

Effect of brighteners on hydrogen evolution during zinc electroplating from zincate electrolytes

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Hydrogen evolution during zinc electrodeposition on a steel substrate from zincate electrolytes containing different additives was studied using various experimental techniques. The hydrogen evolution reaction is limited by the electron transfer step. Hydrogen evolution is most intensive during the first seconds from the beginning of electrodeposition due to the lower overpotential of hydrogen on steel as compared with that on zinc. The evolved hydrogen is dissipated in three ways. Most is dissipated to the atmosphere via gas bubbles at a constant rate. Some is dispersed in the electrolyte some diffuses into the steel substrate, predominantly at the commencement of deposition. The additives affect both the total amount of evolved hydrogen and its distribution. The highest amount of hydrogen is evolved in the presence of the anisaldehyde bisulphite containing composite additive. The highest amount of hydrogen included in the substrate and remaining in the electrolyte corresponds to the use of the Na-*N*-benzylpicotinate containing additive. In this case blistering is observed.

Keywords: *zinc deposition, hydrogen evolution, brighteners, zincate electrolyte*

1. Introduction

During the electrodeposition of many metals from alkaline electrolytes, including zinc plating from zincate electrolytes, the process is accompanied by the evolution of hydrogen and, depending on the composition of the electrolyte and plating conditions, the current efficiency may vary over a broad range [1]. The codeposited hydrogen on the surface of the electrode can penetrate into the substrate metal and alter its mechanical properties [2]. Zinc belongs to the class of metals in which the solubility of hydrogen atoms is negligible and their diffusion is hindered. 0.5 μm thick bright zinc coatings form an effective diffusion barrier against hydrogen penetration, that is, the critical amount of hydrogen which eventually may cause hydrogen embrittlement is evolved during the electrodeposition of the initial atomic layers [3]. On the other hand, hydrogen which has already penetrated into the metal substrate during the pre-treatment or the initial zinc plating stages can diffuse in the reverse direction, accumulate between the substrate metal and the compact zinc layer and may create blisters in the zinc coating [4, 5]. These processes can be influenced strongly by the organic compounds used as brighteners which, as well known, may enhance or inhibit the hydrogenation [2].

The present paper shows some characteristics of hydrogen evolution during the electrodeposition of zinc from zincate electrolytes, determined by various experimental techniques, as well as the effect of brighteners from two classes of organic compounds, aromatic aldehydes and pyridine derivatives, on the distribution of hydrogen in the substrate, the electrolyte and the atmosphere.

2. Experimental details

The investigations were carried out in a basic electrolyte (BE) containing 0.12 M ZnO and 3.25 M NaOH. Zinc coatings electrodeposited from this electrolyte are spongy and have poor adhesion to the substrate. The basic additive (F) for the deposition of compact and smooth coatings was the additive 'Protolux' 518 (Schering Galvanotechnik AG, now Atotech Deutschland GmbH) in absence of brightener component.

The brighteners anisaldehyde bisulphite (AA) (0.5 g dm^{-3}) and Na-*N*-benzylpicotinate (N) (1 ml dm^{-3} of a 33–36% solution) were added to the electrolyte containing the additive (F).

Part of the experiments were carried out using a rotating ring disc electrode (RRDE) [6] with a VA system CVA-1 (Scientific and Manufacturing Union 'Burevestnik', Russia). A thermostated 60 ml cell with a Hg/HgO reference electrode and two Pt

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counter electrodes was used. The working electrode was a steel disc ($r_1 = 2.5$ mm) and a gold ring ($r_2 = 2.75$, $r_3 = 3.75$ mm). The ring current (I_R) due to the oxidation of hydrogen at a sufficiently high positive potential is proportional to the amount of hydrogen evolved on the disc and can be used as its quantitative measurement [7]. The measurements were carried out at a rotation speed (ω) within the range 350–3800 rpm. The electrolyte was purged with argon 30 min before, and during, the experiment. A description of the experimental setup is given elsewhere [8].

