Characteristics of acetate based zinc bath and deposits

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Zinc electrodeposits offer protection to steel against atmospheric corrosion both by galvanic and shielding effects. The cyanide process for zinc electrodeposition is increasingly being replaced by chloride and many other non-cyanide formulations. The search for a better zinc plating electrolyte is therefore a continuing process. In this paper the authors present details of zinc plating from an acetate electrolyte together with the deposit properties. The addition of thiaminehydrochloride to the plating bath improves the surface morphology of zinc electrodeposits. The X-ray diffraction data obtained for electrodeposited zinc showed it to be polycrystalline in nature with an hexagonal structure. Analysis by scanning electron microscopy demonstrated a uniform and pinhole-free surface.

Keywords: Acetate, Zinc, Electrodeposition, Polycrystalline ferroxyl, Thiaminehydrochloride, Gelatin

Introduction

Zinc is electrodeposited from acid baths,[1–3] non-cyanide based alkaline baths[4,5] and from highly toxic cyanide baths. Various attempts have been made to develop different types of improved acid baths.[6,7] A review of the literature shows that electrodeposition of zinc from an acetate bath has not been investigated, apart from the use of acetate as a minor component of zinc plating baths.[8,9] In this paper, the structure and surface morphology of the zinc deposits obtained from acetate based zinc plating solutions are presented.

Experimental

Cold rolled steel plates ($5 \times 7{\cdot}5 \times 0{\cdot}1$ cm) were degreased with trichloroethylene and electrocleaned cathodically for 2 min in alkaline solution composed of 35 g dm^{-3} NaOH and 25 g dm^{-3} Na_2CO_3 at 353 K. The plates were then washed in running water, followed by a 10 s dip in 5 v.-% H_2SO_4 solution, with subsequent thorough washing with a final rinse in distilled water. Zinc was electrodeposited on the steel plates in the presence and absence of additives in an acetate bath. The composition of the plating baths is shown in Table 1. The plating solutions were highly stable clear solutions with no visual degradation observed even after storage for an extended period of 5 years. Electrodeposition was carried out using a 99·99% purity zinc anode. Solution mixing was effected by a magnetic stirrer. The microhardness of the deposits was measured using a diamond pyramid of square base and with an angle of 136° between the vertex of the two opposite faces, yielding the microhardness of the deposit in kg mm^{-2} (LECO Microhardness Tester M 400). The surface of the deposits was followed using an X-ray diffractometer (JEOL JDX 8030) (Cu K_α radiation). The surface morphology was investigated at $\times 2000$ magnification with a scanning electron microscope (SEM).

Results and discussion

For the acetate based electroplating baths a 90–98% cathode current efficiency was observed for current densities of 2–3 A dm^{-2}. The throwing power and coverage were excellent with the maximum throwing power of the bath 21–23%, comparable to that of the cyanide bath. The zinc deposits from the additive free plating solution were uniform and white, whereas those in the presence of thiaminehydrochloride were bright and those in the gelatin containing baths were bright with a yellow tinge.

Adhesion of the zinc deposits obtained in presence and absence of additives from the acetate based bath was tested by subjecting the plated specimens to standard bend tests. The coating neither cracked nor peeled. A ferroxyl test to show the presence or absence of pores in the deposits did not reveal any blue spots on deposits above 6 μm thickness, thereby indicating that above that thickness the deposits were non-porous.[10]

X-ray diffraction (XRD)

XRD measurements were carried out on the different zinc deposits. Figure 1*a* shows the XRD spectra of the deposit obtained from bath A at 303 K. In this, the (103) plane was predominant with peak intensities corresponding to the other crystal planes reduced.

