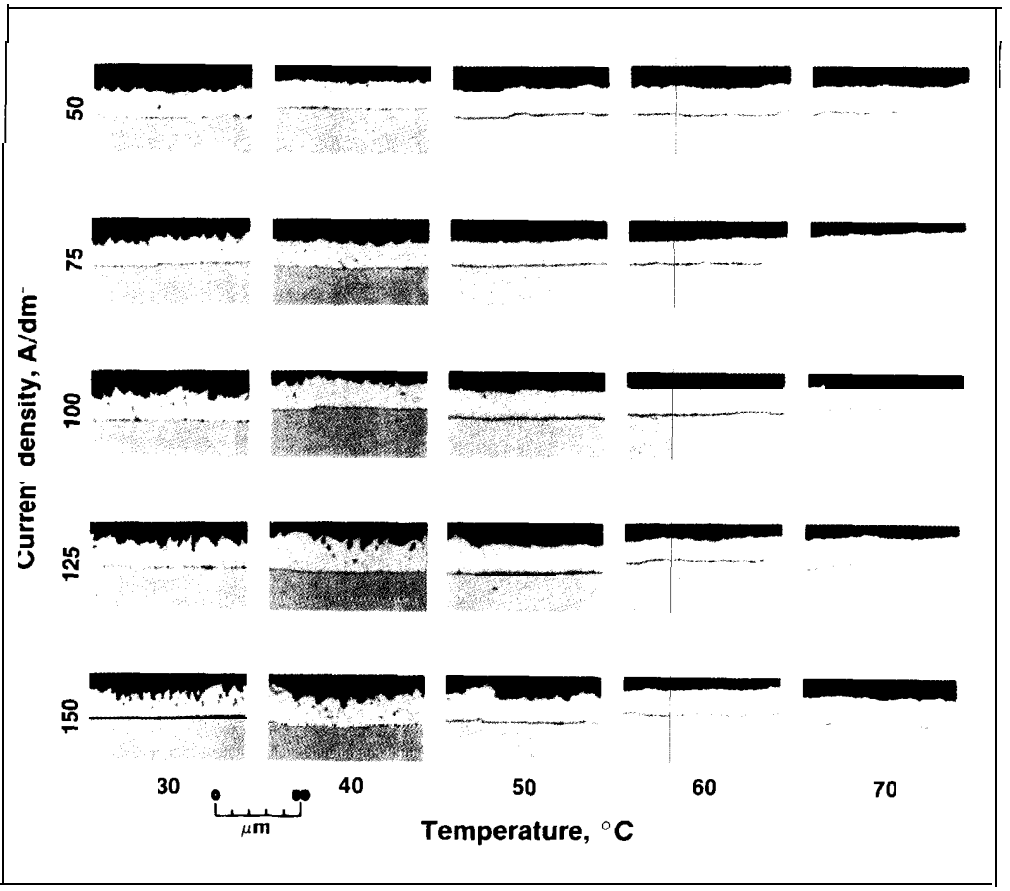

Fig. 2—Cross sections of zinc deposits obtained at different temperature and current densities.

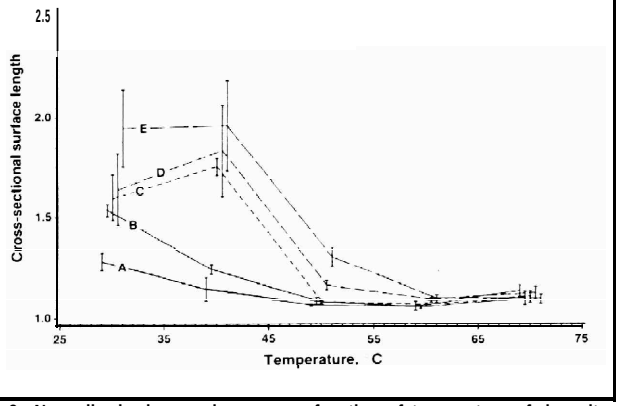

Fig. 3—Normalized microroughness as a function of temperature of deposits produced at (A) 50 A/din', (B) 75 A/din', (C) 100 A/din', (D) 125 A/dm², and (E) 150 A/din'.

diminished. Figure 7 illustrates the roughness values of plated samples as a function of the plating temperature and current density; three roughness zones are separated by lines a and b. Such roughness variation with temperature may be related to the amount of zinc ion at the surface.

