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# **Ductility and Crystallographic Structure of Zinc Foils Electrodeposited from Acid Zinc Sulfate Solutions**

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### ABSTRACT

A study of the relation between electrodeposition process parameters, structure and ductility of electrodeposited zinc foils was carried out. A stretching test was used to determine the ductility of zinc coatings after stripping them from the substrate. Depending on the relative texture coefficient coatings appeared to be more or less ductile. A loss of ductility when the pH of the electrolyte exceeds 4, was identified as due to zinc hydroxide precipitates. These particulates precipitate at the cathode and/or at the anode, then are transferred to the vicinity of the cathode where they can be codeposited with zinc.

Zinc and zinc-based coated steel sheets are investigated intensively for applications in the automotive industry. Much attention has been paid to the improvement of the corrosion resistance of zinc and zinc-based layers, but only a limited amount of work has been published on the relationship between their formability and their structure and the electrodeposition parameters used. In a previous paper<sup>1</sup> a correlation between the cathodic overpotential, the crystallographic texture, and the ductility of electrodeposited copper foils was reported.

Literature data on the effect of the crystallographic texture on the formability of zinc or zinc-based coated steel sheets are contradictory. Lindsay et al.<sup>2</sup> reported on the relation between crystallographic texture and formability based on laboratory and industrially produced samples. The zinc coatings electrodeposited under laboratory conditions from a sulfate electrolyte were of two types. Coatings with basal (00.1) planes oriented parallel to the surface of the substrate easily underwent a substantial elongation under deep drawing. Coatings with pyramidal (10.X) planes oriented parallel to the surface of the substrate quickly underwent intergranular or transgranular fracture under conditions of deep drawing and bending. On the contrary, commercial zinc deposits electrodeposited from a sulfate electrolyte having their pyramidal (10.X) planes oriented parallel to the surface of the substrate, also retained their integrity under conditions of deep drawing and bending. Lindsay et al. suggested that the difference in performance between industrial and laboratory zinc coatings could be related to the grain size. Rangarajan et al.3 reported that thicker electrogalvanized zinc coatings had a marked texture on the surface with a larger percentage of grains with (11.2) planes parallel to the surface. They concluded that with this texture, the basal planes, being the primary slip planes in hexagonal close-packed (hcp) zinc, were favorably oriented for high resolved shear stress when

subjected to uniaxial tension. They observed that as these coatings were strained the grains with the (11.2) planes parallel to the surface slipped and rotated, causing a significant change in texture. So in contradiction to the results of Lindsay et al., Rangarajan et al. found the (11.2) texture to be favorable for plastic deformation. Pak and Meshii<sup>4</sup> investigated nine sets of commercial pure zinc electrogalvanized steel sheets provided by seven different plating lines in five steel companies. No details of the plating conditions were presented. They found two types of textures. In the first type the basal plane was inclined about 30° to the substrate and the (10.3) plane was the surface plane. In an axisymmetric forming test these specimens showed no cracking. For another type of specimen the inclination of the basal plane could not be determined exactly, because of the limitation of the texture measurement method, i.e., Schulz reflection method. The authors estimated that the (11.0) plane was parallel to the surface of these samples, and thus showed a prism texture. These specimens all cracked during the axisymmetric forming test.

Concerning the influence of microstructure on ductility, Rogers<sup>5</sup> stated that the following structural effects must be considered: the nucleation of voids, dislocation interaction, the presence of holes and particles, and the embrittling effect of a special distribution of the softer phase in a twophase system. It is known that particles such as solid organic or inorganic substances, additives, and side-reaction products present in the plating bath may codeposit with zinc during electrodeposition. The inclusion of such particles in the coatings affect ductility. However until now no report on the influence of particles or anodic reaction products on the ductility of zinc coatings has been published.

A study on the ductility of electrodeposited zinc coatings without substrate was carried out. The effect of electrodeposition conditions, such as pH value and current density, on crystallographic texture, morphology, and codeposition of second-phase particles were investigated. Further, the

