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Electrochemical preparation of amorphous Fe–P alloys

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Optimum conditions have been established for the electrodeposition of amorphous Fe–P alloys from sulphate electrolytes, containing complex-forming additives (glycine and oxalic acid) and sodium hypophosphite. It was shown that the increase of pH, current density and glycine content in the plating solution leads to a decrease of the amount of phosphorus in the Fe–P alloy. The cathodic current yield decreases with the increase of glycine concentration in the electrolyte. Small amounts of Cu^{2+} and Mn^{2+} act as brighteners. Sodium hypophosphite exerts a depolarizing effect on the alloy formation process. This effect is more pronounced at low hypophosphite concentrations and low cathodic current densities (CCD). The measurement of the cathodic potential during the deposition of the investigated alloy provides no evidence for a concentration change of phosphorus in the electrodeposited layers. No qualitative alterations of the surface morphology of the amorphous coatings studied have been established as the composition of the alloy and the plating conditions are changed.

1. Introduction

Amorphous alloys are a relatively new material, offering a specific combination of properties and they have attracted keen interest during the last two decades.

The electrochemical synthesis of these materials appears to be highly competitive as compared with other methods for their preparation. A characteristic peculiarity of this method is the possibility of changing the composition of the alloys within a broad range and to select and control the required thickness of the coating.

The most widely studied and used electrodeposited amorphous alloys are the nickel–phosphorus group. The number of electrolytes known to have been used for the deposition of Fe–P amorphous alloys is small. These alloys are deposited exclusively from acidic electrolytes containing an iron salt (chloride, sulphate or sulphamate), a hypophosphite of an alkaline metal, as well as a buffer and complex-forming additives (ammonium chloride, fluoride or sulphamate, L-ascorbic acid, boric acid, etc.) [1–3].

The present paper is aimed at the determination of the conditions for the deposition of uniform and smooth amorphous Fe–P coatings and the effect exerted by the different components in the electrolyte upon the composition and some properties of the deposits.

The first step was to check whether an amorphous alloy can be deposited from a rather simple iron plating electrolyte by only adding the amorphism-causing additive – phosphorus.

Kudryavtzev and Smirnova [4] have proposed glycine as a buffer additive to the sulphuric acid-containing iron plating electrolyte. Existing data provide evidence that glycine acts as a complex-forming additive in nickel and zinc plating electrolytes [5, 6]. The proposed electrolyte also contains oxalic acid as a stabilizer of iron ions. The authors recommend keeping the glycine concentration less than $15\,g\,l^{-1}$, in order to retain high current yield. If this concentration is surpassed, the quality of the iron deposits deteriorates, becoming brittle and having substantial internal stress.

2. Experimental details

The optimization of the conditions for amorphous alloy plating and the determination of a convenient electrolyte was carried out by setting up a plan according to the complete factor experiment method [7]. A linear model, described by an equation of the type

$$y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{23}x_2x_3 + b_{13}x_1x_3 + b_{123}x_1x_2x_3 \qquad (1)$$

was accepted.

The design matrix was set according to a specific scheme, so that during the experiment all possible combinations can be achieved on two levels of the factors. The upper level of each factor is designated as (+1), while the lower is (−1).

The calculation of the regression coefficients was carried out using

$$b_i = \frac{1}{N}\left(\sum_{n=1}^{N} y^{(n)}\,\tilde{x}_i^{(n)}\right) \qquad (2)$$

where N is the number of experiments, $y^{(n)}$ is the experimental value of the output parameter and $\tilde{x}_i^{(n)}$ is the coded value of the experimental factors x_i at the nth experiment.

