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Anodic behaviour of amorphous electroplated alloy coatings

M. KJUCHUKOVA, G. RAICHEVSKI, S. VITKOVA

Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1040, Bulgaria

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The anodic behaviour of electrodeposited amorphous Fe–Ni–P alloy coatings with different Ni : Fe ratios has been studied. It is established that the content of P on the surface of the coatings after their dissolution in acidic medium increases considerably. The change in composition and morphology of the alloys along the depth of the cracks when different potentials are applied to the samples immersed in 0.5 M H_2SO_4 is traced. The presence of a peculiar topography of the surface layer emerging after anodic dissolution is shown.

1. Introduction

Amorphous metals and alloys are very promising new materials, due to their unique physico-chemical and mechanical properties. It is well known that the corrosion resistance of amorphous metal coatings depends to a considerable extent on their composition and microstructure [1, 2]. The selection of the composition of amorphous alloys offers the possibility of controlling the corrosion resistance. Therefore, it is important to investigate the effect of the composition of certain amorphous alloys upon their anodic behaviour. In order to explain the results obtained, it is necessary to trace the change in the surface composition of the coatings following anodic treatment in a convenient corrosion medium, used as a model.

Similar investigations carried out with metallurgically prepared amorphous alloys have been reported in the literature. Kawashima, Asami and Hashimoto [3] have established that amorphous Ni–18P alloy samples, when immersed in 1 M HCL or 0.5 M H_2SO_4 solutions, form a surface film of nickel phosphate, while in the case of crystalline nickel a passive film of hydrated nickel oxi-hydroxide is formed. The authors presume, that this is due to the formation of nickel phosphate, which hinders the build-up of a passive nickel hydroxide film.

By applying accurate X-ray photoelectron spectroscopy, Diegle *et al.* [4–6] have established in high P^+ concentration and elementary phosphorus in the surface layer of amorphous Ni-20P coatings following polarization in 0.2 M HCL or 0.1 M H_2SO_4, but no traces of Ni^{2+} were observed. The authors considered that, in this case, passivation is a result of the adsorption of hydrophosphate ions. Habasaki *et al.* [7] have provided evidence that this phenomenon is a result of the higher value of the nickel dissolution rate constant as compared with that of phosphorus.

The enrichment of the surface with phosphorus has also been established with Fe–40Ni–14P–6B samples [8, 9]. However, the anodic behaviour of electrodeposited coatings has not been adequately considered.

Ratzker and Pratt [10] have established that nickel phosphate is formed on the surface of electroplated Ni–P amorphous alloys, when anodically treated in a neutral Hank solution. This is the result of a selective dissolution of nickel and enrichment of the surface with phosphorus. It is suggested, that phosphate is not formed as a result of the oxidized bulk phase of Ni_3P. Investigations of the anodic behaviour of electrodeposited amorphous Ni–P and Fe–P alloys in borate solutions [11] have established that phosphorus does not exist in the passive film.

This study is aimed at the investigation of the anodic behaviour of amorphous electrodeposited Fe–Ni–P alloys containing various Ni–Fe ratios.

2. Experimental details

The amorphous electrodeposited alloys were obtained in a thermoregulated electrolytic 500 cm^2 cell with recirculation stirring. The coatings were about 20 μm thick, deposited on to copper substrates with area 1 cm^2. The thickness was estimated by weighing the samples. The appearance of the coatings was smooth, light-coloured and semibright. The amorphous state was confirmed with the aid of a Philips X-ray diffractometer, using CuK_α radiation at a convenient range of incident angles.

The electrolyte composition and plating conditions [12] of the Ni–18P alloy were as follows (in $g\,dm^{-3}$): $NiSO_4 \cdot 7H_2O$ – 75, $NiCL_2 \cdot 6H_2O$ – 75, Na-citrate – 20, $NaH_2PO_2 \cdot H_2O$ – 10, saccarin – 4, H_3PO_4 – 16 $ml\,dm^{-3}$ at pH 1.4, $T = 60°C$ and c.d. $= 7\,A\,dm^{-2}$.

The Fe–14P alloy was deposited from a rather simple electrolyte containing $FeSO_4$, glycine and oxalic acid [13].

The three-component amorphous coatings were deposited in the basic electrolyte to which different amounts of $FeSO_4$ were added. The composition of the various electrolytes (in $g\,dm^{-3}$) was as follows: Basic electrolyte (BE) $g\,dm^{-3}$: $NiSO_4 \cdot 7H_2O$ – 45, $NiCL_2 \cdot 6H_2O$ – 45, Na-citrate – 20, glycine – 10, $NaH_2PO_2 \cdot H_2O$ – 10, saccarin – 2, pH 2, $t = 60°C$,

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Table 1.

