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Microthrowing power of electrolytes for the deposition of nickel–iron alloys. I. Components determining the levelling effect of nickel–iron plating electrolytes

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The microthrowing power of an electrolyte for plating nickel–iron alloy deposits containing organic additives of the Classes I and II was investigated in an effort to determine the contribution of each component of the system. The levelling versus concentration relationships were evaluated for each additive and the iron ions in the electrolyte both separately and in combination. The results show that the main levelling additives in this system are the brightener Class II as well as the iron component in the presence of saccharin.

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1. Introduction

Data on the microthrowing power of electrolytes for the deposition of alloys are very scarce. The levelling effect of baths for the deposition of several widely used alloys has been studied [1–3], but information about the mechanism of the levelling processes in these complex electrolyte systems is still not available. On the basis of general considerations, it can be presumed that the presence of a second codepositing ion in the system will tend to change the microdistribution pattern of the coating on the cathode. A convenient model for the investigation of the microthrowing power of alloy deposition electrolytes is the nickel–iron alloy plating bath, since this is based on the well studied bright nickel plating compositions [4].

The present investigation considers an electrolyte for the deposition of bright protective–decorative Ni–Fe alloy coatings, which is now widely used in plating practice.

As in the case of the standard bright nickel plating formulations it contains organic additives, brighteners of Classes I and II according to the classification proposed by Saubestre [5], but differs in having a lower metal concentration and a lower content of organic complex-forming compounds.

Several papers [6–8] dealing with the problems of nickel–iron alloy plating point out as an advantage of this process the improved levelling as compared with that of the conventional bright nickel deposition bath. Our study is aimed at the establishment of the effect exerted by the different components of this complex system upon the microthrowing power.

2. Experimental details

The composition of the investigated electrolytes was: 100 gl^{-1} $NiSO_4 \cdot 7H_2O$; 70 gl^{-1} $NiCl_2 \cdot 6H_2O$; 38 gl^{-1} Ni (metallic); 45 gl^{-1} H_3BO_3; 10 gl^{-1} Na-citrate; 10 gl^{-1} Na-gluconate; 0 to 30 gl^{-1} $FeSO_4 \cdot 7H_2O$; 0 to 6 gl^{-1} Fe (metallic); 0.5 to 7 gl^{-1} saccharin as a Class I brightener; 0 to 0.4 gl^{-1} Class II additive. Plating conditions: pH 3.2; temperature 60° C; cathodic current density 5 $A\,dm^{-2}$) air bubbling.

The Class II additive is a mixture of compounds with a general formula ROR′H and RSO_3H. R and R′ are butyndiol derivatives. Saccharin as a Class I brightener and the above mentioned compounds are often encountered in the patented formulations for Ni–Fe plating baths [9].

The alloy coating was plated onto cathode substrates with a model microprofile (a gramophone record nickel master mould) with V-shaped grooves 30 μm deep (Fig. 1). The

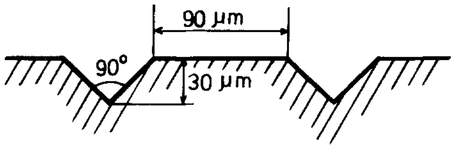

Fig. 1. Drawing of the model microprofile of the cathodes used.

average thickness of the alloy coating was approximately 20 µm. The levelling was checked by profilometric measurements of the roughness of the samples prior to and after plating with a Perthen meter and evaluated by the following equation [10]:

$$L = \frac{R_a^1 - R_a^2}{R_a^1} 100\% \qquad (1)$$

where R_a^1 is the initial roughness and R_a^2 is the final roughness.

The reproducibility of the measurements was ± 1% levelling, provided the hydrodynamic conditions and the geometry of the test cell were kept constant.

