

# *Microthrowing power of electrolytes for the deposition of nickel-iron alloys. II. Levelling effect of iron in nickel-iron electrolytes and its microdistribution in the alloy coating*

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Investigations were aimed at demonstrating and clarifying the levelling effect of the iron component in a saccharin-containing nickel-iron alloy plating electrolyte. The results provide evidence that levelling probably follows the adsorption-diffusion mechanism proposed by Kardos and Foulke, as well as by Edwards and Watson. Microprobe analysis shows that the microdistribution of iron in the alloy deposit is not uniform, its content being higher in the alloy plated on the micropeaks of the cathode profile. A quantitative evaluation of the non-uniform distribution of iron is proposed and a linear empirical relationship has been established between this calculated value and levelling determined by profilometric measurements.

## 1. Introduction

The levelling additives used in plating are in most cases organic compounds. Literature sources describe cases when several inorganic ions display a levelling effect [1-3]. The mechanism by which these additives influence levelling has been investigated in only a few cases, and evidence is still lacking. In Part I of our study [4] it was shown that the introduction of an iron component to the saccharin-containing nickel plating bath enhances the levelling effect substantially. On the basis of the experimental data presented it can be concluded that in the presence of saccharin the iron content behaves as a levelling agent in the nickel-iron plating electrolytes. The present investigation is aimed at elucidating the levelling mechanism of iron in these electrolytes and at determining the microdistribution of iron in the alloy coatings deposited on a model microprofile.

## 2. Experimental details

The composition of the electrolytes studied was:

100 g l<sup>-1</sup> NiSO<sub>4</sub> · 7H<sub>2</sub>O; 70 g l<sup>-1</sup> NiCl<sub>2</sub> · 6H<sub>2</sub>O; 45 g l<sup>-1</sup> H<sub>3</sub>BO<sub>3</sub>; 10 g l<sup>-1</sup> Na-citrate; 10 g l<sup>-1</sup> Na-gluconate. To this bath composition, referred to as the basic electrolyte (BE), were added saccharin, a Class II brightener described in Part I and different amounts of FeSO<sub>4</sub> · 7H<sub>2</sub>O. The deposition conditions, the model cathodes with a defined microprofile, as well as the technique for the determination of the levelling effect are identical with those described in Part I. The polarization curves of the alloy deposition were determined potentiodynamically using a flat platinum electrode. The cathode potentials were measured against a saturated calomel electrode. The distribution of iron in the alloy coating was determined by microprobe analysis of crosscuts of the samples, using a Jeol Superprobe 733 unit. Semiquantitative scanning methods were applied for the study of the surface and quantitative analysis was applied to points within the scan lines. The crosscuts were polished and slightly etched in an effort to avoid the selective dissolution of the surface layers. The point analyses were performed with a 1 μm-diameter electron beam.

### 3. Results and discussion

All the iron in the electrolyte is in the form of citrate and gluconate complexes and it can be presumed that its behaviour during plating is similar to that of the organic levelling additives. According to the adsorption–diffusion mechanism demonstrated in the case of organic levelling agents [2, 5–8], an additive can lead to positive levelling if it exerts an inhibitive effect upon the plating process and if the metal deposition rate is at least partly controlled by its diffusion to the cathode.

Fig. 1 shows the deposition polarization curves of nickel–iron alloy coatings plated in baths containing different amounts of iron. The decrease of current at a given potential caused by the increase of iron in the electrolyte shows that it exerts an inhibitive effect upon the deposition process.

Fig. 2 presents the polarization curves obtained on flat electrodes at two different rates of mechanical agitation for each iron concentration. In all cases the intensification of agitation enhances the inhibitive effect. This provides evidence that the alloy deposition is controlled by the mass transfer of the inhibitor (the iron complex) toward the cathode. On the basis of these results it can be concluded that the levelling effect of iron in nickel–iron plating baths probably follows the adsorption–diffusion mechanism.

During plating the concentration field of the

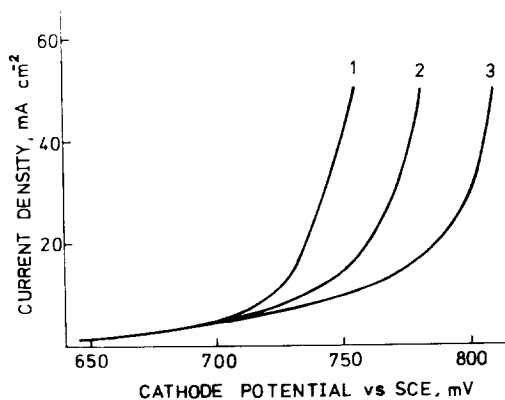


Fig. 1. Current–potential relationships of an electrolyte with composition BE + 4 g l<sup>-1</sup> saccharin + 0.1 g l<sup>-1</sup> brightener Class II to which are added different amounts of iron ions: (1) 0 g l<sup>-1</sup>; (2) 2 g l<sup>-1</sup>; (3) 3 g l<sup>-1</sup>.

