STUDY OF SALT FORMATION ON AN ACTIVE IRON ELECTRODE IN PHOSPHATE SOLUTIONS

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Prior to an explanation of the patterns of active iron electrode solution in phosphate solutions at pH > 4, the assumption was expressed in [1] that the electrode surface was partially covered with iron phosphate in the process of solution. It was assumed that the mechanism of coating formation was spatial (due to supersaturation of the solution in the vicinity of the electrode) and consisted of two layers: a thin protective layer next to the metal and an outer, thicker layer without protective properties. According to [1], the deposit must form initially on particular sectors of the surface only, and the probability of deposition must decrease as the rate of solution mixing increases, ultimately to zero (when the critical velocity of disk electrode rotation ω_{cr} = 2700 rpm is reached). Microscopic observation in the process of polarization proved not sensitive enough to reveal the patterns of growth of the protective salt layer. Formation of the salt layer becomes perceptible after the change in anode current (presumably caused by formation of the thin deposit layer) is completely over.

In the present work, the "Cameca" MS-46 x-ray microanalyzer was used to study salt deposits on iron test piece surfaces after polarization for a specified period in 0.165 M phosphate solution (pH 5.5) at constant potentials (−0.40 and −0.42 V normal hydrogen equivalent). In each case the test piece was washed twice in distilled water and dried in air at room temperature after polarization. The distribution of phosphorus and oxygen over the surface was then determined by measuring the absolute intensity of their characteristic radiations in multiple linear mechanical scanning.

Phosphorus and oxygen can be detected after a minute of polarization in particular surface sectors of test pieces which have dissolved without solution mixing; the ratio of radiation intensities from these elements at each point (with deduction of the background corresponding to the content of these elements in the initial iron test piece) remains approximately constant (Fig. 1). An increase in polarization time to 3 min is accompanied by a substantial increase in the number of such sectors (Fig. 2,* curve 1). Even more prolonged polarization leads to a further increase in phosphorus and oxygen radiation intensity, and both these elements are found at any point on the surface (with an accuracy up to 1 μ, the working diameter of the electronic microprobe).

Phosphorus and oxygen are detected only after more prolonged polarization on test pieces which have dissolved during mixing (rotating disk). Thus the phosphorus and oxygen radiation intensities did not exceed the background values after polarization at ω = 330 rpm for 3 min (Fig. 2, curve 3). These elements could be detected only after 5 min of polarization (curve 2). In this case, however, an increase in solution time (e.g., to 15 min) is accompanied by an increase in the number of sites on the surface where phosphorus and oxygen can be detected (curve 4).

An increase in the speed of disk rotation is invariably accompanied by an increase in the time of polarization required for phosphorus and oxygen surface analysis to give a positive result. At ω = 2780 rpm, phosphorus and oxygen could not be detected on the surface at any of the t durations studied (see, e.g., curve 5 in Fig. 2 for t = 15 min).

* Only the phosphorus distribution curves are shown in Fig. 2. The ratio of phosphorus to oxygen at all points on the surface is constant in this case also.

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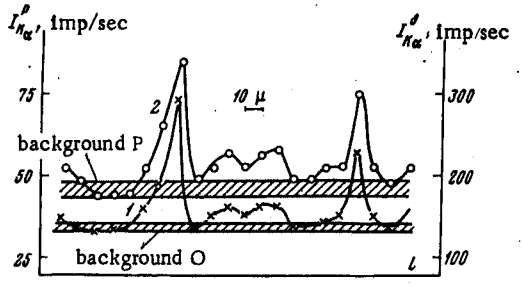