The polycrystalline nature of the deposit was observed with 'd' values in agreement with the standard values given in JCPDS File No. 40831 Zn*. The XRD pattern showed a simple hexagonal structure with lattice parameters $a=2{\cdot}655$ and $c=4{\cdot}946$. A (c/a) ratio of 1·862 was

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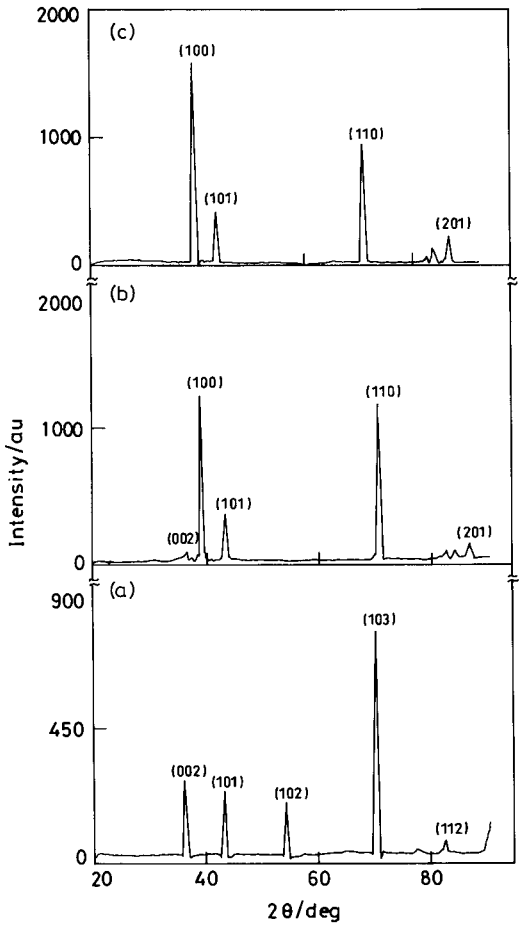


a bath A; *b* bath B; *c* bath C

1 Typical XRD patterns for zinc deposits obtained at 303 K

Table 1 Bath composition

	Bath A	Bath B	Bath C
Zinc acetate / g dm^{-3}	200	200	200
Potassium acetate / g dm^{-3}	60	60	60
Boric acid / g dm^{-3}	40	40	40
Aluminium chloride / g dm^{-3}	30	30	30
Thiaminehydrochloride / g dm^{-3}	–	3	–
Gelatin / g dm^{-3}			3
pH	5	5	5
Temperature / K	303	303	303
Current density / A dm^{-2}	2	2·5–4	2·5–4

found, which was in good agreement with the values reported earlier[11] (Tables 2 and 3).

In zinc deposits obtained from the thiaminehydrochloride containing bath B the (100) plane was the most predominant as in the deposit from the gelatin containing bath C (Fig. 1*b*,*c*).

When the bath temperature was raised to 313 K, the deposits from the thiaminehydrochloride containing electrolyte (bath B) and the gelatin containing electrolyte (bath C) showed the (101) plane to have the most intense signal (Fig. 2*a*–*c*), showing the preferential orientation along the (101) plane. The intensity of the (100) planes was reduced in these deposits.

Scanning electron microscopy

Deposits obtained from bath A

The surface morphology of the zinc electrodeposits obtained in the different baths were analysed using scanning electron microscopy (SEM). Figure 3*a* shows an SEM micrograph at a magnification of $\times 2000$ for zinc deposited from bath A at 303 K and pH 5. Platelets with a layered structure were observed. The occurrence of such layers may be understood in terms of the interdependence between the local overvoltage (as determined by electrical parameters, bath composition and substrate morphology), current efficiency and surface energy of the crystal planes.[12–14] Slightly larger platelets were noted for the deposit obtained at 313 K (Fig. 3*b*).

Deposit obtained from bath B

The deposit obtained at 303 K from bath B containing thiaminehydrochloride yielded a fine grained deposit structure, free from surface defects as shown in Fig. 4*a*. Deposits at 313 K produced a larger grain size (Fig. 4*b*).

