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Abstract

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POINTS OF ZERO CHARGE OF CERTAIN METALS AND ALLOYS

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In a number of works ([1,2]) the fruitfulness of the concepts of the points of zero charge of metals ([3]), as physicochemical constants characteristic of a given metal, was shown.

In the course of investigating the potentials of zero charge of metals ($\varphi_{\text{z.c.}}$), it was found that the value of $\varphi_{\text{z.c.}}$ of a given metal depends on a number of factors. Using the mercury-thallium system as an example, it was shown ([4]) that $\varphi_{\text{z.c.}}$ changes depending on the ratio of the components in the amalgam. In work ([5]) a list was given of the factors under whose influence $\varphi_{\text{z.c.}}$ of metals changes; among these factors are the composition and state of the metallic phase. In the present work an attempt was made to measure potentials of zero charge in order to obtain new data on the dependence of $\varphi_{\text{z.c.}}$ on the composition and state of metals.

As objects of investigation we chose single-crystal zinc (faces (0001) and (0101)) and iron-nickel alloys. The zinc electrodes were prepared from chemically pure zinc, redistilled four times in vacuum, by growing single crystals according to a slightly modified method of Polubin and Froiman ([6]). The total impurity content in the specimens did not exceed $10^{-4}\%$. The iron-nickel alloys were obtained by electrodeposition from solutions of chloride salts, repeatedly purified and recrystallized, using additionally refined iron and nickel anodes. The content of impurities of other metals in the alloys did not exceed $2 \cdot 10^{-4}\%$.

The electrolytes used had the following composition and properties: Σ Fe^{+2}, Ni^{+2} 100 g/l (as metal); citric acid 15 g/l; pH 4.0 ± 0.2; $t = 70°$; $D_k = 40$ a/dm^2.

Without dwelling in detail on the method of electrodeposition of iron-nickel alloys, in the present work we shall confine ourselves only to pointing out that, in order to obtain alloys of the compositions for which the data are given in Fig. 3, it was necessary to prepare baths with a definite content of components for each alloy separately. Measurement of the capacitance of the double layer on the indicated objects was carried out with alternating current by means of a combined bridge ([5]) (a slightly modified version of the Dolin and Ershler circuit

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

([7]). All measurements were made in 0.2 *N* Na_2SO_4 with the addition of sulfuric acid to pH 3.2. In the work all precautionary measures necessary when carrying out measurements of double-layer capacitance ([8,5]) were used.

Some results of the measurements are presented in Figs. 1, 2, and 3.

Figure 1 gives the capacitance-potential curves of a zinc electrode, from which it is seen that the potential of zero charge changes depending on the structure of the metal. For the face (0001) $\varphi_{\text{z.c.}} = -0.60$ V, and for the face (0101) $\varphi_{\text{z.c.}} = -0.68$ V. In the literature, for zinc the value $\varphi_{\text{z.c.}} = -0.63$ V is given, corresponding to a polycrystalline surface formed, according to the data obtained, both by microcrystals with faces (0001) and by faces (0101).

Apparently, depending on the packing density of the atoms in the crystal lattice of the metal, the work function of the electron from it also changes,

Fig. 1. Dependence of the double-layer capacitance of a single-crystal zinc electrode on the potential in a solution of 0.02 N Na_2SO_4 + H_2SO_4 (pH 3.2): 1 –face (0001); 2 –face (0101)

Fig. 2. Dependence of the double-layer capacitance on iron-nickel alloy electrodes on the potential in a solution of 0.02 N Na_2SO_4 + H_2SO_4 (pH 3.2): 1 – 5% Fe; 2 –25% Fe

and consequently also the φ_{pzc} of the metal. The lower packing density of zinc atoms in the (0101) face causes an easier electron emission (as compared with the (0001) face) and thereby shifts φ_{pzc} toward negative values.

When measuring the points of zero charge of amalgams and alloys, it must be borne in mind that a change in the surface concentration of one of the components for various reasons (anodic dissolution, high exchange currents) may lead to the obtaining of nonreproducible data. From this standpoint, the most reliable data are those obtained in measuring the points of zero charge of alloys of metals with small exchange currents, and for precisely this reason, in studying the points of zero charge we confined ourselves to alloys of iron with nickel, which have very small exchange currents.

Fig. 3

Figure 3: Fig. 3

Fig. 3. Dependence of the potential of zero charge of iron-nickel alloys on composition (at pH 3.2)

In Fig. 2 are shown (selectively) the capacitance-potential curves of iron-nickel alloys in dilute solutions, and in Fig. 3 —the dependence of the potential of zero charge of iron-nickel alloys on their composition.

Measurements of φ_{pzc} of pure metals, also obtained by electrodeposition, gave good agreement with the data available in the literature ([9,10]). In view of the fact that for such metals as iron and nickel a dependence of the metal's potential of zero charge on the amount of adsorbed (absorbed) hydrogen ([5]) (or on pH) is characteristic, all measurements were carried out under conditions of strictly constant pH and duration of preliminary cathodic polarization at $D_k = \text{const}$.

In the case presented by us (Fig. 3), a rather sharp change in φ_{pzc} is observed with an increase in the alloy content of the metal having the more negative value of φ_{pzc}, and already at 25% iron in the alloy φ_{pzc} becomes practically equal to the potential of zero charge of pure iron.

The monotonicity of the curve of the dependence of the potential of zero charge of an alloy on its composition is, in our view, evidence that the iron-nickel alloys obtained by electrodeposition are solid solutions; in the case of formation of any compounds of the type Fe_xNi_y, a sharp change in the electron work function and a nonmonotonic course of the dependence of $\varphi_{\text{p.z.c.}}$ would have to be observed (the composition of the alloy would be disrupted).

Thus, it may be considered that, in the absence of factors capable of disrupting the monotonic change in the potential of zero charge as a function of alloy composition, the potential of zero charge of the latter, even at relatively low concentrations of iron, is determined by the electron work function of iron—a metal possessing a more negative value of $\varphi_{\text{p.z.c.}}$.

The data presented in this work clearly illustrate the necessity, when measuring potentials of zero charge, of taking into account the state and composition of the metallic phase.

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Note: Figure translations are in progress. See original paper for figures.