The value and sign of each regressive coefficient provide information about the contribution of a given factor and the direction in which it affects the initial

Table 1. Design matrix and experimental data

Exp. no.	$\tilde{x}_1$	$\tilde{x}_2$	$\tilde{x}_3$	x_1	x_2 *($A\,dm^{-2}$)*	x_3 *($g\,l^{-1}$)*	*P content in the alloy (wt%)*	*Structure*	*Current yield (%)*
1	+	+	+	2.2	10	12	8.7	Am > Cr	69
2	−	+	+	1.6	10	12	10.3	Am	36
3	+	−	+	2.2	4	12	8.5	Am = Cr	54
4	−	−	+	1.6	4	12	15.5	Am	14
5	+	+	−	2.2	10	5	8.1	Cr > Am	92
6	−	+	−	1.6	10	5	14.6	Am	52
7	+	−	−	2.2	4	5	13.8	Am > Cr	72
8	−	−	−	1.6	4	5	16.9	Am	25

Am, amorphous; Cr, crystalline.

parameter, respectively. The statistical processing of the results and the checking of the adequacy of the regression equation were performed according to a procedure, described in [7]. The finding of the x_1 values, when y acquires extremums within the limits of the x_i changes, was achieved by the Box–Wilson [8] method.

The coatings were deposited in a 500 ml cell under intensive stirring. ARMCO anodes were used and the coatings were plated onto 4 cm^2 or 1 cm^2 copper or platinum substrates. The content of P and Fe was determined by microprobe analysis, while the structure of the coating was checked by X-ray diffraction methods.

The polarization curves under galvanostatic conditions were traced vs an SCE reference. The voltage–time curves of the iron–phosphorus-coated cathodes were registered on a chart recorder. Each polarization curve was traced at least 3 times, each time using a fresh electrolyte. The cathodic potential values at the respective current density are the mean figures of the experimental runs at a maximum deviation of the separate values of less than ± 20 mV.

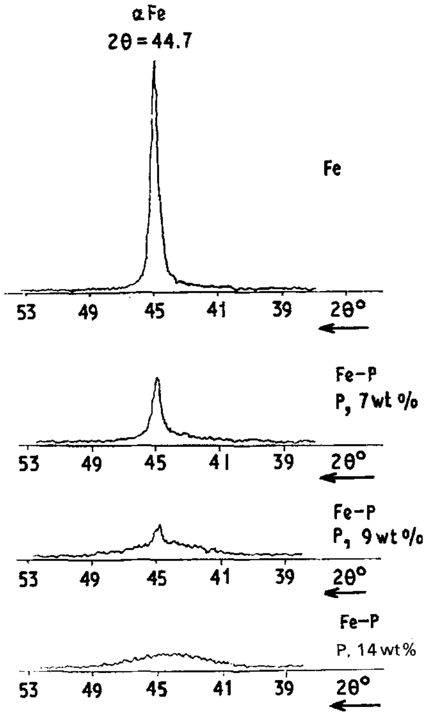

Fig. 1. Diffractograms of iron and iron-phosphorus coatings with different phosphorus content determined with K–Cu$_\alpha$ radiation.

3. Results and discussion

The design matrix for a complete factor experiment and empirical data are presented in Table 1. The diffractograms characteristic of the deposited coatings with various phosphorus contents and the corresponding amorphous, crystal or mixed structures are shown in Fig. 1.

The initial parameters for the complete factor experiment were the phosphorus content in the coating (y_1) and current yield (y_2), while the independent variables were pH of the electrolyte (x_1), cathodic current density (CCD) (x_2) and glycine concentration in the solution (x_3).

The rest of the factors were fixed at constant values as follows: temperature of the electrolyte, 40° C; $FeSO_4 \cdot 7H_2O$, 200 g l^{-1}; $NaH_2PO_2 \cdot H_2O$, 7 g l^{-1}; oxalic acid, 0.5 g l^{-1}.

After eliminating several insignificant interactions, the following regression equations were derived:

$$y_1 = 12.05 - 2.27\tilde{x}_1 - 1.62\tilde{x}_2 - 1.3\tilde{x}_3 \quad (3)$$

$$y_2 = 51.99 + 20.04\tilde{x}_1 + 10.62\tilde{x}_2 - 8.5\tilde{x}_3 \quad (4)$$

Equation 3 shows that the strongest effect upon phosphorus content is exerted by the pH of the electrolyte. The increase of pH, CCD and glycine content in the solution led to a decrease of phosphorus in the alloy. Equation 4 suggests that the increase of CCD and the decrease of the acidity of the medium improve the current yield, while high glycine content lowers the current yield, probably as a result of the complex-forming effect of glycine.