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			,	r								Relative	intensity I	$I/I_0$	í.						
Specimen no.	Cell	Нď	$(A/dm^2)$	p.d. (mm)	(mm) 1	${}^{K_a}_{(\mu m)}$	(00.2)	(10.0)	(10.1)	(10.2)	(10.3)	(11.0)	(11.2)	(20.1)	$(10.4)_{-}$	(20.3)	(10.5)	(11.4) (2	21.0) (:	21.1) (21	.2)
- بـ د ا	44	2.0	202	1.35	33.4	0.94	5.98	1.80	100.00	21.56	13.14	0.00	8.54 4.40	1.66	0.00	5.26 0.40	0.83 8 60	6.89 11 86	0.00	0.00 3	.67
50 1	۹.	30,00	t≫ t	1.10	30.6	1.15	2,84	12.53	100.00	18.00	14.41	79.73	99.86	4.57	0.00	6.93	0.00	11.31	5.65 4	12.05 10	52
4	4	4.0	101	1.01	28.1	0.45	100,00	2.43	0.00	0.69	1.82	0.00	0.00	0.00	0.23	0.00	0.87	0.28	0.00	0.00 0	.00
υ,	4	$\frac{1}{4.1}$	01	0.58	37.7	2.33	100.00	0.00	22.52	17.24	26.40	0.85	7.78	0.00	4.50	3.51	5.86	9.77	0.00	0.00 0	73
6	V	4.5	2	0.50	32.4	2.43	100.00	4.41	35.08	8.69	14.04	2.02	4.21	1.48	$\frac{2.11}{2.11}$	2.24	3.48	3.37	0.00	1.39 0	00
7	4	4.5	2	0.42	35.5	2.14	83.56	23.05	100.00	23.46	28.83	7.19	18.16	4.26	3.14	6.49	3.34	4.52	0.00	3.51 5	44
œ	4	5.2	2	0.31	37.0	2.54	100.00	2.42	58.97	42.93	58.70	2.38	19.25	0.00	6.81	6.36	11.41	14.65	0.00	0.00 1	.61
9	4	3.2	4	1.33	27.9	0.61	48.87	0.00	7.19	20.80	100.00	0.00	5.70	0.00	13.39	0.00	14.36	41.79	0.00	0.00 0	0.00
10	4	ວ ເບັ	4	1.16	25.6	1.03	73.04	0.00	100.00	36.79	54.40	1.69	22.66	0.00	5.80	8.16	10.30	21.74	0.00	1.63 3	30
11		3.7	.4	1.17	34.9	0.87	100.00	0.00	36.84	26.75	90.80	9.18	40.00	0.00	3.09 9.09	8.01	19.76	102.90	0.00	1.01 1	0.0
12	<>	10 CA 20 CA	44	1.28	26.7	0.07	14 33	0.00	14.27	43.11	100.00	0.00	38.07	0.00	9.54	0.00	16.29	96.89	0.00	0.00 0	.00
14	V.	4.5	4	0.40	32.6	2.82	100.00	0.00	21.59	16.05	28.51	0.00	6.01	0.00	4.81	1.50	7.67	9.04	0.00	0.00 0	.00
15	4	5.1	4	0.34	27.8	1.75	100.00	0.00	16.67	15.11	31.41	0.87	3.50	0.00	5.19	2.11	6.63	7.73	0.00	0.00 2	.77
16	V	5.1	4	0.31	36.4	4.50	100.00	1.37	30.56	15.42	22.59	1.36	5.19	0.00	0.00	3.55	6.55	9.02	0.00	0.73 1	30.0
17	14	5.6	44	0.33	34.0	0.91	100.00	0.00	2.66	5.60	18.61	0.00	90 en	9.00	3.07 3 20	0.50	ว.49 ว.50	98.90 98.90	0,00	1 4 0 C	00 00
10	15	0.0	р н <sup>с</sup>	40.1 80.1	10.0	0.92	100.00	0.00	0.01	1 10	11 00	0.00	1 10	0.00	3 <u>1</u> 0 0	0.10	200	8 00	0 00	0 00 0	00
06 6T	rj h	ມ ບ ⊃ ⊂	- 3 8	1.15	31.0 31.4	0.70	100.00	0.60	1.73	0.40	1.20	0.00	0.00	0.00	1.60	0.00	5.50	0.00	0.00	0.00 0	
21	Ч	4.0	4	1.16	52.3	1.48	0.00	0.00	30.64	6.30	7.50	31.80	100.00	0.00	0.00	3.00	0.00	9.90	0.90	11.40 26	.29
22	Ъ	4.0	8	1.17	41.2	1.41	3.50	0.00	48.85	26.90	24.20	5.30	100.00	0.00	2.10	5.40	5.00	34.30	0.00	8.20 12	.49
23	ਸ਼੍ਰ	4.0	12	1.23	39.1	0.87	0.00	0.00	8.65	4.20	1.30	7.00	100.00	0.00	0.00	1.10	0.00	6.70	0.00	4.00 15	.19
24	Ч	5.3	4	0.28	35.4	1.16	100.00	0.00	8.76	10.80	32.40	0.60	6.30	0.00	3.90	1.90	3.30	12.50	0.00	0.00 0	1.00
25	Ч	5.3	0	0.46	38.3	1.72	100.00	0.00	11.73	12.90	30.10	0.90	4.00	0.00	4.30	0.80	8.20	11.60	0.00	0.00 (	1.62
26	Ч	5.3	12	0.53	35.7	1.63	100.00	0.00	1.09	4.70	13.10	0.00	0.70	0.00	3.30	0.00	0.40	00.7	0.00	0.00 0	1.00
					ASTM 4	-831	53	40	100	28	25	21	$^{23}$	17	లు	8	6	11	U)	3 6	-
c. d., current den	sity; p.	.d., pen	etration dep	oth; t, th	ickness;	R <sub>a</sub> , aver:	age rought	ness; I/I <sub>0</sub> ,	intensity o	f certain p	lane reflec	ction, I, di	vided by t	hestrong	est intensi	ity, I <sub>0</sub> , amo	ong 15 pla	ne reflec	tions (in S	%); V, vert	ical
cell; F, flow cell.	read to be	· , F				47	C							(		:	1				

Table I. Electrodeposition conditions and ductility, thickness, roughness, and texture of specimens deposited from an acid zinc sulfate solution.

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effects of crystallographic texture and second phase on ductility were examined.

### Experimental

Zinc coatings were deposited from an electrolyte containing 0.70M ZnSO<sub>4</sub> · 7H<sub>2</sub>O, 0.25M NaSO<sub>4</sub>, and 0.26M NaCl. The pH of the electrolyte was adjusted between 2.2 and 5.6 by addition of a 1% H<sub>2</sub>SO<sub>4</sub> or a 10% NaOH solution. Two types of electrodeposition cells were used, namely, a vertical plates cell (V), and a flow cell (F). The vertical plates cell was a beaker of 1 liter. The cathode was an AISI 316 stainless steel plate 6 imes 10 cm. The anode was an electrolytic zinc plate  $6 \times 10$  cm. The distance between the two plan electrodes was 4 cm. During deposition the electrolyte was agitated with a magnetic stirrer. Deposition was carried out at 28°C and at current densities of either 2 or 4 A/dm<sup>2</sup>, in solutions with different pH values. Before electrodeposition, the stainless steel cathode was passivated in a 40%  $HNO_3$  solution for 8 h, rinsed, first with tap water for 15 min, finally with distilled water. After deposition for an electrical charge of 4320 C, the coatings were peeled from the stainless steel plate for ductility measurements. The thickness of all deposits was ca. 30 µm.