When the zinc ion concentration in the vicinity of the plating surface is decreased, either by an increase in the diffusion-layer thickness or a reduction in the diffusivity of zinc ion, plating will continue preferentially in the direction normal to the surface. This plating results in greater deposition on the portions of the substrate protruding from the surface because the diffusion layer is thinner at protrusions than in recesses. Noruniformity thus becomes self-perpetuating and is further increased by electrical field concentrations on the surface projections.

An increase in temperature results in a reduction of diffusion-layer thickness and an increase in the diffusivity

Table 1
Viscosity, Density, and Kinematic Viscosity of Water

Temp., °C	Viscosity, μ(cp)	Density, g/cm³	Kinematic viscosity	Diffusion-layer thickness[a]	Zinc flux[a]
30	0.7975	0.9957	0.8009	1.0000	1.000
40	0.6529	0.9922	0.6580	0.8946	1.118
50	0.5468	0.9881	0.5534	0.8110	1.233
60	0.4665	0.9832	0.4745	0.7433	1.345
70	0.4042	0.9778	0.4134	0.6875	1.455

[a]Calculated and normalized at 30° C.

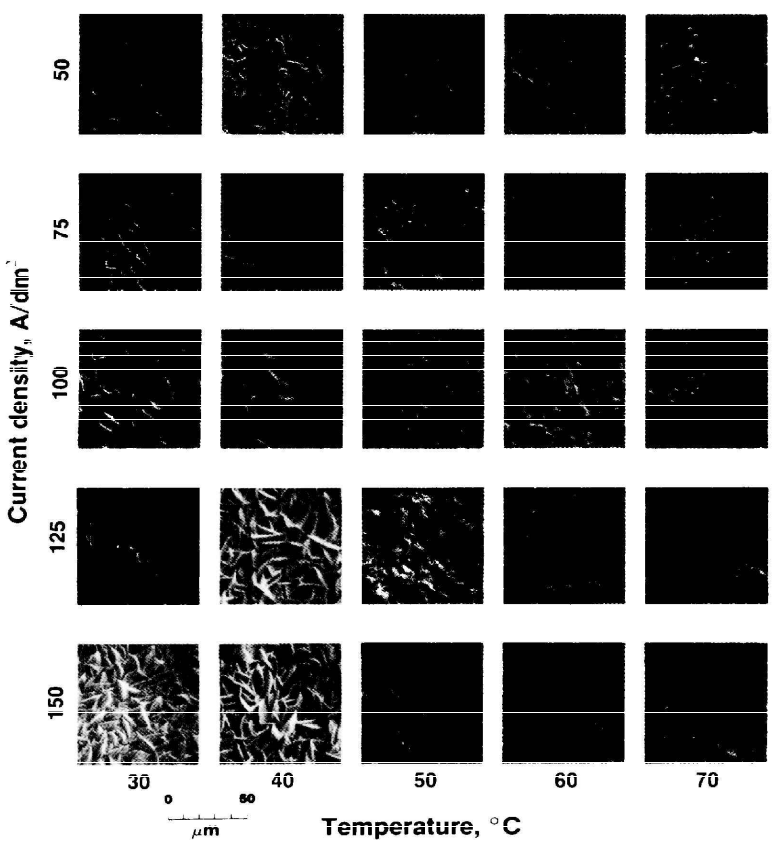

Fig. 4—SEMs of zinc coating surfaces.

of the zinc ion. Equation 1 shows that when solution flow is turbulent, the diffusion-layer thickness varies with the viscosity of the fluid to the power of 17/30 and with the diffusivity, to the power of 1/3. In this study, with a flow rate of 1.7 m/see and a kinematic viscosity of 0.82 x 10^{-2} in./sec, the Reynolds number for fluid flow over a plate becomes:

$$NK_{Re} = d_h U/D = 31{,}100$$

The hydraulic diameter, d_h, is estimated as 1.5 cm because the width of the plate is 16.5 cm (W) and the gap between the electrodes is 0.8 cm (T), resulting in a flow area of 13.2 cm^2, which is equivalent to $d_h = 20WT/W+T$.[19] Because the Reynolds number is much greater than 10,000, the electrolyte flow in this study is considered to be turbulent.[14]

Using Eq. 1, the diffusion-layer thickness is estimated for different temperatures. Table 1 lists the viscosity, density,[20] kinematic viscosity, and calculated, normalized diffusion-layer thickness at 30° C. Using Eq. 2, the normalized zinc ion flux, with respect to the value at 30" C, may be estimated, assuming the variation of diffusivity from 30 to 70° C is negligible. The last column in Table 1 lists the calculated values of the normalized flux. The limiting current density (i_L) during plating should be proportional to the flux of zinc ions at the plating surface. Using Fukuda's equation,[14] the limiting current density was estimated to be about 200 A/dm^2 at 30° C. Taking this value and the data in the last column of Table 1, i_L Values from 30 to 70° C were calculated and plotted in Fig. 8 together with isoroughness lines a and b. Both lines a and b and the limiting current density increase with increasing temperature.