Electrolyte	*Alloy composition (at %)*		
	Fe	*Ni*	*P*
I	1	82	17
II	4	80	16
III	22	64	14
IV	50	32	18

c.d. = $7\,A\,dm^{-2}$.

Electrolyte I: BE + $5\,g\,dm^{-3}$ $FeSO_4 \cdot 7H_2O$

Electrolyte II: BE + $8\,g\,dm^{-3}$ $FeSO_4 \cdot 7H_2O$

Electrolyte III: BE + $30\,g\,dm^{-3}$ $FeSO_4 \cdot 7H_2O$

Electrolyte IV: BE + $100\,g\,dm^{-3}$ $FeSO_4 \cdot 7H_2O$

The surface morphology and the chemical composition of the samples were determined using a Jeol microprobe X-ray analyser.

The composition of the three-component Fe-Ni alloy coatings is presented in Table 1.

All samples were treated in 0.5 M H_2SO_4 at room temperature. The potentials were measured against a saturated sulphate electrode (SSE). Potentiodynamic anodic polarization curves were traced for all compositions and automatically registered with a chart recorder at potential scanning rate $1\,mV\,s^{-1}$. The coatings were sufficiently thick, as evidenced by the microprobe analysis, which gave no traces of copper.

3. Results and discussion

The potentiodynamic polarization curves of different amorphous coatings in 0.5 M H_2SO_4 are shown in Fig. 1. The anodic behaviour of all Fe-Ni-P containing coatings is considerably different as compared with that of the amorphous Ni-18P deposit. (Fig. 1, curve 1). The tendency toward passivation of the double Ni-P alloy has been observed by several authors [3-9]. In the medium investigated here, Ni-18P is self-passivated (no active region of anodic dissolution is observed).

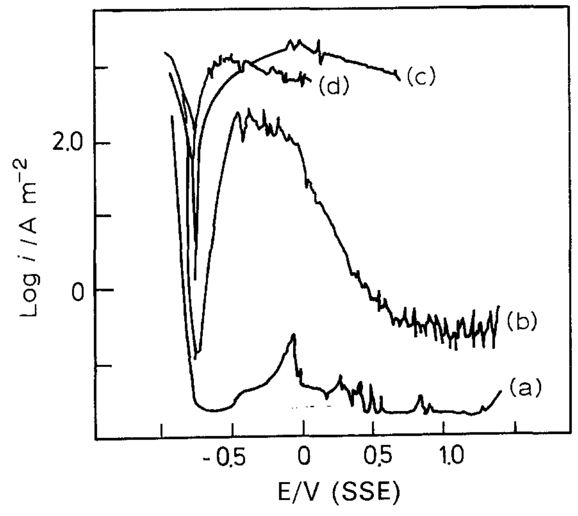

Fig. 1. Potentiodynamic polarization curves of amorphous alloy coatings in 0.5 M H_2SO_4 E/V(SSE): (a) Ni-18P, (b) Ni-1Fe-17P, (c) Ni-50Fe-18P and (d) Fe-14P.