In the flow cell (F), the solution was circulated at a mean flow speed of 4 liter/min. The solution was pumped through the bottom of the inner cell ( $8 \times 8 \times 14$  cm), and flowed over the top of the inner cell into the outer cell ( $15 \times$  $15 \times 22$  cm). The cathode was made of AISI 316 stainless steel. The anode was the same as the one used in the vertical cell. The cathode of  $6 \times 10$  cm and anode of  $6 \times 10$  cm were vertically suspended in the inner cell at a distance of 6 cm. Before deposition the stainless steel plate was passivated as described above. The electrolyte temperature was  $28^{\circ}$ C. Coatings were deposited at three different current densities (4, 8, and 12 A/dm<sup>2</sup>), and at three pH values (3, 4, and 5.3).



10 µm 199kU 101E3 9946/70 МТМ

Fig. 2. Morphology of zinc coatings deposited in the flow cell from a solution containing  $0.70M ZnSO_4$ ,  $0.25M H_2SO_4$ , and 0.26M NaCl (a, top) at pH 4 and 4 A/dm<sup>2</sup>; (b, bottom) at pH 5.3 and 4 A/dm<sup>2</sup>.

The ductility was determined by the stretching tester as described in Ref. 1. The displacement of the punch head between the point where the load begins to rise, and the end point, where the load suddenly falls down, is called the penetration depth and is used as a measure for the ductility of coatings. The back side of the zinc coatings, *i.e.*, the side in contact with the stainless steel plate during electrodeposition, was pressed against the punch head during the punch test, because the surface roughness of this side was nearly the same for all the samples tested. A lubrication oil (Tonnoil Oil. T. 68, Shell) was used for all measurements. At least three stretching tests were done on each specimen and the mean value of the penetration depths is reported. Re-



Fig. 1. Morphology of zinc coatings deposited in a vertical cell from a solution containing 0.70M ZnSO<sub>4</sub>, 0.25M H<sub>2</sub>SO<sub>4</sub>, and 0.26M NaCl (a, top) at pH 2 and 4 A/dm<sup>2</sup>; (b, bottom) at pH 5.1 and 4 A/dm<sup>2</sup>.

Fig. 3. Effect of pH on the ductility of zinc coatings deposited in a vertical cell from a solution containing 0.70M ZnSO<sub>4</sub>, 0.25M H<sub>2</sub>SO<sub>4</sub>, and 0.26M NaCl at 28°C.  $\Box$ , 2 A/dm<sup>2</sup>;  $\blacksquare$ , 4 A/dm<sup>2</sup>.



Fig. 4. Effect of pH and current density on the ductility of zinc coatings deposited in a flow cell from a solution containing 0.70M ZnSO<sub>4</sub>, 0.25M H<sub>2</sub>SO<sub>4</sub>, and 0.26M NaCl at 28°C.  $\bigcirc$ , 4 A/dm<sup>2</sup>;  $\blacksquare$ , 8 A/dm<sup>2</sup>;  $\blacktriangle$ , 12 A/dm<sup>2</sup>.

producibility of the stretching test is 4% as discussed in Ref. 1.

The thickness of specimens was measured with a Fisher Multiscope. The roughness of specimens was measured with a Form Talysurf. When the roughness average,  $R_a$ , is divided by the thickness of the specimen, the roughness factor  $\alpha$  is obtained. The roughness factor describes the initial surface irregularity of a specimen.<sup>1</sup>

The crystallographic texture was measured with an x-ray diffractometer (XRD) (Philips). Cu-K<sub> $\alpha$ </sub> radiation was used. The 2 $\theta$  range was from 30° to 140° and a scanning rate of 1°/min was applied. Similar to Bérubé's method,<sup>6</sup> twenty



Fig. 5. Brittle (a, top) and ductile (b, bottom) fractures on electrodeposited zinc foils obtained at different plating conditions. (a) Fracture with a small dome after stretching test, as experienced for specimens deposited at pH 5.3; (b) fracture with a bigger dome after stretching test, as experienced for specimens deposited at pH 3.



Fig. 6. Details of the fracture on the electrodeposited zinc foils induced by the stretching tests. (a, top) A detail of specimen in Fig. 5a; (b, bottom) a detail of specimen in Fig. 5b.

reflection lines were monitored. However, since the diffraction lines of (00.2), (00.4), and (00.6) are considered as the second-, fourth-, or sixth-order diffraction of the basal plane, and the diffraction lines of (20.0), (20.2), and (20.4) are the second-order diffraction of (10.0), (10.1), and (10.2) planes, only 15 reflection lines have been considered here. For each reflection plane (hk.l), the ratio  $R_{(hk.l)}$  was first calculated as follows

$$R_{\rm (hk,l)} = \frac{I_{\rm (hk,l)}}{I_{\rm p(hk,l)}}$$
[1]

where  $I_{(hk,l)}$  is the relative intensity of the (hk.l) reflection peak and  $I_{p(hk,l)}$  is the relative intensity of the corresponding (hk.l) reflection peak for a powder zinc sample according to the ASTM card index 4-831. Then the relative (hk.l) texture coefficient was calculated.  $RTC_{(hk,l)}$  is defined as

$$RTC_{\text{(hk,l)}} = \frac{R_{\text{(hk,l)}}}{\sum R_{\text{(hk,l)}}} \times 100\%$$
<sup>[2]</sup>

where  $\sum R_{\text{(hk,l)}}$  is the sum of the 15  $R_{\text{(hk,l)}}$ .  $RTC_{\text{(hk,l)}}$  expresses the percentage of the relative intensity of a given orientation (hk.l) among the 15 crystallographic orientations of the sample studied. A value of  $RTC_{\text{(hk,l)}}$  greater than 6.7% (100% divided by 15) indicates a preferred orientation of this (hk.l) plane as compared with the zinc powder sample of which all crystallographic orientations are randomly distributed. For example, if the relative intensity of the (00.2) reflection plane of a specimen,  $I_{(00.2)}$ , is 10.60, and  $I_{p(0.2)}$  for the zinc powder sample is 53 according to the ASTM card, the corresponding ratio  $R_{(00.2)}$  obtained is 0.20. In the same way if the other 14  $R_{(hk,l)}$  are calculated, and the sum of all 15  $R_{(hk,l)}$  is 2.00, the relative texture coefficient of the (00.2) reflection planes,  $RTC_{(00.2)}$ , is 10%. Since this  $RTC_{(00.2)}$  is larger than 6.7%, (00.2) is a preferred orientation for this specimen.