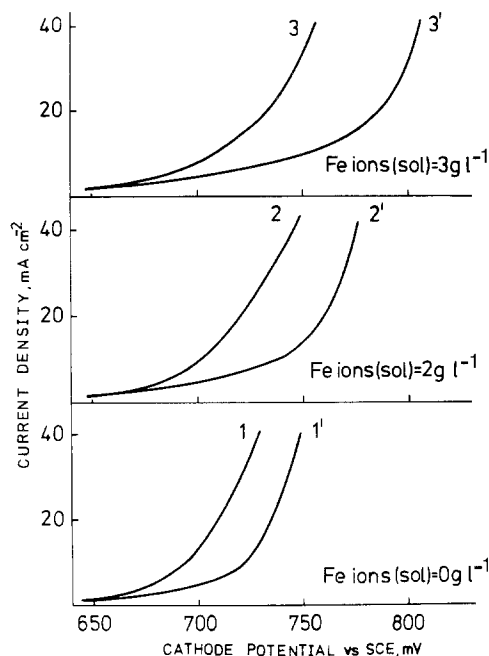


Fig. 2. Current–potential relationships for two different mechanical agitation rates of the electrolyte. Curves 1 to 3 at 50 r.p.m.; curves 1' to 3' at 350 r.p.m. for electrolytes corresponding to Curves 1 to 3 in Fig. 1.

levelling agent in the vicinity of the cathode is not uniform and is similar to the primary current field. As a result, the coating at the micropeaks must contain much more levelling agent (or its decomposition products) inclusions as compared with the microgroove regions. The experimental confirmation of this conclusion is considered very important as an evidence for the validity of the levelling mechanism. However, even with the aid of updated analytical techniques, it appears that the task is difficult, due to the low concentrations of organic levelling additives and the fact that the products of their transformation are not always included in the coating or are included in very small amounts. Watson and Edwards [2] have solved this problem qualitatively. By applying various etching techniques to crosscuts they have obtained different colouring of the coating on the micropeak regions which they attribute to the presence of larger amounts of incorporated addition agents at these sites.

The nickel–iron system offers a more accurate solution of this problem since the entire amount of levelling agent, in this case iron, which reaches

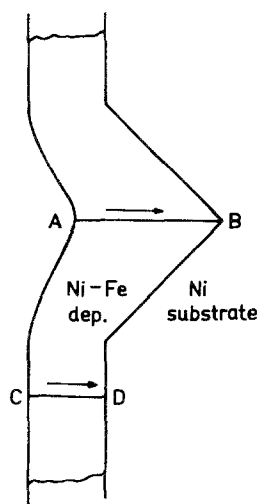


Fig. 3. Scanning lines for microgrooves AB and for micropeak CD.

the cathode surface is included in the coating. Each layer of the deposited coating contains information about the distribution of the levelling additive upon the microprofile at the given moment. This information can be obtained sufficiently accurately by checking the crosscut of the alloy coating by microprobe analysis. The semiquantitative analysis of iron and nickel by scanning along the lines AB and CD in Fig. 3 can be further backed by quantitative analysis data for the alloy at points situated at even intervals along AB and CD.

The results will show the distribution of the levelling agent upon the given microprofile at the beginning of the plating and, on the other hand, the change of this distribution when the grooves are filled during the deposition process.

Figs 4a and b show the scan-line profiles of iron and nickel in a coating deposited from a bath containing the BE and  $4 \text{ g l}^{-1}$  saccharin +  $2 \text{ g l}^{-1}$  Fe upon cathodes with a defined microprofile described in Part I. It can be seen in Fig. 4a that the iron content in the alloy increases from the bottom of the groove towards the surface, the curve comprising an initial linear region and a plateau. The alloy on the protruding part shows no significant change in composition along its depth (Fig. 4b). It can be presumed that at the point where the plateau appears the diffusion limitations for the access of iron to the cathode decrease considerably and the cathode surface becomes equally available with respect to the iron component in the electrolyte.

In Fig. 5 of Part I [4] it was shown that the appearance of a maximum in the levelling versus iron ion concentration curve for a nickel-iron plating electrolyte containing saccharin is characteristic for the relationship between levelling and the amount of the levelling agent. This relationship is explained by the creation of sufficiently strong inhibitive effect on the metal deposition process and the localization of this effect on the micropeaks [5-7]. An experimental confirmation of this presumption can be obtained by microprobe investigations of coatings deposited from electrolytes containing different amounts of levelling agent, i.e. iron ions. Data presented in Table 1 are obtained from samples deposited from electrolytes containing amounts of iron, corresponding to the ascending, descending and near maximum regions of Curve 1 (Fig. 5 in Part I [4]). Levelling data are obtained by direct profilometric measurements by the method described in Part I.