Each of the y_1 and y_2 values are the arithmetic mean of three parallel measurements.

The control based on Fisher's criterion [7] shows that Equation 3 is adequate while Equation 4 is inadequate. The Box–Wilson method offers the possibility of searching for an optimum even in the case of inadequacy of the regression equations. In our case, the optimum conditions are those which simultaneously meet the following requirements: the amount of P in the coating must ensure amorphous structure and cathodic current yield must be relatively high.

Table 2. Influence of hypophosphite concentration in the electrolyte on the chemical composition of Fe–P alloys and their structure

pH	*CCD* ($A\,dm^{-2}$)	$NaH_2PO_2 \cdot H_2O$ *concentration* ($g\,l^{-1}$)	*Phosphorus content in the coating (wt%)*	*Structure*
2	5	1	7	Cr
2	7	3	13.6	Am
2	7	7	11	Am
1.8	10	10	12	Am

Optimization according to the Box–Wilson method gave the following results: glycine, $8.5\,g\,l^{-1}$, pH, 2, CCD, $7\,A\,dm^{-2}$.

The advantage of this electrolyte is the possibility of depositing from it amorphous coatings at higher pH values and lower hypophosphite concentration in the electrolyte. Under these conditions, the latter is stable with regard to pH, formation of precipitates and alloy composition. The alloy coatings are uniform, smooth and light-coloured. The complete factor experiment does not use the sodium hypophosphite content as an independent variable, in spite of literature data which claim that is should be one of the major factors determining the phosphorus content in the alloy. Routine preliminary experiments have shown that hypophosphite concentrations above $3\,g\,l^{-1}$ do not exert a substantial influence on the phosphorus content and the structure of the alloy (Table 2).

We felt it necessary, however, to check accurately the effect of hypophosphite on the alloy formation process.

It can be seen in Fig. 2 that the addition of hypophosphite to the electrolyte, regardless of concentration or current density, exerts a depolarizing effect on the alloy formation process as compared with the electrodeposition of pure iron. This effect, according to the literature, is the sole result of the alloy formation [9–11]. In this case it may be expected that depolarization will be enhanced as phosphorus content in the alloy coating increases and, presumably, the increase of hypophosphite in the electrolyte will cause a similar effect.

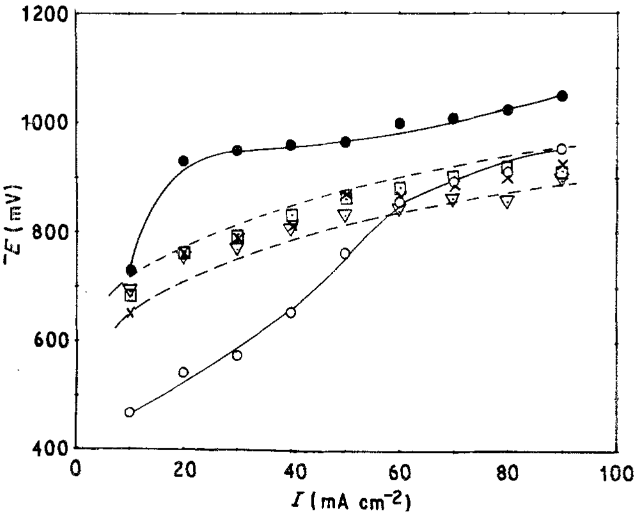

Fig. 2. Polarization curves traced during the deposition of iron and iron–phosphorus alloys from an electrolyte containing ($g\,l^{-1}$): $FeSO_4 \cdot 7H_2O$, 200; glycine, 8.5; oxalic acid, 0.5; and different amounts of $NaH_2PO_2 \cdot H_2O$; ●, 0; ○, 1; △, 5; ×, 10; □, 15. Electrodeposition is carried out at 40° C at pH = 2.