The morphology of the specimens and of the fracture surfaces obtained in the punch test were examined by a scanning electron microscope (SEM) (Philips 515). A JEOL 200-CX transmission electron microscope (TEM) was used at 200 kV to characterize the zinc deposits and the precipitates that remained in the electrolyte after electrodeposition. The precipitates and powders scratched from cathode's were put in copper grids with carbon film for direct TEM observation.<sup>7</sup> From x-ray photoelectron spectroscopy (XPS) (VG Scientific Escalab 220i XL) additional data were obtained. Monochromatized Al-K<sub>a</sub> radiation was used as x-ray source. The ion-beam etching was carried out at 5 kV and 2  $\mu$ A for 100 min, and the etch area was 4  $\times$  4 mm. Then atomic concentrations of Zn and O by monitoring the Zn2p3 and O1s in the specimens were determined.

The electrodeposition conditions, the ductility, thickness, roughness, and texture results for the different zinc foils produced in either the vertical cell or the flow cell are listed in Table I.

# Results

Coating appearance and morphology.—The main morphological features of specimens deposited in both the vertical cell and the flow cell change when the pH of the electrolyte exceeds 4. Two types of morphology were identified, and are shown in Fig. 1 and 2. At pH values between 2.0 and 4.0 the specimens have a ledged structure, independent of the electroplating cells used. (Fig. 1a and 2a). The morphology of specimens deposited in both cells at >pH 4.5 shows fine flakes appearing together with many crystallites having hexagonal facets facing the surface (Fig. 1b and 2b).

Within the range of electroplating conditions used, the effects of current density and cell geometry on morphology are insignificant.



Fig. 7. Appearance of the through-coating fracture. (a, top) Transcrystalline cleavage in brittle specimens as in Fig. 5a; (b, bottom) ductile dimples of ductile specimens as in Fig. 5b.

Effect of plating conditions on ductility.—The dependence of ductility of the zinc electrodeposited on bath pH is shown in Fig. 3 for the vertical cell and in Fig. 4 for the flow cell. It appears that the ductility of the zinc foils varies widely with pH in both cells. Specimens deposited at pH between 2 and 3.5 are much more ductile than those deposited at >pH 4.5.

Fractography of specimens after stretching test.—After stretching the electrodeposits, two types of fracture can be distinguished as shown in Fig. 5. The specimens with low penetration depth show a small dome, Fig. 5a, while those with high penetration depth show a bigger dome as is shown in Fig. 5b. Details of the cracks are shown in Fig. 6 for the less ductile specimen (Fig. 6a) and for the ductile specimen (Fig. 6b). In Fig. 6a the crack runs through all the thickness of the deposit, the region adjacent to the crack has not deformed significantly, and the zigzag crack is composed of straight segments and apparently runs along crystal facets. In Fig. 6b a crack runs also through the thickness of the deposit but a deformation of the deposit in the zone adjacent to the crack can be seen clearly.

The corresponding two types of the through-coating fracture are shown in Fig. 7a and b. Transcrystalline cleavage (Fig. 7a) can be seen in the case of brittle specimens as shown in Fig. 5a, while in Fig. 7b dimples can be seen on the fracture surface of ductile deposits as the one shown in Fig. 5b.

Texture of specimens.—The relative intensities and the relative texture coefficients, (RTC) are listed for the 15 reflection planes of all specimens in Tables I and II. The *RTC* values of the (00.2), (10.2), (10.3), (11.2), (10.4), (10.5), and (11.4) reflection planes are often larger than 6.7% and change with pH and electrodeposition conditions. The *RTC* of the (10.0), (20.1), or (21.0) reflection planes are never larger than 6.7%. The other reflection planes occasionally have an *RTC* much larger than 6.7%, but are normally not the preferred orientations. However, no general relationship between *RTC* and pH value appears.

#### Discussion

Effect of texture on ductility.—First the assumption proposed by Lindsay et al.<sup>2</sup> was examined. Therefore in Fig. 8a the ductility of our specimens was plotted against the *RTC*<sub>(00.2)</sub>. At first glance, it seems that no relation between the ductility and the  $RTC_{(00.2)}$  exists. However, if only the ductility of the specimens in the upper part in Fig. 8a is considered, *i.e.*, for the specimens deposited at  $\leq$ pH 4, the ductility decreases with the  $RTC_{(00.2)}$ . (That the specimens can be divided into two groups based on pH of deposition is discussed later.) This tendency is opposite to the assumption proposed by Linsay et al. Next, the assumption proposed by Rangarajan et al. was examined. The ductility of our specimens now is plotted against the  $RTC_{(11.2)}$ , in Fig. 8b. No relationship between ductility and  $RTC_{(11.2)}$  is observed even for the specimens deposited at  $\leq$  pH 4. Thus, neither the hypotheses proposed by Lindsay et al.<sup>2</sup> nor the conclusions on the experiments by Rangarajan et al.,<sup>3</sup> are satisfactory explanations of the results obtained here.