The amount of hydrogen evolving to the atmosphere during the deposition of zinc was measured in a bell-type cell (Fig. 1). The reliability of the measurement was checked by determination of the quantity of hydrogen evolved during electrolysis in an electrolyte containing 3.25 M NaOH at a current density (c.d.) of 2 A dm^{-2} (Fig. 2). Under these conditions, 9.5 ml hydrogen should be evolved in 10 min. The measured quantity of 9.4 ml is in a good agreement with the theoretical value. The curve does not pass through the origin of the coordinate system, since some time elapses until the hydrogen bubbles travel through the electrolyte column to the top of the burette.

The amount of hydrogen included in the substrate and the coating was determined by vacuum extraction using the Exalograph EA 1 apparatus (Fa. Balzers).

The effect of additives on the penetration of hydrogen into the steel substrate was investigated by the Devanathan–Stachurski method [9]. The experiments were carried out in a cell with two compartments, separated by $50 \mu\text{m}$ thick iron membrane with an area of 2.4 cm^2 (Fig. 3). The polarization compartment of the cell, where the membrane acts as a cathode, was filled with the studied electrolyte and the ionization compartment with a 0.2 M NaOH

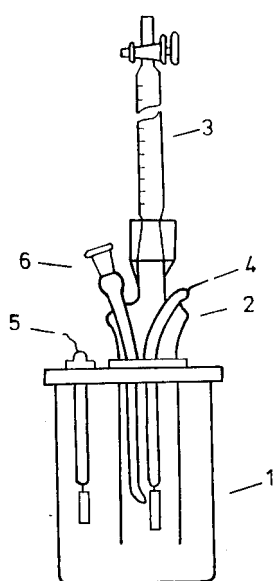


Fig. 1. Bell-type cell for the measurement of hydrogen dissipated in the atmosphere. Key: (1) electrolytic cell, (2) glass bell, (3) burette, (4) working electrode, (5) counter electrode, (6) reference electrode.

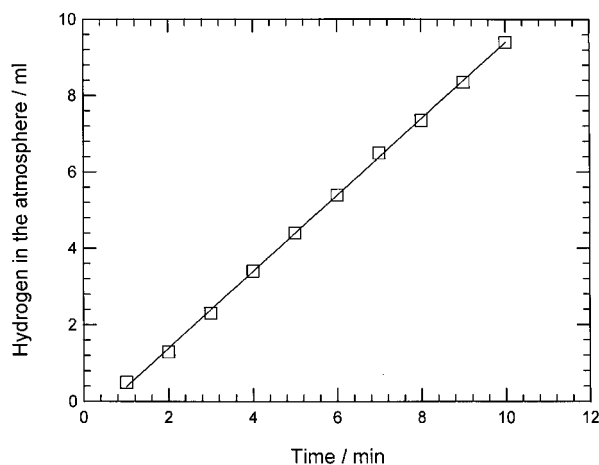


Fig. 2. Amount of hydrogen evolved in the atmosphere vs duration of electrolysis of a solution containing 3.25 M NaOH at cathodic c.d. of 2 A dm^{-2} .

solution. The cathodic side was potentiostatically polarized. The anodic side of the iron membrane, coated in advance with a $0.15\text{--}0.20 \mu\text{m}$ Pd layer, was kept at a constant potential of $+0.05 \text{ V}$ vs a Hg/HgO reference electrode. The oxidation current (I_H) registered at the ionization side of the membrane is a measure of the amount of hydrogen penetrating into the substrate. Each compartment of the cell had its own reference Hg/HgO electrode and Pt counter electrode. The electrolyte was purged with Ar for several hours before starting the experiment. A detailed description of the experimental procedure is given elsewhere [10]. The zinc deposition current efficiency was determined gravimetrically.