Figure 8 seems to imply that at the higher temperatures the surface will remain smooth as the plating current density approaches the limiting current density. A further refinement of this implication considers the effect of temperature on diffusivity. As the temperature increases, the diffusivity of zinc ions in the diffusion layer increases (Table 2). The increased diffusivity results in a further increase in the flux of zinc ions arriving at the plating surface and thus an increase in the limiting current density as the temperature increases. As shown in Fig. 8, the increased limiting current density will cause an increase in the slope of the i_l line and push it towards i_L', which has a slope similar to that of lines a and b. Because these lines have similar slopes, the ratio of the applied plating current density to the limiting current density determines the microroughness of the plated surface. When the plating current density was about 25 percent of the limiting current density, the microroughness was 1.30 as measured by the cross-sectional surface-roughness scale (line b).

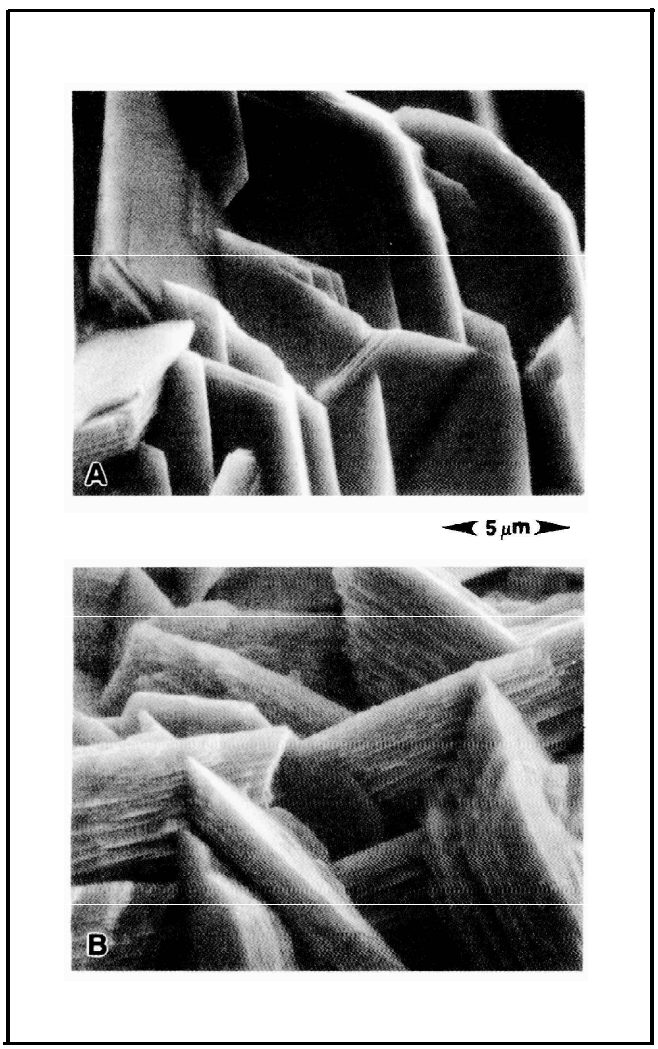

Fig. 5—High-magnification electron micrographs of zinc deposited at 30° C and (a) 50 A/dm^2 and (b) 150 A/dm^2.