The starting point for the hypotheses stated by Lindsay *et al.*<sup>2</sup> and Rangarajan *et al.*<sup>3</sup> is the generally accepted view<sup>8</sup> that at room temperature crystals of zinc deform essentially by basal slip and that the stress-strain behavior is influenced by the orientation of the basal plane relative to the tension axis prior to deformation. This orientation determines to a large extent the plastic strain the crystal undergoes before fracture. Accordingly, if the basal planes of a zinc crystal are parallel to the sample surface, the resolved shear stress on these planes is zero and stress is infinitive to start slip. Therefore, the specimens with a (00.2) texture cannot be deformed. Similarly, if the prism plane, (10.0), or any of the (XX.0) planes of a zinc crystal are parallel to the sample surface, *i.e.*, that the basal planes of the zinc crystal are perpendicular to the sample surface,

	ical Society	, mc.
22222222222222222222222222222222222222		No.
0.558 0.558 0.258 0.258 0.228 0.25	1.35 1.10 1.01	p.d. (mm)
$\begin{array}{c} 0.0675\\ 0.0675\\ 0.0675\\ 0.0225\\ 0.025\\ $	0.028	Q
222 0.427 2322 0.425 2322 0.425 2356 25425 25425 252 0.556 25455 252 0.556 2556 2556 2556 2556 2556 2556 2556	23.4 0.3 23.4	(00.2)
0.000400040000000000000000000000000000	0.9 2.6 2.6	(10.0)
33004000000000000000000000000000000000	21.0 5.0 2.0	(10.1)
2557767077276762889772857 2649584227762888577757	16.2 4.4 1.1	(10.2)
11111111111111111111111111111111111111	111.1 2.9 3.2	(10.3)
000412000000000000000000000000000000000	0.0 0.0	(11.0)
487-6778-784 855-67-07-07-877-67-84 855-62-07-92-92-764 862-62-07-92-92-764-50-63-20 862-07-92-92-07-76-45-06-32	7.8 21.9 0.0	(11.2)
-4400000000000000000000000000000000000	0.0 0.0 0.0	RTC (%) (20.1)
20212 2020 20212 2	20.2 0.0 3.4	(10.4)
сторгародовина 40%гоагодоби соосе 4че 40%гоагодоби сососе 2000 40%гоагодоби сососе 2000 40%гоагодоби сососе 2000 40%го 20000 40%го 2000 40%го 20000 40%го 2000000000000000000000000000000000000	$13.8 \\ 0.6 \\ 4.4 \\ 0.0$	(20.3)
12. 12. 12. 12. 12. 12. 12. 12.	2.9 17.8 6.3	(10.5)
$\begin{array}{c} 11.2\\ 12.2\\$	13.2 5.2	(11.4)
	0.500	(21.0)
0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0	23.5 0.0	(21.1)
$\begin{array}{c} \begin{array}{c} 1.5\\ 2.5\\ 2.5\\ 2.5\\ 2.5\\ 2.5\\ 2.5\\ 2.5\\ 2$	1.7 1.7 0.0	(21.2)

Table II. Penetration depth, roughness factor, α, and relative texture coefficient of specimens, (RTC%), deposited from an acid zinc sulfate solution.



Fig. 8. Relationship between penetration depth and (a) *RTC* of (00.2); (b) *RTC* of (11.2).

the resolved shear stress on these planes is zero, and the crystal cannot be deformed. Only when the basal planes of zinc crystals make an angle with the substrate surface, can zinc be deformed. Ideal deformation behavior can be expected in crystals of which the angle between the basal plane and the tension axis lies between  $10^{\circ}$  and  $80^{\circ}$ .<sup>8</sup> So, to investigate the effect of the crystallographic texture on the deformation of zinc coatings, we suggest that each group of



Fig. 9. Crystallographic orientations in zinc hcp crystals.



Fig. 10. Relationship between penetration depth and sum of RTC of (00.2), (10.0), (11.0), and (21.0) for specimens deposited at 2 to 12 A/dm<sup>2</sup> and pH 2 to 5.6 in different cells. pH 2 to 4,  $\Box$  vertical cell; flow cell; pH 4.1 to 5.6,  $\triangle$  vertical cell,  $\blacktriangle$  flow cell.

grains, of which the inclination of basal planes to the surface of substrate is between 10° and 80°, contributes to the ductility of the whole specimen. The grains with an orientation (10.1), (10.2), (10.3), (11.2), (10.4), (20.3), (10.5), (11.4), (20.1), (21.1), or (21.2) satisfy the inclination condition. Some of these orientations are presented schematically in Fig. 9. Schmid and Boas, as quoted by Honeycombe,<sup>8</sup> calculated a series of theoretical stress-strain curves. From these calculations it seems that the deformation is different for different angles between the slip basal plane and the tension axis. The larger strain is obtained when the angle between the basal plane and the tension axis is between 45° and 60°. Although the contribution of individual grains to the total ductility is different, in a first approximation, we assume that their contributions are equal. The percentage of each kind of grain to all grains is related to the relative texture coefficient. The sum of the RTCs of (10.1), (10.2), (10.3), (11.2), (10.4), (20.3), (10.5), (11.4), (20.1), (21.1), and (21.2) planes can be selected and designated as an index for available deformability. Alternatively, the sum of RTCs of (00.2), (10.0), (11.0), and (21.0) planes can be selected and designated as an index for nonavailable deformability.