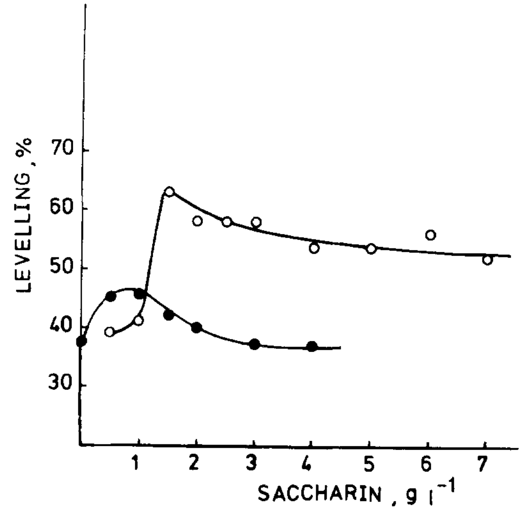

Fig. 3. Levelling as a function of the saccharin concentration (●) Curve 1, BE, (○) Curve 2, BE + 3 g l^{-1} Fe.

3. Results and discussion

The investigated electrolyte for the deposition of nickel–iron alloys can be considered as a system comprising the following components:

1. Basic electrolyte BE ($NiSO_4$, $NiCl_2$, H_3BO_3, Na-citrate, Na-gluconate)
2. Iron complex (for the present the effect of the nature of the complex-forming compound upon levelling will not be considered)
3. Class I additive, saccharin
4. Class II additive, ROR′H + RSO_3H

The basic electrolyte displays an ideal microthrowing power, i.e. the deposited coating repeats the profile of the substrate. The measurements carried by the method mentioned above show a 23 to 25% levelling, due to the so-called geometric levelling [11]. The real levelling effect is obtained by the presence of the other three components in the electrolyte formulation. In order to evaluate the contribution of each

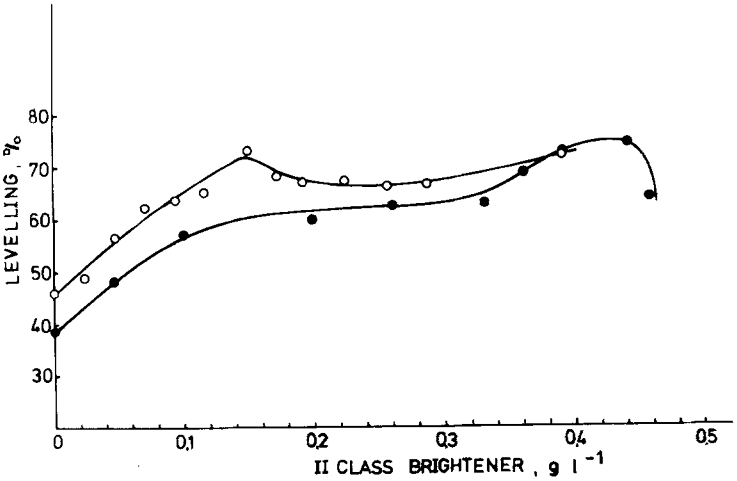

Fig. 2. Levelling as a function of the concentration of the Class II brightener. (●) Curve 1, BE + 4 gl^{-1} saccharin, (○) Curve 2, BE + 4 gl^{-1} saccharin + 2 gl^{-1} Fe.

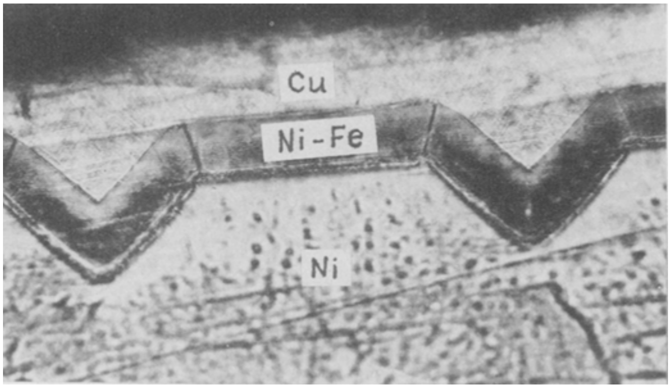

Fig. 4. Geometric levelling obtained in an electrolyte composition BE + 2 gl^{-1} Fe.

individual component to the overall levelling the relationship between the respective concentration and levelling was traced using single additives or additives in combination. Fig. 2 Curve 1 shows the relationship between concentration and levelling effect of the Class II additive in the presence of saccharin. The introduction of iron to the electrolyte improves the levelling (Curve 2).