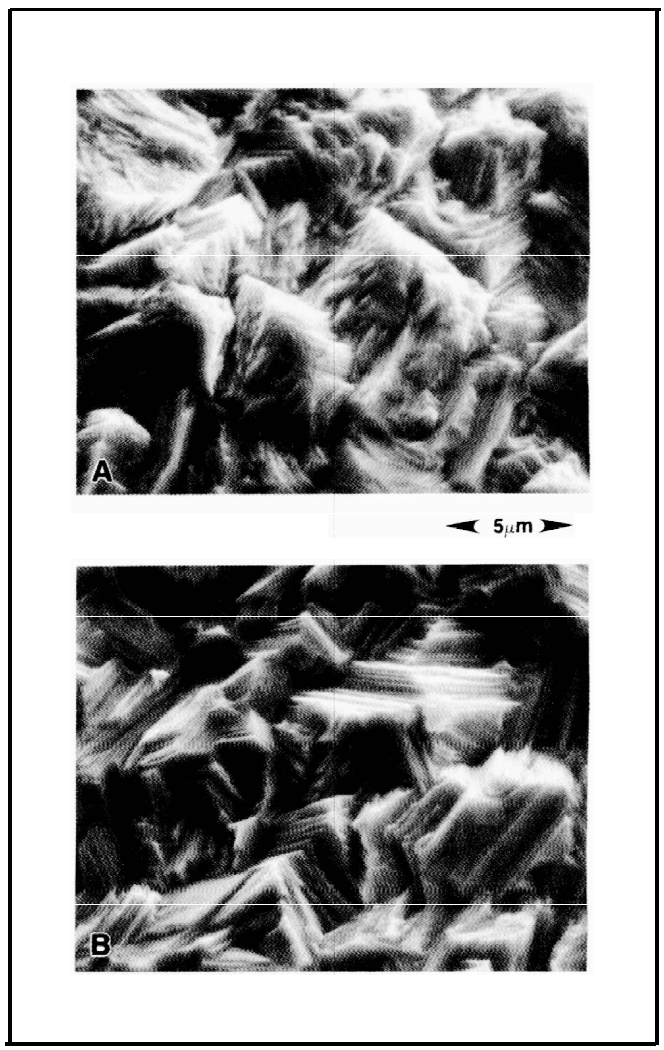

Fig. 6—High-magnification electron micrographs of zinc deposited at 70C and (a) 50 A/dm^2 and (b) 150 A/dm^2.

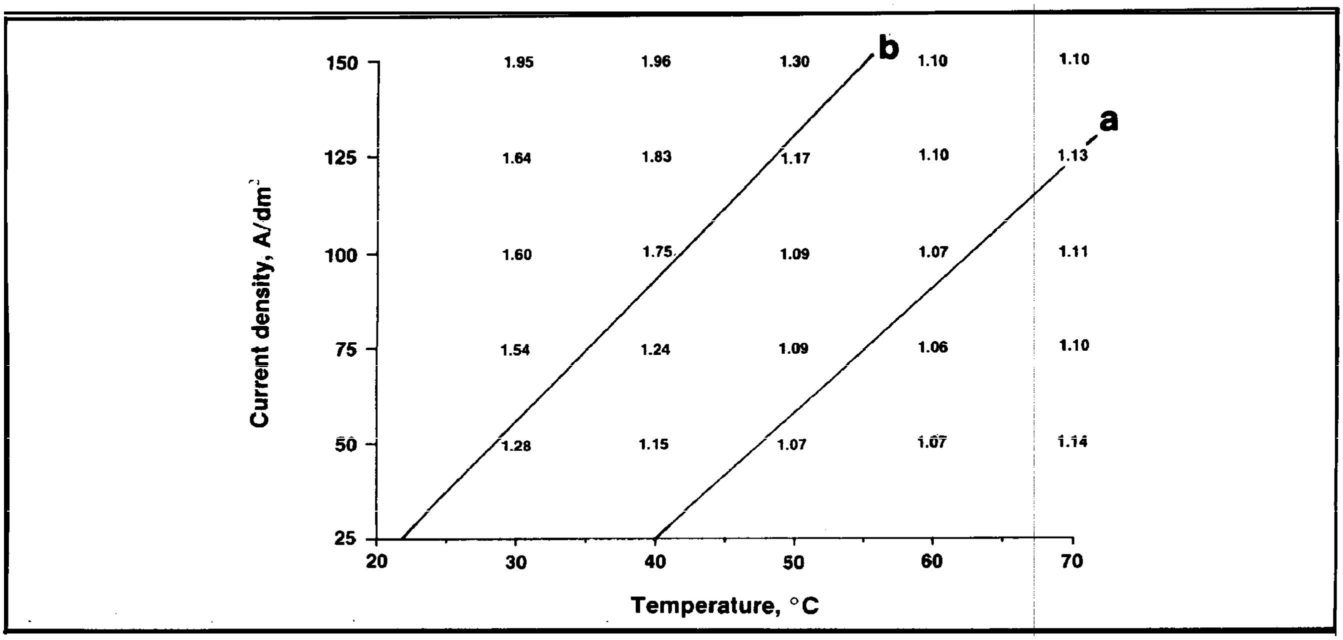

Fig. 7—Microroughness of zinc as a function of temperature and current density; lines a and b are isoroughness lines approximately equal to 1.1 and 1.3 on the normalized roughness scale.