For the specimens deposited in the flow cell and the vertical cell at pH 2 to 4, and identified as ductile specimens, the penetration depth is plotted against the sum of RTC of (00.2), (10.0), (11.0), and (21.0) planes in Fig. 10. It appears that the ductility decreases with this index for nonavailable deformability and that a linear relationship with 99% confidence is obtained. The striking influence of >pH 4 is discussed in the next Section. The angle between a (11.3) plane and the basal plane is 55.1° and that the angle between a (11.1) plane and the basal plane is 74.9°. However, the lines of (11.1) and (11.3) cannot be obtained, because the diffraction intensities of these planes are zero. The (22.2) line and (22.6) line were out of the XRD measurement range. In addition, although it is assumed that at room temperature crystals of zinc deform essentially by basal slip, other less essential slip processes on pyramidal and on prismatic planes, or twinning may occur. These factors interfere with the linear relation. Microstructural features such as the grain size also interfere with the linear relation. Pak and Meshii however concluded that this influence is secondary.<sup>4</sup> In a first approximation, the linear relationship between ductility and the sum of RTCs of the (00.2), (10.0), (11.0), and (21.0) planes did appear.

It is interesting to analyze the contradictory conclusions obtained by Lindsay *et al.*,<sup>2</sup> Rangarajan *et al.*,<sup>3</sup> and Pak and Meshii<sup>4</sup> referring to this assumption of the existence of an index of available deformability. The results obtained by Pak and Meshii, based partly on estimations of the texture, support our assumption. The experiments by Rangarajan *et al.* showed that the grains with the (11.2) planes parallel to the surface slipped and rotated with applied strain. Since they only deposited zinc coatings with a strong







Fig. 11. TEM photomicrographs of particles scratched from zinc sample no. 16, deposited at pH 5.1. (a, top) Bright-field photograph and corresponding electron diffraction pattern of  $\epsilon$ -Zn(OH)<sub>2</sub>; (b, middle) diffraction pattern of the phase formed from  $\epsilon$ -Zn(OH)<sub>2</sub> by electron-beam heating in TEM; hexagonal structure with lattice parameters a = 5.011 Å and c = 7.693 Å; and (c, bottom) bright-field photograph and corresponding electron diffraction pattern of ZnO.



(11.2) texture, they concluded that the (11.2) texture was a favorable texture for plastic deformation. However, their experimental data for electroplating zinc coatings with a thickness between 10 and 13  $\mu$ m show that the grains with the (10.1) or (10.2) texture also slipped and rotated as a function of strain. However due to limitation in their experimental conditions they could obtain only the (11.2) texture which was a favorable texture for plastic deformation, and the (00.2) texture which was unfavorable for plastic deformation.

The experiments by Lindsay *et al.* showed that the zinc deposits with a (00.1) texture produced in their lab and the commercial zinc deposits with a (10.X) texture both had good deformability properties. That the commercial zinc

deposits with a (10.X) texture have good forming properties is in agreement with the present assumptions and results. Similarly, the zinc deposits with a (10.X) texture produced in their lab should have good deformability properties. The deformability of these coatings was low. These coatings however were deposited at pH 4.5. Our results (Fig. 3 and 4) show that the ductility of zinc coatings deposited at  $\geq$ pH 4.5 is lower than the ductility of coatings deposited at <pH 4. Lindsay *et al.* attributed the difference of formability between laboratory and commercial specimens with a similar texture to a different grain size. It is unreliable to determine a grain size from topographical SEM pictures. Since Lindsay's samples with (10.X) texture were deposited at pH 4.5, it may be assumed that the lower

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Fig. 12. SEM fracture surface of brittle zinc, specimen no. 16, deposited at pH 5.1. Hexagonal feature and flakes can be seen on the surface.

ductility arises from precipitates codeposited with the zinc (see next point of Discussion), and is not primarily related to the texture. Concerning the deformation of zinc deposits with a (00.1) texture, Lindsay et al. did not give quantitative data. Otherwise, a comparison of the deformability of deposits with either a (00.1) texture or a (10.X) texture could have been performed. They also did not give the original data of the XRD measurement, nor mentioned whether the given data were normalized against the zinc powder sample with random orientation. Only 7 orientations were mentioned, and it is particularly difficult to understand how the (00.1) line could be calculated since the structure factor of (00.1) diffraction planes in a hexagonal crystal is zero. Further, not only the percentage of the orientation of (00.1) was taken into account but also the orientation of (00.2). So, obviously the method or the calculation was incorrect, because the percentage of the orientation of (00.1) should be nearly equal to the percentage of the orientation of (00.2), if the percentage of the orientation of (00.1) can be obtained. Thus, the data of the estimated percentages for different orientations as recorded in the paper by Lindsay et al. are doubtful, and one must be careful with their conclusion that the zinc coating with the (00.1) texture has good forming properties.

Effect of pH value on ductility.—As mentioned above (Fig. 3 and 4), zinc foils deposited in the flow cell and the vertical cell at >pH 4.0 are the least ductile. This brittleness however cannot be attributed to a higher sum of *RTC* of (00.2), (10.0), (11.0), and (21.0), as appears from Fig. 10. The low ductility of these specimens deposited at  $\geq$ pH 4.5 thus



Fig. 13. Apparent current efficiency of zinc deposits from an acid zinc sulfate solution at different pH values. ○ 2 Å/dm<sup>2</sup>; + 4 Å/dm<sup>2</sup>; ■ 8 Å/dm<sup>2</sup>.

cannot be explained simply by a change of the crystallographic texture.

It has been reported<sup>1</sup> that the initial surface irregularity of a specimen, *i.e.*, the roughness factor, influences the ductility of thin metallic foils under biaxial stress. A larger roughness factor  $\alpha$  may cause the ductility of specimens to be reduced, especially if  $\alpha > 0.04$ . In Table II 9 of 11 specimens with lower ductility are rougher, and their roughness factor  $\alpha > 0.04$ . But there are two specimens with roughness factor < 0.04.

SEM investigation shows that flakes are present in the coatings deposited in both cells at  $\geq$ pH 4.5, but not in the coatings deposited at  $\leq$ pH 4. Therefore, the decrease of ductility may be attributed to a second phase codeposited with the zinc.