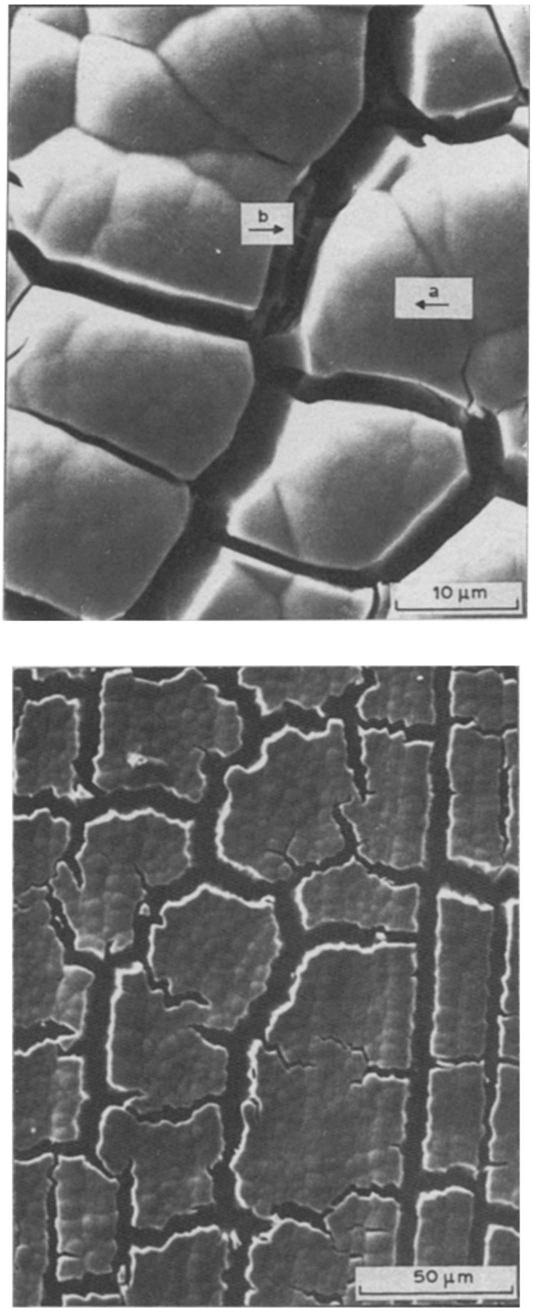

Fig. 2. SEM micrographs of the Ni-4Fe-16P amorphous alloy surface, treated in 0.5 M H_2SO_4: (a) at E = −0.74 V for 3 min at different sites (Table 2, sample 3.1a and b); (b) at E = −0.47 V for 2 min (Table 2, sample 3.2).

The Ni-50Fe-18P and Fe-14P alloys are characterized as being slightly prone to passivation (in fact a real passive region is not observed) and i_d > $0.1\,A\,cm^{-2}$ (curves 3 and 4). A similar behaviour is displayed by alloys Ni-4Fe-16P and Ni-22Fe-14P (absent in Fig. 1). The only exception is the alloy with a very small iron content (1 at. %), curve 2, which is very prone to passivation after reaching E = 0.5 V. In addition, the self-dissolution currents ($i_s = 10^{-5}\,A\,cm^{-2}$) and critical current density $i_{cr} = 4 \times 10^{-2}\,A\,cm^{-2}$ at E_a = 0.0 V are smaller by an order of magnitude as compared with the rest of the alloys. It may be presumed that on the surface of alloys containing Fe less than

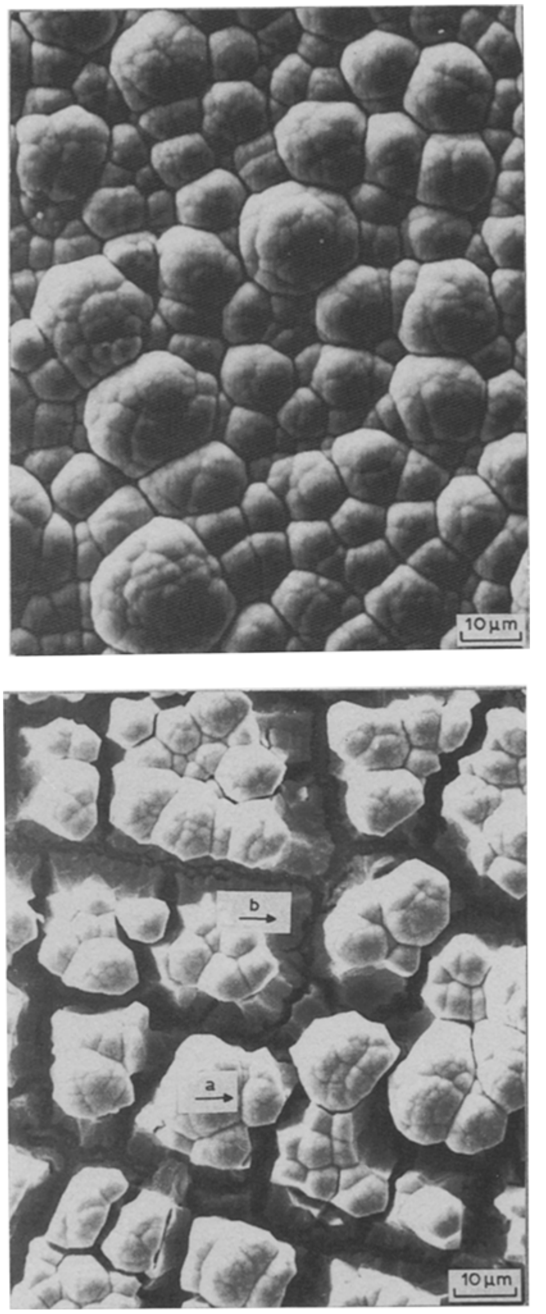

Fig. 3. SEM micrographs of the Ni–50Fe–18P amorphous alloy: (a) untreated sample; (b) a and b, treated in 0.5 M H_2SO_4 at $E = -0.70$ V for 3 min at different sites.