It is significant that the most pronounced depolarization effect (ΔE) is observed at low hypophosphite concentrations ($1\,g\,l^{-1}$) and current densities up to $6\,A\,dm^{-2}$. Within the other concentration range (5–$15\,g\,l^{-1}$) the polarization curves are confined to the region contained by the broken curves (see Fig. 2). At higher current densities ($6\,A\,dm^{-2}$) and $1\,g\,l^{-1}$ hypophosphite, the polarization curves remain within the same area.

In order to clarify the effect exerted by hypophosphite upon the depolarizing effect, Fig. 3 shows the changes of ΔE as a function of hypophosphite concentration at three of the most characteristic current densities. It is noted that at low concentrations of hypophosphite, as current density increases, ΔE decreases abruptly. This effect is most pronounced within the range 4–$7\,A\,dm^{-2}$. According to the complete factor experiment data, higher current densities give lower phosphorus content in the alloy. But if we consider the change of ΔE as a function of hypophosphite concentration, it may be expected that at low current densities and low $NaH_2PO_2 \cdot H_2O$ content in the electrolyte (high ΔE), the amount of phosphorus in the alloy will increase, while at high current densities (7–$9\,A\,dm^{-2}$) the phosphorus content should remain constant as hypophosphite concentration is changed within the range 1–$7\,g\,l^{-1}$ (constant ΔE). Our experiments show that in coatings deposited at $1\,g\,l^{-1}$ hypophosphite and current density $7\,A\,dm^{-2}$ ($\Delta E \approx 330\,mV$), the amount of incorporated phosphorus is

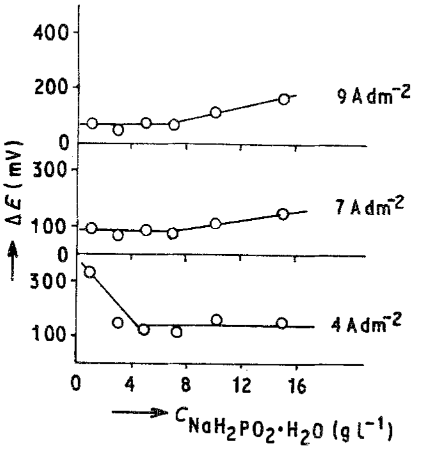

Fig. 3. Depolarization effect ΔE vs $NaH_2PO_2 \cdot H_2O$ concentration in the electrolyte, traced at current densities 4, 7 and $9\,A\,dm^{-2}$. Basic electrolyte and deposition conditions as in Fig. 2.

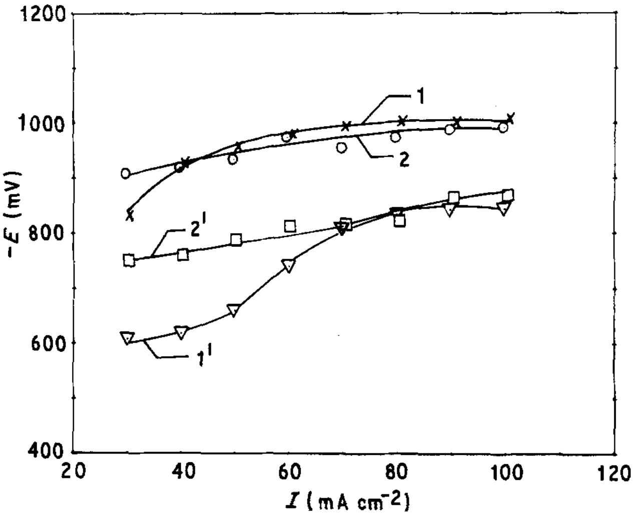

Fig. 4. Polarization curves traced during the deposition of iron and iron–phosphorus alloy. Curves 1 and 2 – in the absence of hypophosphite; 1', 2' – 7 g l^{-1} hypophosphite; 1, 1' – 5 g l^{-1} glycine; 2, 2' – 10 g l^{-1} glycine. Basic electrolyte and deposition conditions as in Fig. 2.