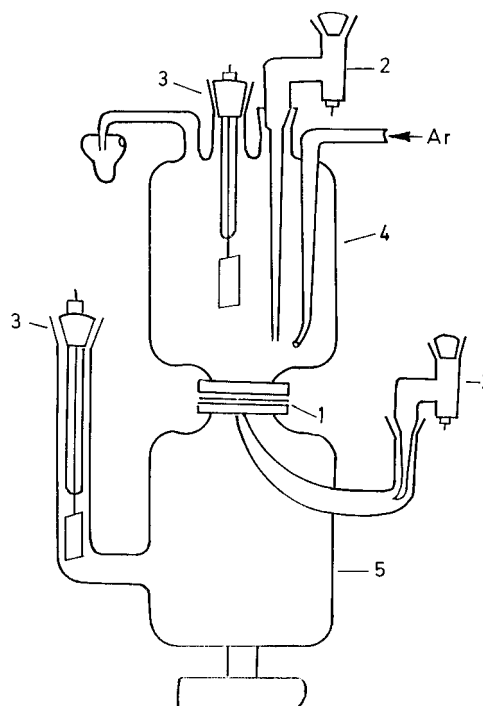


Fig. 3. Hydrogen penetration cell by the Devanathan–Stachurski method. Key: (1) working electrode, (2) reference electrodes, (3) counter electrodes, (4) polarization compartment of the cell, (5) ionization compartment of the cell.

All experiments were carried out at 25 °C.

3. Results and discussion

3.1. Effect of plating conditions on the codeposition of hydrogen

Previous investigations using the RRDE method have shown that zinc deposition from zincate electrolytes in the absence of brighteners is diffusion limited and stirring leads to an increase in zinc current efficiency [11]. The relationships between the ring current (I_R) and $\omega^{1/2}$ at various disc potentials E_D are shown in Fig. 4. The rate of hydrogen evolution does not depend on the rotation speed of the electrode within the investigated potential range. According to the theory, this relationship suggests that the rate determining stage of the hydrogen evolution process is electron transfer [7].

The substrate plays an important role in hydrogen evolution. The potentiodynamic curves $I_R = f(E_R)$ for the additive-free electrolyte at constant potential of -1.5 V for steel and zinc are shown in Fig. 5. In the latter case zinc was electroplated in advance onto the steel disc under galvanostatic conditions. When zinc is deposited onto the steel disc, higher I_R values as compared with those measured during deposition on a zinc disc were registered, due to the lower hydrogen overvoltage on iron. This is why the most intensive evolution of hydrogen occurs during the initial stages of zinc deposition onto steel (Fig. 6), in agreement with results by other authors [12]. The I_R against time curves were obtained under galvanostatic conditions at the steel disc. The ring current exceeds zero when the disc electrode is switched off ($I_{R,0}$), presumably due to the oxidation of dissolved hydrogen. When the disc electrode is switched on, the ring current shows in the first seconds of electrodeposition a maximum, followed by a decrease and remains almost constant during the following several minutes to the end of the experiment (about 20 min).

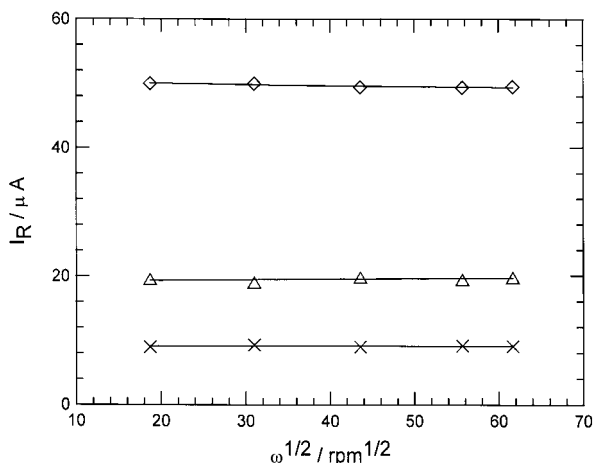


Fig. 4. Ring current against rotation speed of the electrode at different potentials of zinc deposition onto the disc from the additive-free electrolyte. $E_R = 0.15$ V. Key: (x) $E_D = -0.8, -1.2$ V; (Δ) $E_D = -1.4$ V; (\diamond) $E_D = -1.6$ V.