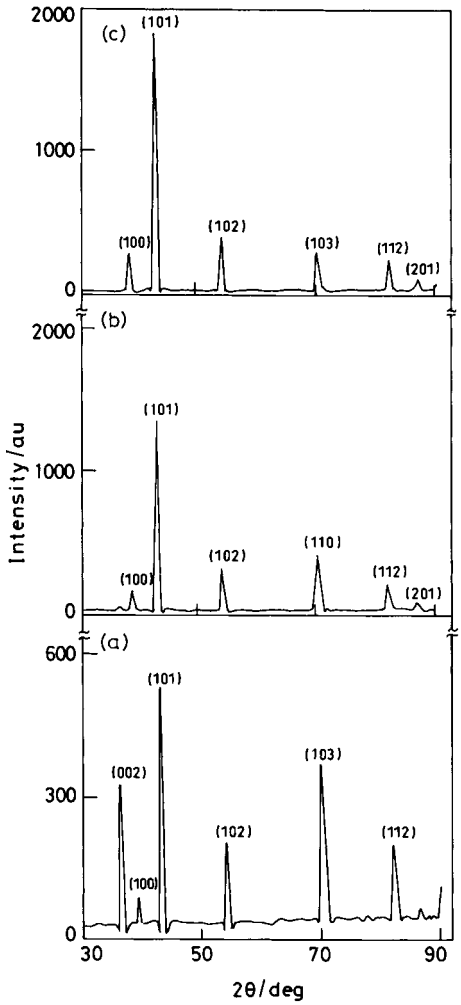
Deposit obtained from bath C

SEM investigation of the deposit obtained at 303 K from bath C containing 3 g dm^{-3} gelatin showed structure consisting of small spherical grains (Fig. 5*a*).

The surface morphology of the deposit obtained at 313 K from bath C (Fig. 5*b*) showed a fibre-like structure. Clusters of non-uniform large nodules growing on the surface were detected.[15]

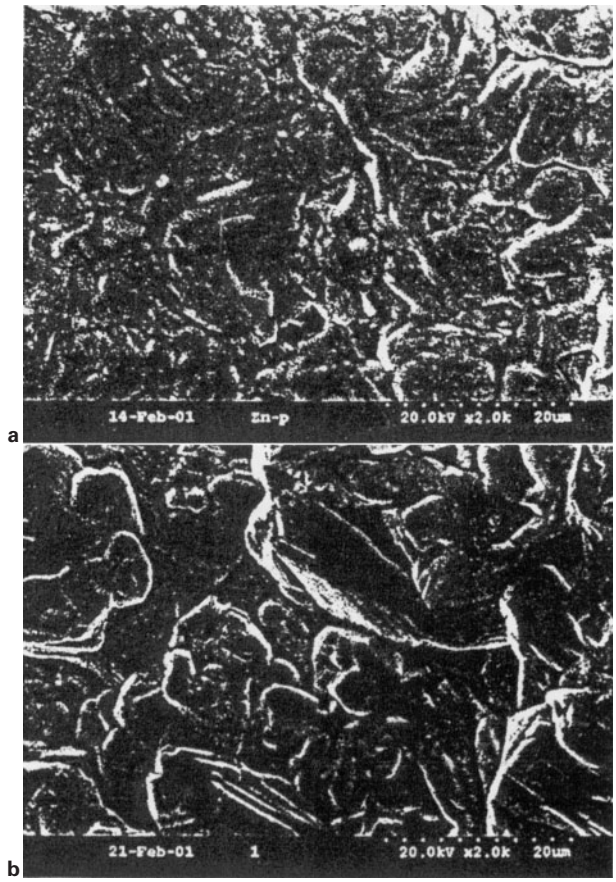
Table 2 X-ray diffraction data for electrodeposited zinc obtained from baths A, B and C at 303 K and at pH 5

				Lattice parameters / μm			
Bath	*d* (observed)	*d* (standard)	*hkl*	*a*	*c*	*c*/*a* ratio	Structure
A	2·473	2·473	002	2·655	4·946	1·862	Hexagonal
	2·088	2·091	101				
	1·685	1·687	102				
	1·340	1·342	103				
B	2·473	2·473	002	2·6708	4·908	1·837	Hexagonal
	2·313	2·308	100				
	2·091	2·091	101				
	1·333	1·332	110				
	1·123	1·124	201				
C	2·308	2·308	100	2·665	4·897	1·837	Hexagonal
	2·088	2·091	101				
	1·331	1·332	110				
	1·122	1·124	201				



a bath A; *b* bath B; *c* bath C

2 Typical XRD patterns for zinc deposits obtained at 313 K



a

b

a 303 K at a current density of 2 A dm^{-2}; *b* 313 K at a current density of 2 A dm^{-2}