Fig. 3 shows the levelling effect for saccharin which, in the absence of iron ions in the electrolyte (Curve 1), is as poor as the case of standard nickel plating baths [4]. The combination between saccharin and the iron complex leads to a substantial enhancement of the levelling effect (Curve 2). This is a further confirmation of the positive effect which iron exerts on the microthrowing power of the electrolyte. However, the fact that the iron complex alone does not exert an intrinsic levelling effect is very important, i.e. the formulation basic electrolyte + iron complex displays a geometric levelling only (Fig. 4).

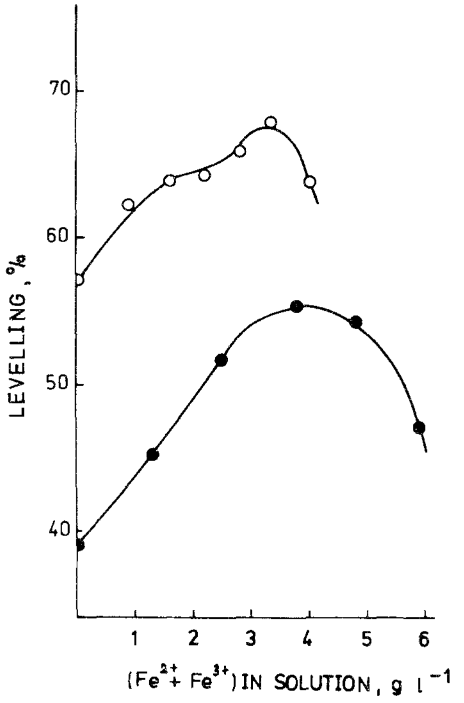

Fig. 5. Levelling as a function of the concentration of iron ions in the electrolyte. (●) Curve 1, BE + 4 gl^{-1} saccharin, (○) Curve 2, BE + 4 gl^{-1} saccharin + 0.1 gl^{-1} brightener Class II.

Fig. 5 presents the relationship between levelling and concentration of Fe^{2+} and Fe^{3+} in solutions containing only saccharin (Curve 1) and saccharin + Class II additive (Curve 2). The occurrence of a levelling maximum is inherent to levelling additives and has been considered in detail by Kardos [11, 12], and Watson and Edwards [13]. A similar relationship has been obtained by Kruglikov *et al.* [14] for a nickel–iron plating electrolyte containing the additives saccharin, citric acid, sodium laurylsulphate and polyvinyl pyrolidone, but no special attention has been attached to this phenomenon.

4. Conclusions

Table 1 summarizes data taken from the concentration relationships. The results presented illustrate the following conclusions about the contribution of each component in the electrolyte to the overall levelling effect of the nickel–iron alloy plating electrolyte:

1. The iron complex does not display a levelling effect if no organic additives of the Classes I and II are present (Table 1, No. 2).

Table 1. Data taken from concentration relationships

Electrolyte No.	*Iron in solution* *(gl^{-1})*	*Saccharin* *(gl^{-1})*	*Class II additive* *(gl^{-1})*	*Levelling effect* *(%)*
1. Basic electrolyte	–	–	–	geometric
2. Basic electrolyte	2	–	–	geometric
3. Basic electrolyte	–	4	–	38.5
4. Basic electrolyte	2	4	–	49
5. Basic electrolyte	–	–	0.15	52
6. Basic electrolyte	2	–	0.15	53
7. Basic electrolyte	–	4	0.15	60
8. Basic electrolyte	2	4	0.15	73

2. Saccharin alone as an additive to the basic electrolyte exerts a slight levelling effect only (Table 1, No. 3).

3. The combination of the two components, iron complex and saccharin increases the levelling effect (Table 1, No. 4).

4. The combination between the iron complex and the Class II additive does not enhance the levelling effect as compared with that of the basic electrolyte and the Class II additive (Table 1, No. 5 and No. 6; the data are obtained from single experiments). These results suggest that the presence of saccharin in the solution is a necessary condition for the iron ions to act as a levelling agent.

5. The introduction of the iron complex to an electrolyte, containing additives of the Classes I and II further increases the levelling effect.

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