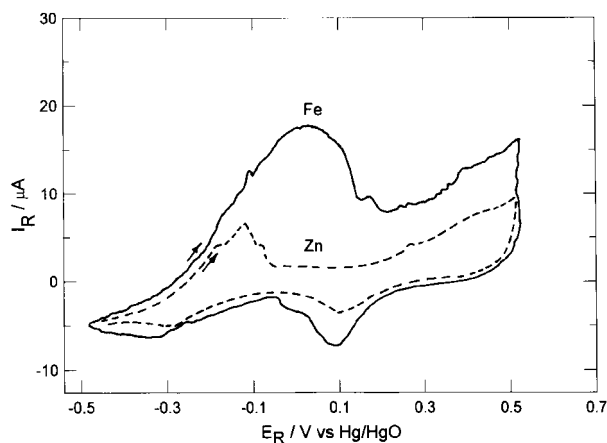


Fig. 5. Potentiodynamic curves of the ring during zinc deposition from the additive-free electrolyte onto different substrates at disc potential of -1.5 V, $\nu = 5$ mV s $^{-1}$, 960 rpm.

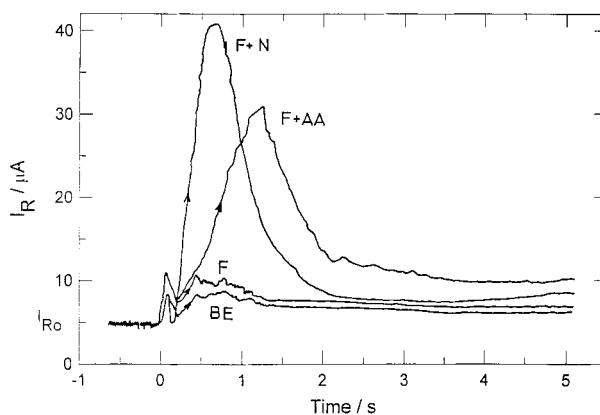


Fig. 6. Effect of the additives on the ring current during zinc deposition onto a steel disc at cathodic c.d. of 3 A dm $^{-2}$, 960 rpm.

The amount of evolved hydrogen increases abruptly when each of the brighteners are added to the electrolyte containing additive F. During the initial stage the most intensive hydrogen evolution is observed in electrolyte containing Na-*N*-benzylnicotinate. For electrolytes containing anisaldehyde bisulphite the maximum evolved hydrogen is reached after a period of time and higher plateau currents are registered. This behaviour is in agreement with data for zinc current efficiency (Table 1).

The amount of evolved hydrogen depends on the basic components of the zincate electrolyte. Their effect on the ring current at constant disc potential of -1.5 V is shown in Fig. 7. The increase in ZnO content (at constant NaOH concentration), as well as the decrease in NaOH content (at constant ZnO concentration) decrease the amount of evolved hydrogen.

Table 1. Current efficiency of zinc in different electrolytes at cathodic current density 2 A dm $^{-2}$ and 30 min deposition without stirring