7 wt% and the coating is crystalline, while at 7 g l^{-1} hypophosphite (ΔE = 80 mV) the amount is 11 wt% and the alloy is amorphous (see Table 2).

Within the range 3–8 g l^{-1} hypophosphite, a decrease of the depolarization effect is generally observed as current density increases, without alterations of the ΔE values when hypophosphite concentration is changed. The constant ΔE value at the given current density suggests a constant phosphorus content in the alloy. The identical P content data in Table 2, determined within this concentration range, confirm this suggestion. The stable deposition of amorphous alloy coatings is possible just within this concentration range. At high hypophosphite content (15 g l^{-1}) no decrease of ΔE is observed as current density increases, which is contradictory to data derived by the complete factor experiment.

The depolarization effect of phosphorus is probably related to the incorporation mechanism by which it is included in the cathodic coating. This mechanism has been investigated by Vachidov [12] in the case of amorphous nickel–phosphorus alloys.

We have no grounds to presume that this mechanism is not also valid in our case. It is suggested that in this case, in addition to the alloy formation process, another phenomenon is present, which may be related to adsorption and the mechanism by which phosphorus is separated from the hypophosphite ion.

Polarization curves were traced at different glycine (Fig. 4) and ferrous sulphate concentrations (Fig. 5) in the solution. It may be noted from Fig. 4 that the polarization curves in the absence of hypophosphite, and at two different glycine concentrations, are similar and suggest that glycine does not affect the electrodeposition of pure iron.

The polarization curves in the presence of hypophosphite at various glycine contents differ substantially at low current densities. The depolarization effect at low glycine concentrations is more pronounced, which means that as glycine content increases, the amount of phosphorus in the alloy decrease. This result is confirmed by the complete factor analysis, which states that this relationship is improbable, since the effect of glycine becomes noticeable at low cathodic current densities only. When the latter surpass 7 A dm^{-2}, ΔE remains identical at different glycine concentrations, i.e. it should exert no effect upon the phosphorus content in the alloy coating.

Figure 5 (a and b) shows the polarization curves traced at different ferrous sulphate content in the electrolyte. When the amount of hypophosphite is high (10 g l^{-1}), ΔE is not affected by cathodic current density at both ferrous sulphate concentrations 150 and 280 g l^{-1}, but its value is higher at low content of $FeSO_4 \cdot 7H_2O$. This shows that at lower ferrous sulphate concentrations, an amorphous alloy can also be deposited at lower hypophosphite concentrations. When hypophosphite and ferrous sulphate concentrations are respectively 1 and 280 g l^{-1}, the depolarization effect is more pronounced and clear-cut within a broader current density range (Fig. 5b) as compared