3 SEM micrographs of zinc deposit obtained from bath A

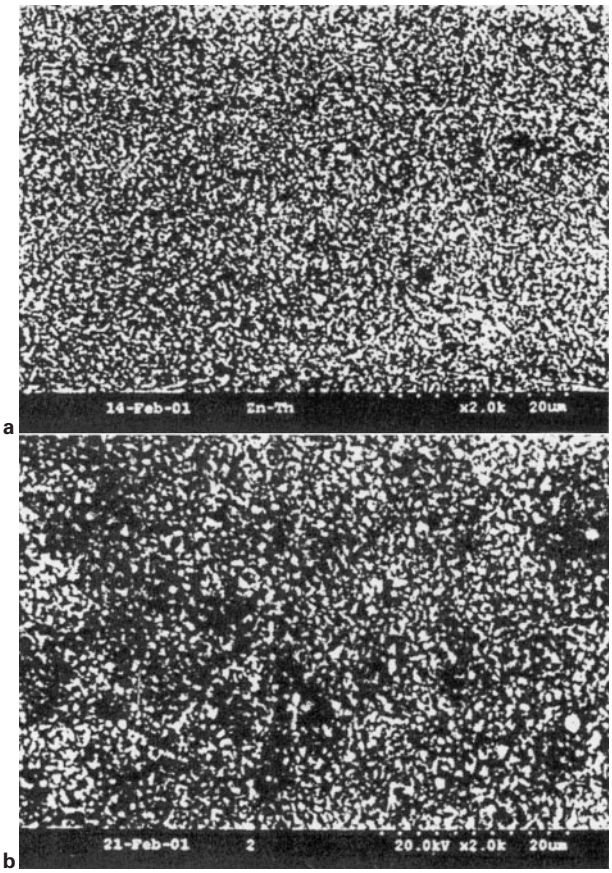
Microhardness

The microhardness values of the zinc deposits from baths A, B and C at different temperatures with an applied load of 25 g are presented in Fig. 6.

The zinc deposit obtained from bath A exhibits comparable values of microhardness at 303, 313 and 323 K although those at the latter two temperatures were low. On addition of thiaminehydrochloride as the electrolyte, bath B, deposits with increased hardness were produced at 303 K. The values for the deposits obtained at 313 K and 323 K were reduced, which may be indicative of decomposition of the additives.

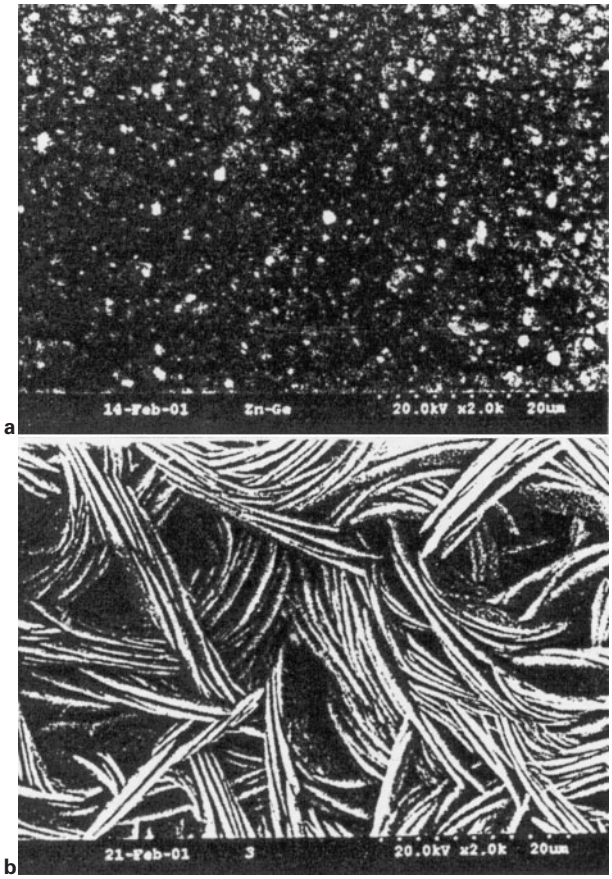
Table 3 X-ray diffraction data for electrodeposited zinc obtained from baths A, B and C at 313 K and at pH 5