Fig. 1

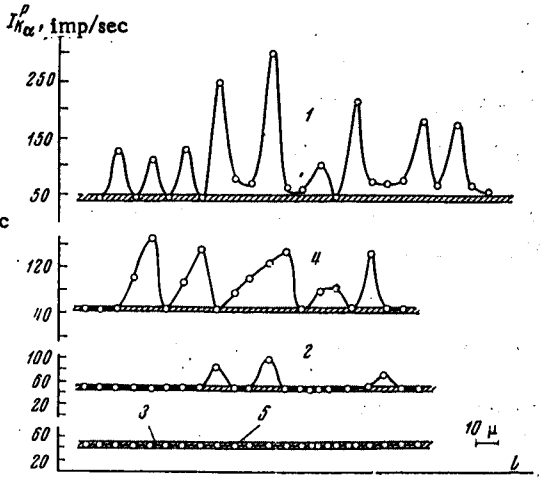

Fig. 2

Fig. 1. Distribution of characteristic x-ray intensity (10 keV, 250 nA) for oxygen (1) and phosphorus (2) over an iron electrode surface after polarization in 0.165 M phosphate solution at pH 5.5 and a potential of −0.4 V for 1 min without mixing.

Fig. 2. Distribution of phosphorus radiation intensity over an iron electrode surface after polarization in 0.165 M phosphate solution at pH 5.5 and a −0.42 V potential: 1) $\omega = 0$, t = 3 min; 2) $\omega = 330$ rpm, t = 5 min; 3, 5) $\omega = 2780$ rpm, t = 15 min (×) and $\omega = 330$ rpm, t = 3 min (○); 4) $\omega = 330$ rpm, t = 15 min.

Thus, in accord with the ideas in [1], deposit formation does indeed begin only in particular surface sectors and an increase in the rate of solution mixing leads to a reduction in the probability of electrode coating with phosphate. The constant ratio of phosphorus to oxygen at any point on the surface shows that the deposit layer does indeed correspond to a phosphate salt in composition and not to an iron hydroxide, the possible formation of which cannot be excluded a priori.

These conclusions should be regarded only as a strong argument in support of the spatial mechanism of phosphate formation because, as was pointed out above, according to [1] the phosphate deposits consist of two layers* but the method used by us does not distinguish these two layers. However, the conclusions are admissible because of the high probability that sectors of the inner (thin) layer are centers of crystallization for the outer (thicker) layer. Having regard to this, and also to the fact that in a number of cases where there is a perceptible drop in current during the experiment, phosphate is not detected† by the x-ray microspectral method on the electrode, one may conclude that the thickness of the protective layer may be less than the limit of sensitivity of this method. Method sensitivity is not susceptible to precise quantitative calculation in the case under examination. The limits of sensitivity of x-ray microanalysis using an electronic probe (0.01-0.5 weight %) given in [2] can be used to evaluate it approximately. At a mean sensitivity of 0.05% in a volume of 1 $\mu^3 = 10^{-12}$ cm^3 (the approximate volume of the sample being analyzed) of weight $P = 10^{-12} d_1$ (g) ($d_1 = 7.8$ g/cm^3, the specific gravity of iron) the amount of phosphorus m determinable is

$$m = \frac{P0.05M_{FeHPO_4}}{100M_P} \approx 2 \cdot 10^{-14} \text{ g} \qquad (1)$$

(M is the molecular weight of phosphorus and iron phosphate).

If it is assumed that the sample being analyzed is approximately cylindrical, and that the dimensions of the coated sectors on the surface exceed the electron beam area (i.e., that the layer sectors being analyzed may be regarded as continuous), the minimum layer thickness l (cm) which can be determined by the method can be found from the relationship

$$m = d_2 \frac{\pi D^2}{4} l, \qquad (2)$$

* It should be remembered that the question is one of porous deposits, not solid deposits.

† This occurs, e.g., at $\omega = 330$ rpm. In unmixed solutions, phosphorus can be detected on the surface even in the initial stages of current drop.

where $d_2 \approx 4$ g/cm^3 is the specific gravity of phosphate and $D = 10^{-4}$ cm is the electron beam diameter. From (2) and taking account of (1) we find $l \approx 7 \cdot 10^{-7}$ cm, which corresponds to several monolayers with the maximum density of phosphate molecule packing. If allowance is made for the fact that the sensitivity of the method may be higher than 0.05% an even smaller value may be assumed for the upper limit of protective phosphate layer thickness.

LITERATURE CITED

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2. L. S. Birks, X-Ray Spectral Analysis Using an Electronic Probe [in Russian], Metallurgiya, Moscow (1966).