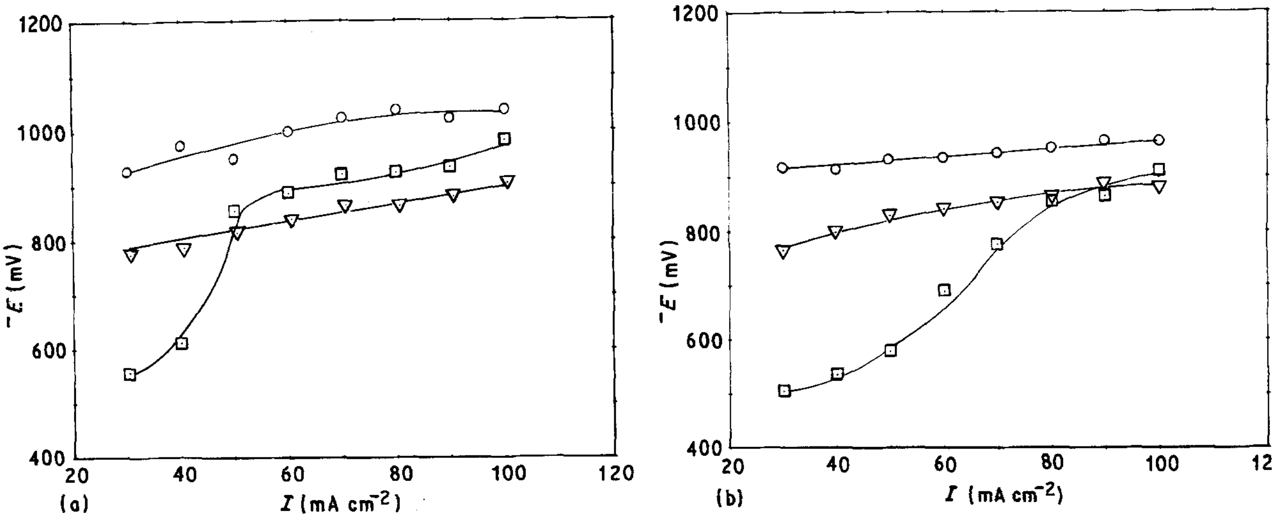

Fig. 5. Polarization curves traced during the deposition of iron and iron–phosphorus alloys from: (a) electrolyte containing (g l^{-1}): $FeSO_4 \cdot 7H_2O$, 150; $Na_2SO_4 \cdot 10H_2O$, 213; glycine, 8.5; oxalic acid, 0.5; hypophosphite: ○, 0; □, 1; △, 10. Deposition conditions 40° C at pH = 2; (b) electrolyte containing $FeSO_4 \cdot 7H_2O$, 280; glycine, 8.5; oxalic acid, 0.5; hypophosphite: ○, 0; □, 1; △, 10. Deposition conditions 40° C at pH = 2.