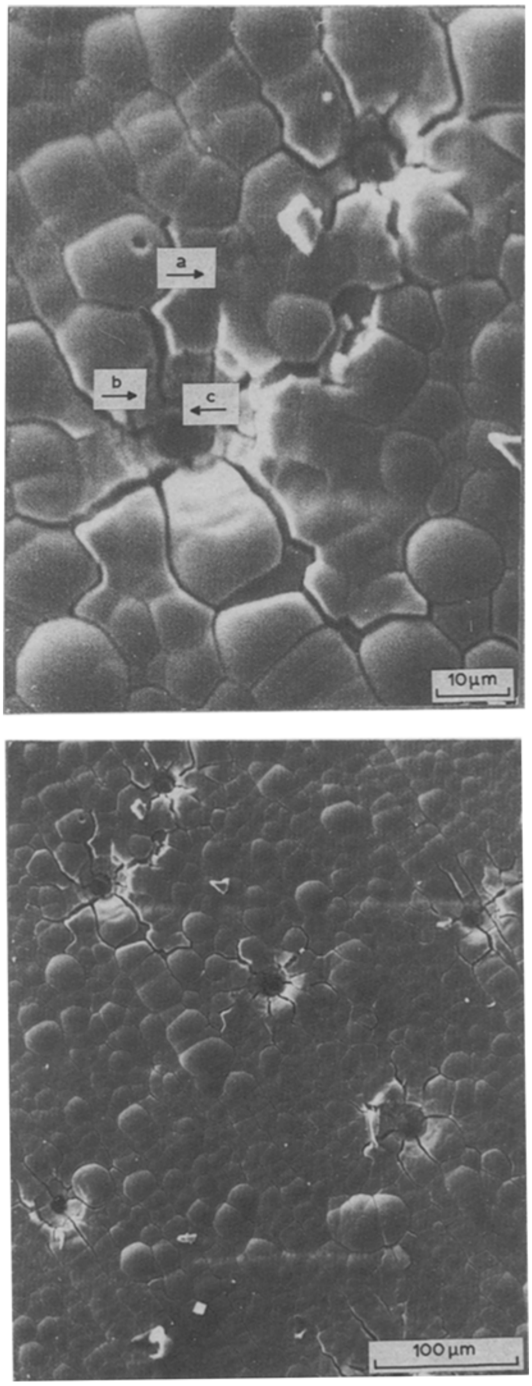

Fig. 4. SEM micrographs of the Fe–14P amorphous alloy treated in 0.5 M H_2SO_4 at $E = -0.60$ V for 2 min at different sites.

4% a partially screening barrier layer is formed, the diffusion through which is limited by the dissolution rate ($i_d = 0.16\,\mathrm{A\,cm^{-2}}$). In the case of Ni–1Fe–17P coatings, at $E = 0$ V, this layer is transformed into a typical oxide passivation film, resulting in a substantial broadening of the passive zone 0.9 V.

The morphology of all studied samples is shown in Figs 2–4. It can be seen that the dissolution of all Fe–Ni alloys proceeds with the formation of a network of cracks or craters with peculiar 'steps' inside. Probably the coatings are deposited with high internal stresses. It was interesting to establish how the composition and morphology of the alloys change along the depth of the cracks and craters when in different corrosion and electrochemical states.

Table 2 shows the change in the chemical composition of the alloy samples after remaining in different electrochemical states. The corrosion potentials, determined from the intercept of the anodic and cathodic curves, does not coincide in all cases with the steady-state potentials, without anodic polarization. The other potentials, presented in Table 2, are introduced by an external source of polarization. It may be seen that the amount of phosphorus on the surface of the sample coatings (with the exception of Ni–18P) after dissolution is considerably higher as compared with the untreated surface. This enrichment with P is on account of nickel depletion (samples 2.1, 2.2, 3.1a, 3.2a, 4.1a and 4.2) or iron depletion (samples 5.1a, 5.2,

Table 2.