By TEM, only Zn was found in specimen no. 1 deposited at pH 2 and specimen no. 10 deposited at pH 3.5. In specimens no. 16 and 17, deposited at >pH 4, Zn,  $\epsilon$ -Zn(OH)<sub>2</sub>, ZnO, and a phase with a hexagonal structure with lattice parameters a = 5.011 Å and c = 7.693 Å were identified (Fig. 11). This phase did not fit any file in the PDF-2 database compiled by JCPDS International Center for Diffraction Data. This phase can be formed from  $\epsilon$ -Zn(OH)<sub>2</sub> by electron beam heating and can transform to ZnO by stronger beam heating. By XPS only Zn was found in specimen no. 1 deposited at pH 2. 15 atom percent (a/o) O was found in specimen no. 16 electrodeposited at pH 5.1. Combining the TEM with the XPS results, we conclude that brittle zinc deposits produced at >pH 4 include zinc hydroxide and zinc oxide.

The fracture surface of the specimen deposited at pH 5.1 shows flakes and hexagonal feature, Fig. 12. These features do not appear in the fracture surface of specimens deposited at lower pH. With reference to the morphology of  $Zn(OH)_2$  and ZnO as shown by TEM, Fig. 11, the flakes are  $Zn(OH)_2$ , while the hexagonal pieces may be zinc oxide or a hexagonal hydroxide, the transformation product of electron beam heated  $\epsilon$ -Zn(OH)<sub>2</sub>.

From solubility data we can calculate whether the precipitation of Zn(OH)2 is likely to occur in slightly acidic electrolyte. The solubility of  $\epsilon$ -Zn(OH)<sub>2</sub> at 25°C is 4.12  $\times$  $10^{-17}$ . <sup>8</sup> In the present study the bulk concentration of Zn<sup>++</sup> is 0.70*M*. If the pH of the solution is 5.3, the concentration product of  $(Zn^{++})$  and  $(OH)^-$  is  $0.28 \times 10^{-17}$  which is less than the solubility product, so precipitation of Zn(OH)<sub>2</sub> is unlikely to occur in the bulk of solution. If hydrogen evolves at the cathode, the pH value rises and the precipitation of Zn(OH)<sub>2</sub> becomes possible at the cathode. However no gas evolution was noticed visually during deposition. Therefore in an additional experiment the current efficiency was determined under different electrodeposition conditions. From the results plotted in Fig. 13, it appears that all the apparent current efficiencies were less than 100% when depositions were carried out at pH 2, while the apparent current efficiencies were larger than 100%, if the depositions were carried out at pH 5.6. The pH value was higher after deposition. For instance, the pH value increased from 4 to 4.7 after 4320 C was passed through the solution, suggesting that there is evolution of hydrogen or that OH<sup>-</sup> was generated during the electrodeposition. Obviously, the pH value in the region adjacent to cathode can be much higher than 4.7 during electrodeposition resulting in the precipitation of  $\epsilon$ -Zn(OH)<sub>2</sub>. It is also possible that Zn(OH)<sub>2</sub> precip-itates at the anode. McGraw<sup>10</sup> has observed that basic zinc salts can precipitate at the anode if the pH value in the bulk was >5.0. In our study the anode was covered by a white powdery product when the electrodeposition was carried out in the vertical cell at  $\geq$ pH 4.5. An XRD pattern of precipitate collected from the anode is shown in Fig. 14, and indicates that the precipitate is  $\epsilon$ -Zn(OH)<sub>2</sub>. The flakelike shape of these precipitates was observed by SEM in Fig. 15. These flakes are similar to the flakes codeposited with zinc at  $\geq$ pH 4.5, (Fig. 1b and 2b). In Fig. 16a flakes adhering to the surface of a zinc crystallite can be seen as well as a flake overgrown by a zinc crystal, Fig. 16b. This figure shows that the zinc deposit has a notch due to precipitated Zn(OH)<sub>2</sub>. Notched grains together with a lot of



Fig. 14. XRD pattern of precipitate collected from anode; Z, peaks of  $\epsilon$ -Zn(OH)<sub>2</sub>; A, peaks of aluminum (sample holder).

precipitated  $Zn(OH)_2$  along the boundaries result in a deterioration of ductility.

By XRD zinc hydroxide, but not zinc oxide, was found in the precipitate. The oxide found by TEM and XPS in the zinc foils deposited at >pH 4 is probably the decomposition product of zinc hydroxide when heated by an electron beam or an ion beam in high vacuum (higher than  $10^{-6}$  Torr).

The low ductility of specimens deposited at >pH 4 is caused by the second phases in the deposits which were codeposited with zinc during electrodeposition.

# Conclusion

Specimens deposited at room temperature and at pH 2 to 4 from an acid zinc sulfate solution are ductile; fractography shows ductile dimples. The specimens deposited at pH 4.5 to 5.6 are brittle and their fractography shows transcrystalline cleavage.

Specimens with the basal planes parallel or perpendicular to the surface are less ductile because the slide of basal planes is impossible when the load axis is lying in the same plane or perpendicular to the plane. A linear relationship between ductility and the sum of relative texture coeffi-



Fig. 15. Morphology of the precipitation collected from anode.

cients of (00.2), (10.0), (11.0), and (21.0) was obtained with a 99% confidence for specimens deposited at pH 2 to 4. The larger strains are obtained when the angle between the basal plane and the tension axis is between  $10^{\circ}$  and  $80^{\circ}$ .



Fig. 16. Flakes (a, top) on a surface of zinc crystallite; (b, bottom) wrapped by a zinc crystallite.