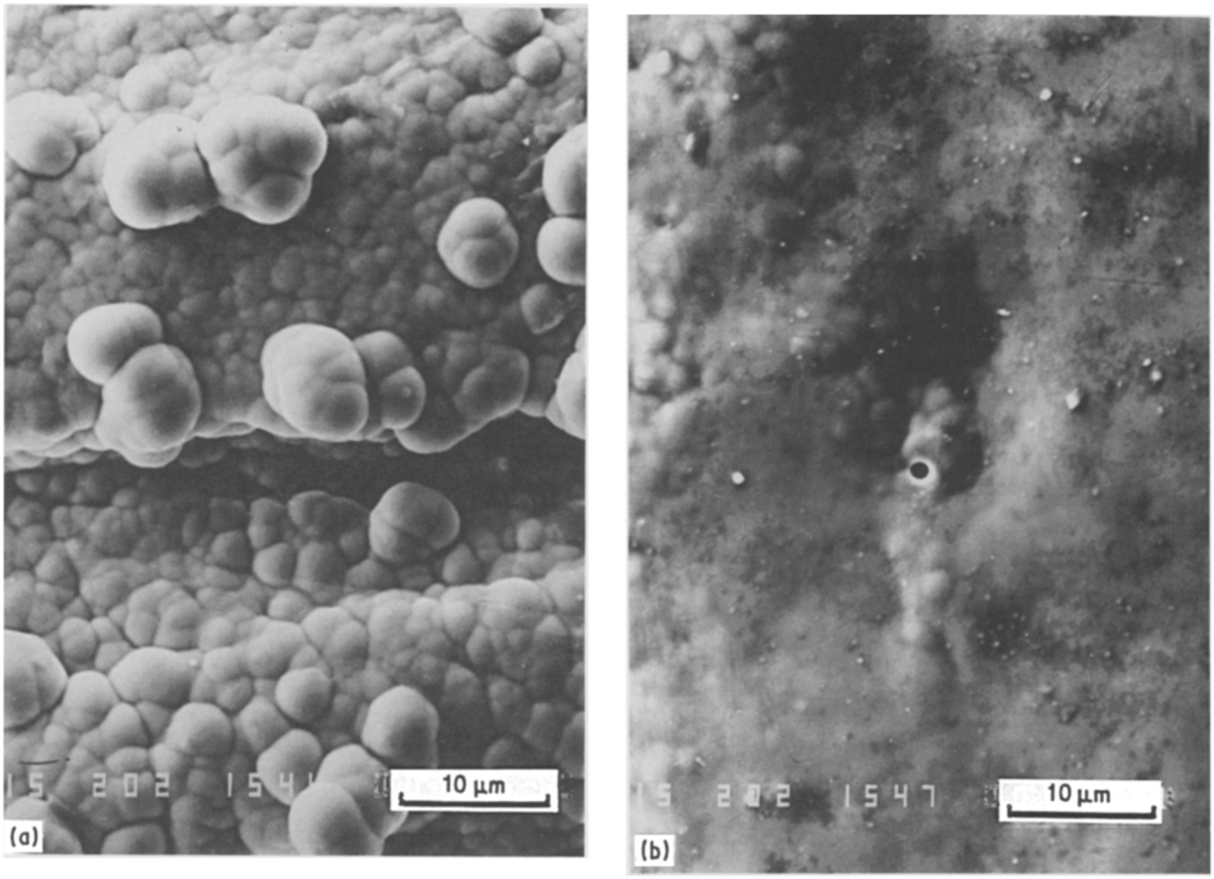

Fig. 6. Scanning electron micrographs of amorphous alloys Fe–P. (a) Fe, 86 wt%; P, 14 wt%; (b) Fe, 86 wt%; P, 13 wt%; Cu, 0.7 wt%.

to ΔE in electrolytes containing the same amount of hypophosphite, but only $150\,\mathrm{g\,l^{-1}}$ ferrous sulphate (Fig. 5a). Thus low concentrations of $FeSO_4 \cdot 7H_2O$ are recommended for the electrodeposition of amorphous iron–phosphorus alloys.

We already have mentioned that literature data report the brightening effect of Cu^{2+} during the electrodeposition of iron–phosphorus alloys. Under our plating conditions, Cu^{2+} also exerts a brightening effect when added to the optimized electrolyte formulation and, moreover, at concentrations of copper sulphate less than those mentioned in the literature [3] – 0.2 instead of $1\,\mathrm{g\,l^{-1}}$. In some cases Mn^{2+}, introduced into the electrolyte as manganese sulphate ($3\,\mathrm{g\,l^{-1}}$), exerted an effect similar to that of copper ions. It turned out that a combination of Cu^{2+} and Mn^{2+}, simultaneously present in the electrolyte, display the maximum brightening effect. The atomic absorption analysis provided evidence that when the electrolyte contains $0.2\,\mathrm{g\,l^{-1}}$ copper sulphate, the coating includes 0.7 wt% copper, while no manganese is detected. The electrodeposited coatings remain amorphous. The electron micrographs of the surface clearly show the smoothing effect of copper and manganese ions (Fig. 6).

4. Conclusions

(1) Optimized conditions have been determined for the preparation of amorphous Fe–P coatings by plating from an electrolyte containing ferrous sulphate, sodium hypophosphite, glycine and oxalic acid. It has been established that amorphous alloys are deposited from this electrolyte at hypophosphite content higher than $3\,\mathrm{g\,l^{-1}}$, pH less than 2.2 and cathodic current density up to $10\,\mathrm{A\,dm^{-2}}$. At pH less than 1.6 current yield is very low. The advantage of the electrolyte developed is that it offers the possibility of depositing amorphous alloys at higher pH values and less hypophosphite in the electrolyte. Under these conditions the electrolyte is stable with respect to pH and alloy composition, no precipitation occurs and the coatings are uniform, smooth and light-coloured.

(2) The addition of hypophosphite to the electrolyte exerts a depolarizing effect on the pure iron deposition process, most pronounced at low hypophosphite concentrations and low current densities.

(3) The complete factor experiment provides the following information: (a) The phosphorus content in the coating is affected most strongly by the pH of the electrolyte. Increase in pH, current density and glycine content in the electrolyte leads to a decrease of phosphorus in the alloy. (b) An increase in current density and a decrease in the acidity of the electrolyte improve the current yield, while high glycine content exerts a reverse effect.

(4) It has been established that a brightening effect during the electrodeposition of amorphous iron–phosphorus coatings from the developed electrolyte can be achieved by the addition of small quantities of Cu^{2+} and Mn^{2+}.

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