Electrolyte	BE + F	BE + F + N	BE + F + AA
Zinc current efficiency/%	63	48	40

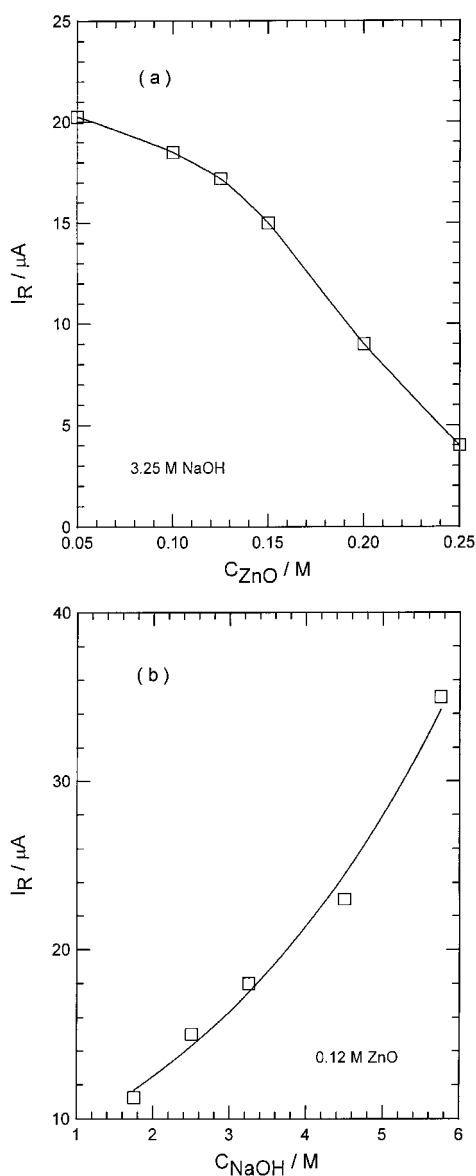


Fig. 7. Ring current vs ZnO (a) and NaOH (b) concentrations during zinc deposition from the additive-free electrolyte. $E_D = -1.5$ V. (I_R values are taken from the potentiodynamic curves I_R/E_R at $E_R = 0.15$ V.)

The decrease in zinc current efficiency at high c.d., inherent to zincate electrolytes, is shown in Fig. 8 for the basic electrolyte with additive F. A slightly decrease in zinc current efficiency with the time is observed, when stirring is not used.

3.2. Distribution of evolved hydrogen

During the deposition of zinc, a part of the hydrogen evolved on the cathode surface passes through the bulk of the electrolyte into the atmosphere. This amount can be measured in a bell cell with a burette (Fig. 1). The results (Fig. 9) show more intensive hydrogen evolution in the presence of additives and are in agreement with data in Table 1.

Some of the codeposited hydrogen diffuses into the substrate. The influence of the additive on the penetration of hydrogen was investigated by the Deva-

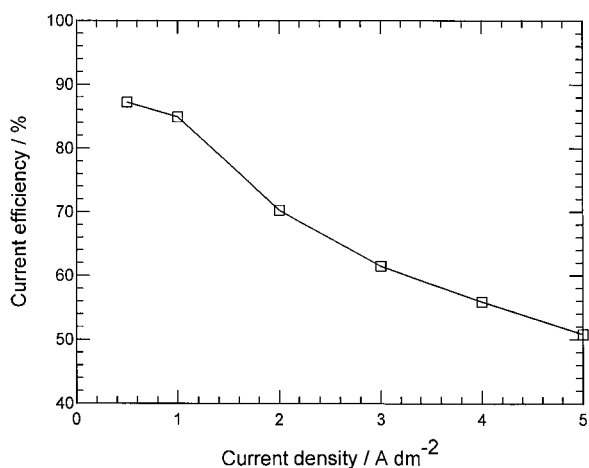


Fig. 8. Current efficiency against cathodic c.d. during zinc deposition from electrolyte containing the additive F (without stirring). Data correspond to 10 min deposition.

nathan–Stachurski method. The relationship between the oxidation current (I_H) and the potential applied to the polarization side of the membrane (E_p) is shown in Fig. 10. In the potential region -1.0 to -1.4 V the curves pass through a maximum. In the presence of the composite additive containing anisaldehyde bisulphite, this maximum is lower compared to the basic electrolyte and to the basic electrolyte containing additive F, i.e. hydrogen penetration through the membrane decreases. The result is in agreement with literature data, claiming that aromatic aldehydes inhibit the hydrogenation of steel both during the pretreatment and zinc plating stages [2]. The highest maximum is observed in the presence of the Na-*N*-benzylpicotinate, containing composite additive, suggesting that this brightener enhances the hydrogenation of the steel substrate.

The vacuum extraction tests confirm these results: maximum hydrogen content was established in samples plated in Na-*N*-benzylpicotinate containing electrolytes (Table 2).