When the pH value of the acid zinc sulfate baths exceeds pH 4, the ductility of zinc deposits deteriorates. The coatings produced at pH 5.3 have a low ductility, i.e., ca. 0.28 to 0.54 mm of penetration depth in the stretching test. The reason is that zinc hydroxide is codeposited with zinc at the cathode. Zinc hydroxide may be precipitated at the cathode, as well as at the anode, from where it is transferred to the cathode.

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# **Electrocatalysis of Anodic Oxygen-Transfer Reactions**

**Evolution of Ozone** 

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#### ABSTRACT

Current efficiencies are compared for the generation of  $O_3$  simultaneously with  $O_2$  during anodic discharge of  $H_2O$  at pure and iron(III)-doped  $\beta$ -lead dioxide film electrodes in phosphate buffer (pH 7.5, 10°C) containing 2.5 mM KF. Also examined is the effect of applied current density. A current efficiency of 14.6% was obtained for the Fe(III)-doped PbO<sub>2</sub> film electrode deposited on an internally cooled (10°C) tubular titanium substrate at a current density of 200 mA cm<sup>-2</sup> as compared to only 6.1% at the undoped PbO<sub>2</sub> electrode under the same conditions. This result is tentatively explained on the transfer of equipation from budgets adverted on Pb(U) sites adverted to the transfer of equipation from budgets adverted on Pb(U) sites adverted to the transfer of equipation from budgets adverted to the transfer of equipation from budgets adverted to the pb(U) sites adverted to the transfer of equipation from budgets adverted to the transfer of equipation from budgets adverted to the transfer of equipation for the transfer of equipation for the same conditions. the basis of a mechanism involving the transfer of oxygen from hydroxyl radicals adsorbed on Pb(IV) sites adjacent to Fe(III) sites to  $O_2$  adsorbed at the Fe(III) sites in the surface of the Fe(III)-doped Pb $O_2$  electrodes.

Ozone  $(O_3)$  is known to be generated simultaneously with O<sub>2</sub> during anodic discharge of H<sub>2</sub>O at several electrode materials in a variety of aqueous media.<sup>1,2</sup> This observation has resulted in the suggestion of numerous possibilities for electrolytic ozonation, including sterilization of water, bleaching of paper, and electrosynthesis. The electrochemistry of  $O_3$  evolution has been discussed<sup>3-10</sup> and only a brief summary is given here.

Relevant reduction half-reactions and their corresponding standard potentials are

$O_3 + 6H^+ + 6e^- \Rightarrow 3H_2O$	$E^{\circ} = 1.51 \text{ V} vs. \text{ NHE}$	[1]
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 $O_2 + 4H^+ + 4e^- \Rightarrow 2H_2O$  $E^{\circ} = 1.23$  V vs. NHE [2]

It is apparent from these  $E^{\circ}$  values that anodic generation of  $O_2$  is thermodynamically favored over generation of  $O_3$ . Strategies to increase the current efficiency for O<sub>3</sub> generation generally include one or more of the following<sup>3-10</sup>: (i)choice of anode materials characterized by large O2-evolution overpotential, e.g.,  $PbO_2$  and glassy carbon (GC); (ii) application of a large anodic current density to achieve a large positive electrode potential; (iii) lowering of temperature; and (iv) addition of an adsorbate, e.g.,  $F^-$ ,  $BF_4^-$ , and  $PF_{\theta}^{-}$ , to block the O<sub>2</sub><sup>-</sup>-evolution mechanism and, thereby, increase the efficiency for  $O_3$  evolution.

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Representative values reported for O<sub>3</sub>-generation efficiency are given in Table I. Notable values are: 21% at  $\beta$ -PbO<sub>2</sub> in 2*M* HPF<sub>6</sub> (750 mA cm<sup>-2</sup>, 0°C), <sup>3</sup> 35% at GC in 7.3*M* HBF<sub>4</sub> (600 mA cm<sup>-2</sup> 0°C), <sup>9</sup> and 45% at GC in 62 weight

# Table I. Reported values of current efficiency for O3 generation during constant-current electrolysis at various electrodes in a variety of media.

Anode	Media	Temp. (°C)	Current density (mA cm <sup>-2</sup> )	Current efficiency (%)	Ref.
Pt	5M H <sub>2</sub> SO <sub>4</sub>	0	200	0.15	3
Ru/Ti	$5M H_2 SO_4$	0	200	0.15	3
$\beta$ -PbO <sub>2</sub>	$2M H_2 SO_4$	0	120	1.1	3
$\beta$ -PbO <sub>2</sub>	$2M  \mathrm{HF}$	0	750	6	3
$\beta$ -PbO <sub>2</sub>	$2M \operatorname{H}_2\operatorname{PO}_4^-$	0	750	3	3
$\beta$ -PbO <sub>2</sub>	2M HClO <sub>4</sub>	0	750	12	3
$\beta$ -PbO <sub>2</sub>	7.3M HBF <sub>4</sub>	0	800	18	3
$\beta - PbO_2$	7.3M HPF <sub>6</sub>	0	400	51	3
β-PbO <sub>2</sub> /Eb <sup>a</sup>	0.52 <i>M</i> K <sub>2</sub> HPO <sub>4</sub> / 0.22 <i>M</i> KH <sub>3</sub> PO 2.5 mM KF (pH 7 5)	0 4/	190	11.7	6
GC <sup>⊳</sup> GC GC	$\begin{array}{c} (511 + .5)\\ 7.3M \ \mathrm{HBF}_4\\ 7.3M \ \mathrm{HBF}_4\\ 62 \ \mathrm{w/o} \ \mathrm{HBF}_4\end{array}$	0 0 ~5	$200 \\ 600 \\ 200$	$22 \\ 35 \\ 45$	$9 \\ 9 \\ 10$

 $Eb \equiv Ebonex^{\otimes}$ .

<sup>b</sup>  $GC \equiv glassy carbon.$