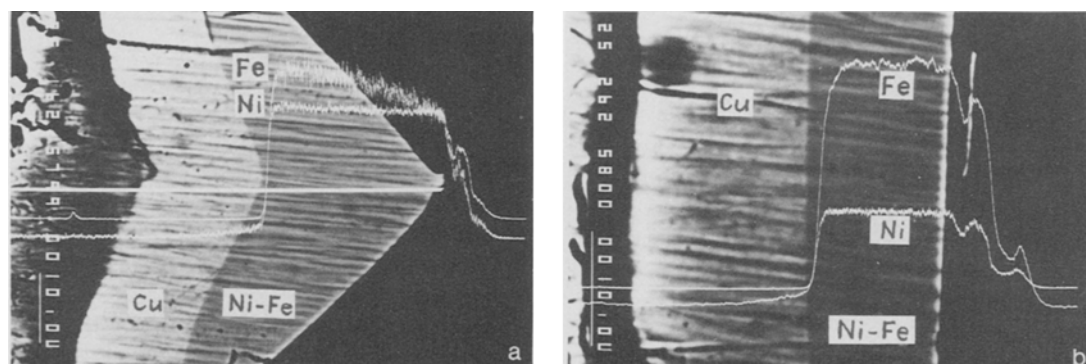


Fig. 4a and b. Scanning line profiles for iron and nickel along the lines (a) AB and (b) CD.

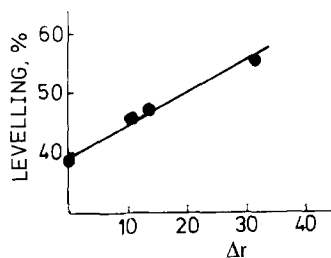


Fig. 5. Relationship between  $\Delta r$  and the levelling effect determined by profilometric measurements.

In order to characterize the inhibiting effect and its localization on the micropeaks we introduce two parameters: the difference,  $\Delta$  and the ratio,  $r$  of the values of iron concentration for a peak and a groove respectively for each sample. The physical meaning of  $\Delta$  is the difference between the degree of inhibition in the two regions of the microprofile since the inhibitive effect is proportional to the amount of inhibitor in the solution (the iron component). When the electrolyte contains no iron or when iron is uniformly distributed along the microprofile,  $\Delta$  is zero. The parameter  $r$  shows the degree of non-uniformity in the distribution of the levelling agent on the microprofile, i.e. the extent to which inhibition is localized on the peaks.

The linear relationship between the levelling effect versus the product of  $\Delta$  and  $r$ , presented in Fig. 5 is of special interest. For  $\Delta r = 0$ , which takes place in the absence of iron in the electrolyte,  $L = 39\%$ . This value is quite close to the intercept value (38.5) of the levelling versus iron concentration curve (Curve 1, Fig. 5, Part I [4]).

Table 2. Some parameters of samples shown in Table 1

Parameters	Solution 1	Solution 2	Solution 3
$Fe_{\text{soln}} \text{ g l}^{-1}$	1.34	3.78	5.88
$L = \frac{R_a^1 - R_a^2}{R_a^1} 100\%$	45.2	55.3	47.0
$\Delta = Fe_{\text{peak}} - Fe_{\text{groove}}$	6.2	16.9	10.7
$r = \frac{Fe_{\text{peak}}}{Fe_{\text{groove}}}$	1.75	1.87	1.29

Note:  $\Delta$  and  $r$  denote the difference and the ratio of iron content in the nearest to the substrate layer (3 to 4  $\mu\text{m}$  thick) on a micropeak and in a microgroove. The values are calculated from the asterisk-marked data in Table 1.

#### 4. Conclusions

1. It is shown that in saccharin-containing nickel-iron alloy plating electrolytes the iron component exerts a levelling effect. The mechanism of this phenomenon is in agreement with the adsorption-diffusion theory advanced by Kardos and Foulke [5-7], as well as by Watson and Edwards [2].

2. Nickel-iron alloy coatings deposited from the electrolyte studied and investigated by electron microscopic methods and microprobe analysis provide evidence that:

(a) The initial distribution of iron on the microprofile is nonuniform, the amount on the peaks is higher. This distribution corresponds to the mechanism of the adsorption-diffusion theory for the localization of an organic levelling agent.

Table 1. Wt% of iron in the alloys

Solution 1		Solution 2		Solution 3	
Along AB	Along CD	Along AB	Along CD	Along AB	Along CD
12.6	14.0	32.5	35.3	43.4	49.5
11.5	—	—	—	—	—
11.0	—	—	—	41.0	—
10.9	—	30.9	—	—	—
10.7	—	—	—	—	—
9.7	—	—	—	39.2	—
9.4	14.4*	—	36.4*	—	48.0*
8.2*	—	19.5*	—	37.3*	—

\* Data points used in Table 2.

(b) With decrease of the initial roughness of the cathode surface the nonuniform distribution of iron becomes less pronounced.

(c) Two parameters for the evaluation of the degree of nonuniformity of iron distribution in the alloy have been introduced and a linear relationship between the levelling effect, determined by profilometric methods, and product of these two indices has been established empirically.

### References

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