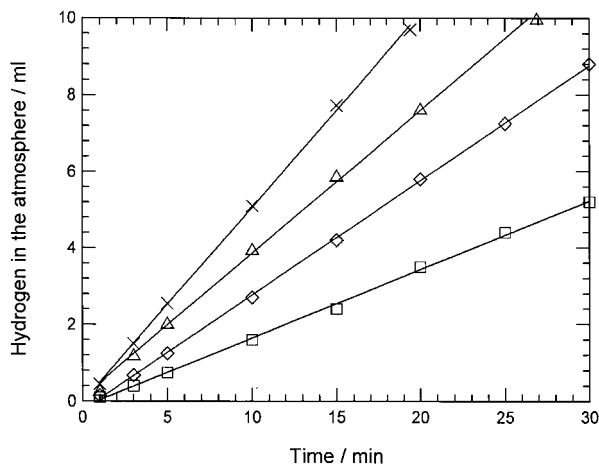


Fig. 9. Amount of hydrogen dissipated in the atmosphere during the deposition of zinc for various electrolyte compositions at a cathodic c.d. of 2 A dm^{-2} . Key: (\square) BE; (\diamond) BE + F; (\triangle) BE + F + N; (\times) BE + F + AA.

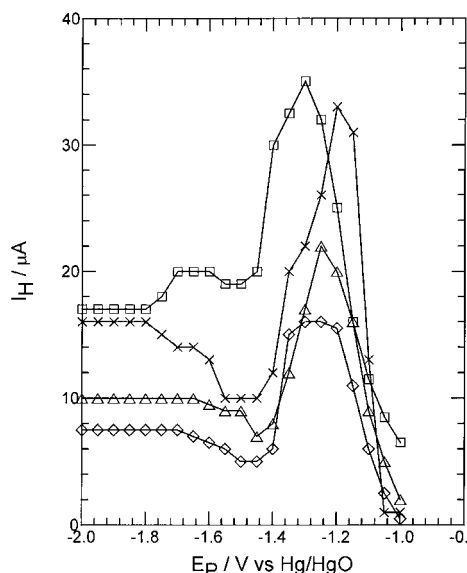


Fig. 10. Effect of the additives on the penetration of hydrogen into the substrate during potentiostatic polarization of the membrane. Key: (x) BE; (Δ) BE + F; (\diamond) BE + F + AA; (\square) BE + F + N.

The initial layers of the zinc coating exert a barrier effect and reduce the penetration of hydrogen through the membrane. In additive-containing electrolytes this effect is enhanced, probably as a result of the more compact coatings as compared with those deposited from the additive-free electrolyte.

The sum of the calculated quantities of electricity consumed for the deposition of zinc, for the hydrogen dissipated in the atmosphere and included in the sample is less than the measured quantity of electricity consumed during the test. The difference suggests that a part of the hydrogen remains in the electrolyte, which is confirmed by the gas bubbles evolved when used electrolytes are mechanically stirred. The hydrogen bubbles formed on the cathode are of different size and stability, depending on the type of additives and their effect on surface tension. For example, in the presence of anisaldehyde bisulphite less numerous, but larger, hydrogen bubbles are formed, whereas in the case of Na-*N*-benzylnicotinate the electrode is covered by fine hydrogen bubbles. In the latter case the amount of the evolved hydrogen remaining in the electrolyte is maximum.

A clear-cut illustration of the distribution of hydrogen evolved during zinc deposition from the electrolytes containing the three combinations of additives is shown in Table 3.

The additives affect both the overall amount of evolved hydrogen and its distribution. Most of the

Table 2. Hydrogen content in samples (substrate and coating) as a function of electrolyte composition at cathodic current density 2 A dm^{-2} and 30 min deposition

Electrolyte	BE + F	BE + F + N	BE + F + AA
Hydrogen content/wt %	0.0091	0.0106	0.0084

Table 3. Effect of the additives on the distribution of evolved hydrogen

Electrolyte	Hydrogen content/ml		
	BE + F	BE + F + N	BE + F + AA
Atmosphere	8.96	11.32	15.05
Electrolyte	1.17	2.50	0.78
Substrate + coating	0.63	0.74	0.56

hydrogen is dissipated into the atmosphere. The highest overall amount of hydrogen is formed in the presence of anisaldehyde bisulphite containing composite additive, that is, zinc deposition efficiency in this electrolyte is the lowest. The highest amount of hydrogen included in the substrate and in the coating, as well as remaining in the electrolyte, is established in the case of Na-*N*-benzylnicotinate containing additive.