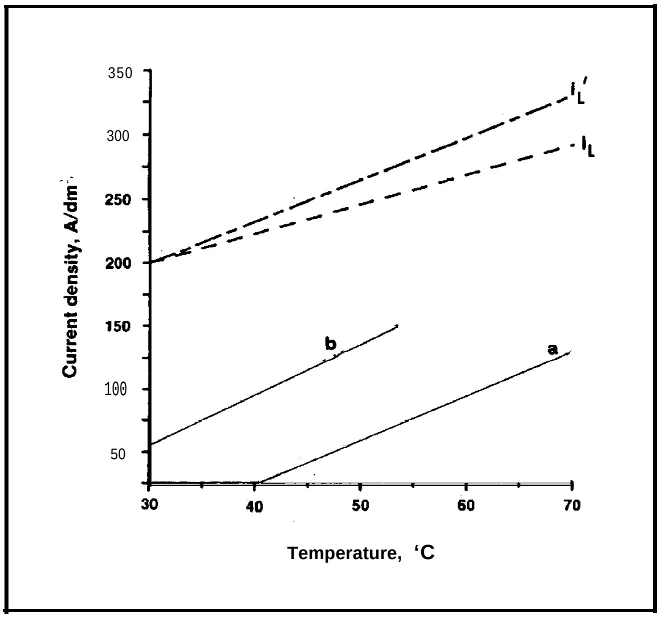

Fig. 8—Limiting current density (i_L) as a function of temperature and turret density isoroughness lines a and b are approximately equal to 1.1 and 1.3 on the normalized-roughness scale.

Table 2
Estimated Diffusivity of Zinc Ion and Limiting Current Densities in Sulfate Electrolytes

Temp., °C	Limiting current density*	Estimated diffusivity, cm²/sec†	Limiting current density‡
30	2000	8.61 × 10 [illegible]	2000
40	2230	[illegible]	2309
50	[illegible]	[illegible]	2629
60	2690	9.46 × 10 [illegible]	2956
70	2910	9.74 × 10 [illegible]	3292

*According to [illegible] and Table 1
†From Perry and Chilton
‡Corrected for diffusivity

Conclusions

The zinc ion supply and consumption rate at the cathode surface are factors determining the surface microroughness of zinc electrodeposits. Microroughness decreases when plating current density is constant as solution temperature is increased. When the ratio of the applied and limiting current densities is about 0.25, microroughness is 30 percent greater than a flat surface, as measured by the cross-sectional surface-length technique described in this paper.

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References

1. A.K. Graham, *Electroplating Engineering Handbook*, 3rd ed., Van Nostrand Reinhold Co., New York, NY, 1971; p. 594-609.
2. Ibid., p. 652.
3. A. Weymeersch, R. Winand and L. Renard, *Plat. and Surf. Fin., 68,56* (Apr. 1981
4. S.P. Keeler and T.E. Dwyer, *SAE Paper 860433, Detroit,* MI (Feb. 1986).
5. T.R. Roberts, unpublished work.
6. W.H. Safranek and C.H. Layer, *Trans. Inst. Met. Fin., 53, 121 (1975).*
7. K. Sate, K. Yamato and K. Iozumi, *Trans. ISIJ,* p. 946 (1983).
8. K. Sakai et al., *Proc. AESF 4th Continuous Strip Plating Symp. (May* 1984).
9. K. Sakai and H. Nakao, U.S. patent 4,491,506.
10. K. Sakai et al., *Iron and Steel Eng.,* p. 49 (Aug. 1985).

11. M. Podrini, U.K. patent application GB2140037A.
12. R. Winand, U.S. patent 4,304,653.
13. T. Sellitto, U.S. patent 4,183,799.
14. J.L. Faltenmier and C.W. Tobias, MS thesis, University of California-Berkeley, Lawrence Berkeley Laboratory Report No. 13057 (1982).
15. S. Fukuda et al., *Nippon KK Technical Report Overseas* No. 31 (1981).
16. J. Hampel, U.S. patent 4,469,565.
17. T.R. Roberts, T.R. Heckard and E.A. Williams, *Proc. AESF Fifth Continuous Strip Plating Symp.* (May 1987).
18. T.R. Roberts, MS thesis, University of Cincinnati (1986).
19. J. Seekely and N.J. Themelis, *Rate Phenomena in Process Metallurgy,* Wiley-Interscience, New York, NY, 1971 ; p. 109, 369,425-427.
20. CRC *Handbook of Physics and Chemistry, 61st* ed., Chemical Rubber Co., Cleveland, OH (1981).
21 R.H. Perry and C.H. Chilton (ed.), *Chemical Engineer's Handbook,* 5th ed., McGraw-Hill, New York, NY, 1973; p. 3-324.

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