Bath	*d* (observed)	*d* (standard)	*hkl*	Lattice parameters / μm		*c*/*a* ratio	Structure
				a	*c*		
A	2·466	2·473	009	2·6578	4·3970	1·8425	Hexagonal
	2·302	2·308	100				
	2·083	2·091	101				
	1·682	1·687	102				
	1·338	1·342	103				
	1·171	1·173	112				
	1·089	1·090	104				
B	2·308	2·308	100	2·6649	4·9568	1·8600	Hexagonal
	2·092	2·091	101				
	1·685	1·687	102				
	1·333	1·332	110				
	1·172	1·173	112				
C	2·308	2·308	100	2·6649	4·8911	1·8354	Hexagonal
	2·088	2·091	101				
	1·685	1·687	102				
	1·340	1·342	103				
	1·171	1·173	112				



a 303 K at a current density of 3 A dm^{-2}; *b* 313 K at a current density of 3 A dm^{-2}

4 SEM micrographs of zinc deposits obtained from bath B



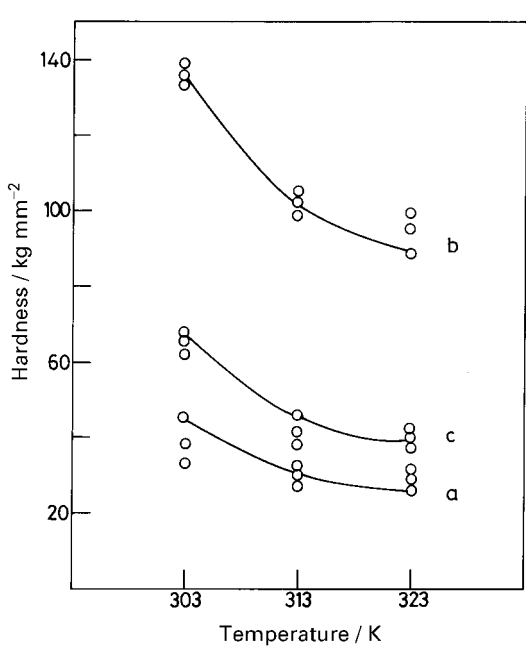
a 303 K at a current density of 3 A dm^{-2}; *b* 313 K at a current density of 3 A dm^{-2}

5 SEM micrographs of zinc deposits obtained from bath C

Curve C (bath C) showed that addition of gelatin to the acetate electrolyte produced deposits with greater hardness values at 303 K. At 313 and 323 K these hardness values again decreased. The greatest deposit hardness was obtained from the bath containing thiaminehydrochloride at all three deposition temperatures.

Conclusions

To avoid the problems associated with zinc deposits from cyanide baths, an electroplating bath based on an acetate solution was developed. Thiaminehydrochloride and gelatin were used as additives in these plating solutions. Inspection of the adhesion characteristics of the zinc deposits from these baths showed them to be good. Ferroxyl indicator tests revealed the absence of pin-holes at and above 6 μm thick deposits. The hardnesses of the zinc deposits were appreciable with a maximum value of 140 HV obtained from the deposits from the bath containing thiaminehydrochloride. XRD patterns revealed the (103) plane to be predominant for deposits from the additive free bath while the introduction of additives changed the structure, the (100) plane being the major fall. At 313 K, the (101) plane dominated in all three baths. Surface morphology studies revealed that at 313 K the deposits from the acetate bath consisted of the grain size of platelets, which increased with temperature. Addition of thiamine hydrochloride to the bath produced fine grained deposits. Increase of temperature of the bath modified the grain size. Gelatin addition to the bath produced deposits with spherical types of deposits at 303 K



a bath A; *b* bath B; *c* bath C

6 Microhardness of the zinc deposits obtained from different zinc plating baths at different temperatures

whereas at 313 K the grain size was modified to a fibre-like structure.

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