No.	*State*	*E*/*V*(SSE)	*Duration of treatment*/*min*	*Log i*/*A m*$^{-2}$	*Chemical composition*/*at %*		
					Fe	*Ni*	*P*
1.	Untreated				–	82	18
1.1	Treated	-0.65	30	-1.7	–	81	19
1.2	Treated	$+1.10$	30	-1.4	–	81	19
2.	Untreated				1	82	17
2.1	Treated	-0.76	20	-1.0	2	71	27
2.2	Treated	$+1.05$	10	-0.6	3	70	27
3.	Untreated				4	80	16
3.1[a]	Treated	-0.74	3	$+2.0$	5	73	22
3.1[b]	Treated	-0.74	3	$+2.0$	8	91	1
3.2[a]	Treated	-0.47	2	$+3.2$	5	68	27
3.2[b]	Treated	-0.47	2	$+3.2$	8	91	1
4.	Untreated				22	64	14
4.1[a]	Treated	$-0,60$	5	$+2.3$	23	55	22
4.1[b]	Treated	-0.60	5	$+2.3$	39	54	7
4.2	Treated	-0.44	2	$+3.4$	23	47	30
5.	Untreated				50	32	18
5.1[a]	Treated	-0.70	3	$+1.5$	34	45	21
5.1[b]	Treated	-0.70	3	$+1.5$	66	33	1
5.2	Treated	-0.46	3	$+3.0$	48	24	28
6.	Untreated				86	–	14
6.1[a]	Treated	-0.72	2	$+2.2$	75	–	25
6.1[b]	Treated	-0.72	2	$+2.2$	97	–	3
6.2[a]	Treated	-0.60	2	$+3.0$	68	–	32
6.2[b]	Treated	-0.60	2	$+3.0$	87	–	13
6.2[c]	Treated	-0.60	2	$+3.0$	92	–	8

The indices a, b and c mark treated samples which have been subjected to microprobe SEM analyses on the surface (a) and in the cracks at various depths (b and c).

6.1a, 6.2a). As already mentioned, a similar selective dissolution of nickel, but followed by the formation of an elementary phosphorus layer, has been established by Diegle *et al.* [4–6], but in the case of metallurgically manufactured Ni–20P alloys.

When the dissolution is carried out in the vicinity of the corrosion potential, the increase in phosphorus content is typically about 40–50% (Table 2, samples 3.1a, 4.1a, 5.1a). When high anodic polarization is applied ($E = -0.44$ V for sample 4.2 and $E = -0.46$ V for sample 5.2) corresponding to the maximum dissolution rate in the active state, the increase in phosphorus content reaches 100% and 55%, respectively.

The Fe–14P alloy displayed an increase in P content up to 80%. The change in the ratio between the alloy components are not observed with the Ni–18P alloy, since it is self-passivated.

It can be generally concluded that the enrichment of the surface of P-containing alloy coatings during anodic treatment proceeds most intensively at high dissolution rates. This may be a result of the bonding of P with Ni separately.

The corrosion process appears to be enhanced in the cracks. It is surprising that at these sites an abrupt decrease of phosphorus content is observed (up to one order of magnitude) as compared with the initial amount in the surface layer (samples with indices b and c). Simultaneously with the depletion of phosphorus a considerable increase in Fe content is observed at these sites. This increase is relatively less pronounced in samples containing higher percentages of Fe (alloys Ni–50Fe–18P and Fe–14P).

Two possible explanations are possible:

(i) Within these regions of very active dissolution, intermetallic Ni$_x$Fe$_y$-type compounds are formed, while P remains in a free unbonded state is, therefore, readily removed.

(ii) The non-uniform topography of dissolution may be the result of the unequipotential surface of the samples. Due to a delayed removal of the dissolution products from the cracks to the bulk solution, it is possible that an additional concentration polarization is initiated at these sites, shifting the potential to more positive values, when phosphides of higher order are formed [14], which are more readily dissolved in this medium.

4. Conclusions

1. Ni–18P amorphous alloy coatings are self-passivated in 0.5 M H$_2$SO$_4$ solutions, while Ni–59Fe–18P and Fe–14P show restricted tendency toward passivation. The only exceptions from this rule are alloys with a very small iron content (1 at %), which are quite prone to passivation.
2. A substantial increase in phosphorus content has been established on the surface of samples containing iron, when they are anodically treated. This effect is

most clear-cut with high dissolution rates and may be a result of the bonding of P with Ni and Fe in the form of phosphides or phosphates.

3. Within the network of cracks in the treated samples, the amount of phosphorus decreases considerably as compared with the concentration on the surface. Simultaneously, a considerable increase in iron content at these sites is observed. This experimental fact may be the result of the formation of intermetallic Ni_xFe_y-type compounds or the appearance of higher order phosphides when more positive potentials are reached.

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