3.3. Formation of blisters in the zinc coating

When bright zinc coatings are deposited from zincate electrolytes, a deleterious effect of blistering is observed in some cases. This effect was also established during the present investigations. Blisters appeared after a certain time in zinc coatings deposited in the presence of a composite additive containing Na-*N*-benzylnicotinate (Fig. 11). It was already known that this additive causes the highest hydrogen evolution and hydrogenation of the substrate early in the initial stages of zinc deposition. Under these conditions, it is possible that part of the hydrogen remains included in the loose structure of the initial zinc layers. It is also possible that electrochemical transformation of the additives and their effect on hydrogen evolution changes during the transition from the steel substrate to the zinc layer. X-ray microanalysis combined with SEM observations showed that under the blisters, a loose zinc coating, less than $0.5 \mu\text{m}$ thick occurs (Fig. 12). X-ray electron spectroscopy (XPS) has also established a higher content of several elements contained in the additives (carbon, nitrogen and sulfur) in this initial layer, as compared to that in thicker zinc

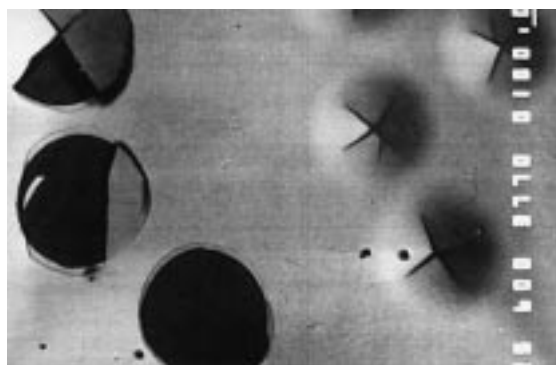


Fig. 11. Defects in the zinc coating. 4.5 mm on the photo corresponds to $100 \mu\text{m}$.

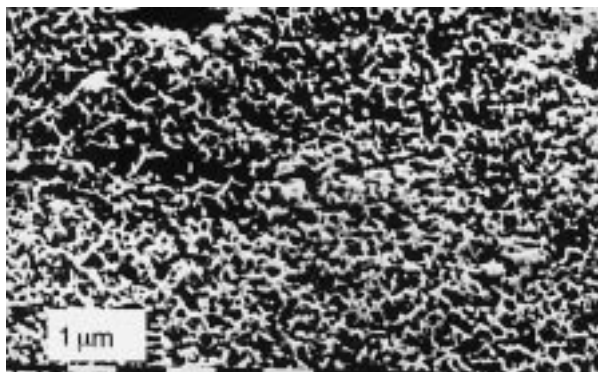


Fig. 12. SEM micrograph of the surface under a removed blister of the zinc coating.

coatings. In addition, within this thickness range X-ray analysis showed an abrupt change in the predominant orientation axes of the zinc coatings.

4. Conclusion

The rate determining stage of hydrogen evolution in additive-free electrolyte is electron transfer. The amount of evolved hydrogen increases at higher cathodic current densities, higher NaOH concentrations and lower ZnO content, as well as in the presence of all tested additives.

The evolved hydrogen is dissipated in three ways: into the atmosphere, into the bulk electrolyte and into the steel substrate. The most substantial part is dissipated into the atmosphere. Additives affect both the total amount of evolved hydrogen and its distribution.

The most intensive hydrogen evolution is observed during the first seconds of electrodeposition due to the lower overvoltage of hydrogen on steel as compared with that on zinc. Part of the hydrogen diffuses

into the substrate and probably remains included in the loose initial zinc layers. After deposition in Na-N-benzylnicotinate containing electrolyte it later contributes to blistering of the zinc coating. Moreover, the differences in the parameters of the initial zinc layers such as high content of several elements deriving from the additives (carbon, nitrogen and sulphur), altered texture and structure, changes in the internal stress, etc., may lead to blistering.

Acknowledgement

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