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Abstract

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ON THE CALCULATION OF DEPOLARIZATION AND SUPERPOLARIZATION EFFECTS IN THE FORMATION OF A GALVANIC ALLOY

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It is known that the discharge of ions of two or several metals into an alloy is accompanied by the phenomenon of depolarization or superpolarization (^{1}). The various theories explaining this phenomenon are qualitative in character. Only N. M. Polukarov and K. M. Gorbunova (^{2}) attempted to calculate the depolarization effect from the change in the partial molar free energy of the metal upon alloy formation. There is no doubt, however, that for a number of cases the thermodynamic approach to calculating alloy-formation effects proves insufficient.

We attempted to calculate the effects of depolarization and superpolarization in the formation of a binary alloy for those cases in which both the deposition of the components into the alloy and their deposition in pure form are described by the equations of the theory of slow ion discharge (^{3}). For simplicity, we shall everywhere take $\psi_1 = 0$. The calculation is based on the method set forth in the work of V. L. Kheifets, A. L. Rotinyan, O. P. Kaltanova, and P. G. Levenfish (^{4}).

Let us write the equation for the deposition of a pure metal in the following form:

$$J_{\mathrm{m}} = K_{\mathrm{m}} a_{\mathrm{m}} e^{-U_0/RT} e^{\alpha_{\mathrm{m}} z F \varphi_{\mathrm{m}}^{\mathrm{nzn}}/RT} e^{-\alpha_{\mathrm{m}} z F \varphi_{\mathrm{m}}/RT}. \tag{1}$$

Here J_{m} is the current density; a_{m} is the activity of metal ions in the electrolyte; U_0 is the activation energy at the potential of zero surface charge (φ^{nzn}); φ_{m} is the cathode potential; z is the valence; R is the gas constant; T is the absolute temperature; K_{m} is the rate constant; α_{m} is the transfer constant.

If, however, the metal is deposited not in pure form but into an alloy, then the alloy-formation effect, expressed by a lowering of the potential energy by the amount $\Delta\Phi$, will lead to a lowering of the activation energy by the amount

$\alpha_\mathrm{c}\Delta\Phi$. During alloy formation the potential of zero surface charge may also change. As for the constant K, in the further derivation we shall, as a first approximation, take it to be independent of the alloy composition.

Then the rate equation for discharge when the metal is deposited into an alloy will take the form

$$J_\mathrm{c} = K_\mathrm{m} a_\mathrm{c} e^{-U_0/RT} e^{-\alpha_\mathrm{c}\Delta\Phi/RT} e^{\alpha_\mathrm{c} zF\varphi_\mathrm{c}^\mathrm{nzn}/RT} e^{-\alpha_\mathrm{c} zF\varphi_\mathrm{c}/RT}, \tag{2}$$

where a_c is the activity of the ions of the depositing metal in the solution for alloy deposition. (Quantities for the deposition of the given metal into an alloy are denoted by the subscript c, and those for deposition of the same metal in pure form by the subscript m.)

From equations (1) and (2), after taking logarithms and solving for the potential of metal deposition into the alloy φ_c, one directly obtains:

$$\varphi_\mathrm{c} = \frac{\alpha_\mathrm{m}}{\alpha_\mathrm{c}}\varphi_\mathrm{m} - \frac{\Delta\Phi}{zF} + \varphi_\mathrm{c}^\mathrm{nzn} - \frac{\alpha_\mathrm{m}}{\alpha_\mathrm{c}}\varphi_\mathrm{m}^\mathrm{nzn} - \frac{RT}{\alpha_\mathrm{c} zF}\ln\frac{a_\mathrm{m}}{a_\mathrm{c}} + \frac{RT}{\alpha_\mathrm{c} zF}\ln\frac{J_\mathrm{m}}{J_\mathrm{c}}. \tag{3}$$

If we compare deposition potentials at equal current densities, the last term of equation (3) becomes zero.

As is easily seen, equation (3) takes into account the change of both thermodynamic and kinetic factors during alloy formation.

We verified this equation using the example of the formation of a Ni—Fe alloy from sulfate solutions. Electrolytically obtained alloys of this system constitute a continuous series of solid solutions ([5]). Consequently, in this case

$$\Delta\Phi = RT\ln\gamma m, \tag{4}$$

where m is the atomic fraction of the component in the alloy and γ is the activity coefficient. According to ([5,6]), the system we studied is close to ideal; therefore in the calculations we take $\gamma = 1$. The zero-charge potentials for pure iron and nickel were taken from work ([7]), and for iron-nickel galvanic alloys from ([8]).

Table 1

Compositions of the electrolytes used (30 g/l H_3BO_3 and 10 g/l NaCl were added to all electrolytes; pH 3)

Electrolyte No.	1	2	3	4	5	6
$FeSO_4$, mol/l	0.19	0.62	–	–	0.19	0.62
$NiSO_4$, mol/l	–	–	1.06	0.63	1.06	0.63

Polarization curves were obtained for the deposition of iron and nickel from electrolytes Nos. 1-4 (see Table 1), and partial polarization curves for the deposition of nickel and iron into an alloy from electrolytes Nos. 5 and 6. The polarization curves obtained, in semilogarithmic coordinates, are rectilinear in the investigated range of current densities (from 0.2 to 2 A/dm^2).

Table 2

Electrolyte No. for obtaining the alloy	Electrolyte No. for depositing the metal	Metal	T-ra, °C	m	$-\varphi$	$-\varphi$	$-a = -\varphi$ at $D_k = 1$ A/dm^2	α	α	$-\varphi$, measured	$-\varphi$, calculated
5	1	Fe	25	0.48	0.380	0.380	0.728	0.37	0.47	0.672	0.673
5	1	Fe	40	0.48	0.380	0.380	0.710	0.40	0.61	0.613	0.612
5	3	Ni	25	0.52	0.320	0.380	0.628	0.37	0.38	0.685	0.672
5	3	Ni	40	0.52	0.320	0.380	0.588	0.39	0.39	0.623	0.640
6	2	Fe	25	0.75	0.380	0.380	0.719	0.46	0.55	0.660	0.668
6	2	Fe	40	0.75	0.380	0.380	0.712	0.43	0.65	0.610	0.617
6	4	Ni	25	0.25	0.320	0.380	0.644	0.37	0.42	0.702	0.665
6	4	Ni	40	0.25	0.320	0.380	0.596	0.43	0.42	0.646	0.653

The values of the constants a (at $J = 1$ A/dm^2) and α are given in Table 2. The last column of the table gives the values of the potentials of metal deposition into the alloy calculated by formula (3), and the penultimate column gives the measured potentials of metal deposition into the alloy. All potentials are given at $J = 1$ A/dm^2. In the calculations we assumed that the activities and φ at 40° are equal to those at 25°. This should not introduce a substantial error into the calculations.

From a comparison of the calculated and measured potential values it is seen that equation (3) is, on the whole, satisfactorily justified.

The effects of depolarization or superpolarization during the deposition of metals into an alloy can be determined by comparing φ and φ , since $\Delta\varphi = \varphi - \varphi$.

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