Electrolytic Deposition of Nickel. A bent cathode used to determine internal stress in a deposit (via a transducer) was being nickel plated in a standard electrolyte. Almost simultaneously with the onset of visible deformation it began to emit signals similar to those shown in Fig. 1.

Thus, all the investigated metals in the usual as-received condition emit ultrasonic signals during trans- or intergranular cracking, pitting, cathodic hydrogen absorption or subsequent hydrogen evolution, and when electroplated. Here, the intensity of the ultrasonic field generated is sometimes so great that there arises an unavoidable question as to the possibility for the existence of a positive, inverse relation between these fields and the intensity of the processes. Such a relation may be based on mechanisms such as a resonant interaction and mutual excitation of irradiated oscillators, and an ultrasonic intensification of diffusion or migration of reaction components (inter- and transgranular and along narrow cracks or pitting canals).

All this fully confirms the necessity for a broad microacoustic investigation of corrosion and electrochemical systems for developing a method to externally diagnose various types of corrosion or corrosion/electrochemical weakening of materials, and to penetrate deeper into the mechanism of such phenomena.

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SELECTIVE IONIZATION OF THE NEGATIVE COMPONENT IN THE DISSOLUTION OF A BINARY ALLOY (TIN—ZINC)

A. P. Pchel'nikov, A. D. Sitnikov, and V. V. Losev

UDC 620.193.01

The selective dissolution of Zn from a Sn, Zn (0.1 at. %) alloy in a solution of 3 M NH_4Cl + 0.01 M HCl was studied by a method of combining electrochemical and radiochemical measurements. The use of a model of the process of selective dissolution of the negative component of a binary alloy, based on the concept of nonequilibrium diffusion of this component in the volume of the alloy, taking the continuous removal of the surface layers of the alloy as a result of their dissolution into account, permitted a quantitative description of the process of selective dissolution of Zn.

The dissolution of components of binary alloys may occur selectively or uniformly, depending on the conditions of electrolysis. Selective dissolution (SD) may be observed both in anodic polarization and corrosion and in cathodic polarization of the alloy. One of the possible mechanisms of SD is the mechanism of volume

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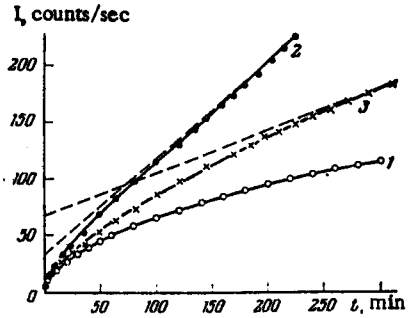

Fig. 1. Change in the radioactivity of a solution with time during cathodic polarization ($\Delta\varphi$ = 100 mV) (1) and during anodic polarization of a Sn, Zn (0.1 at. %) alloy at i (A/cm^2): 2) $1 \cdot 10^{-3}$; 3) $5 \cdot 10^{-4}$ [the points on curves 2 and 3 correspond to the experimental data; the curves were calculated according to Eq. (2)].

diffusion of the components in the alloy. A theoretical consideration of this mechanism [1] shows that the dissolution of the negative component should be limited by its nonequilibrium diffusion from the volume of the alloy to the surface, while the following relationship should be observed between the partial current of dissolution of the negative component i_i and the time t:

$$i_i = K/\sqrt{t}. \tag{1}$$

The correctness of Eq. (1) has been noted for Cu, Au (13-25 at. %) alloys [2], only for a period of several dozen seconds after the beginning of dissolution. In the case of corrosion and anodic polarization of an In, Zn (0.1 at. %) alloy [3], function (1) is observed up to a current density of $1 \cdot 10^{-1}$ A/cm^2. In the case of a higher density, some time after the imposition of anodic polarization, an equilibrium state is reached, characterized by a uniform dissolution of the initial alloy. In general, in the presence of SD, the amount of the negative component passing into solution is a complex function of the time, so that with time the rate of propagation of the diffusion front of this component into the alloy slows down, while the rate of dissolution of the surface layers of the alloy remains constant [3]. In [4] functions were obtained describing the dependence of the integral flux and the value of the coefficient of selective dissolution Z_i^a for the negative component of the alloy on the time for the case when the rate of dissolution of this component is limited by volume dissolution in the solid phase, while the alloy/solution boundary is displaced at a rate V (cm/sec) (let us consider the positive flux from the depth of the alloy):

$$N(t) = \frac{DC_0}{V}\left[(1+2y^2)\operatorname{erf} y + 2y^2 + \frac{2y}{\sqrt{\pi}}e^{-y^2}\right] \tag{2}$$

$$Z^a = \frac{e^{-y^2}}{2\sqrt{\pi}\,y} + \frac{1}{2} + \frac{1}{2}\operatorname{erf} y, \tag{3}$$

where N(t) is the number of g/cm^2 of the negative component that passed into solution in the time t (sec) after the beginning of dissolution; D and C_0 are the diffusion coefficient of this component (cm^2/sec) and its concentration in the alloy (g/cm^3), respectively: $y = (V/2)\sqrt{t/D}$.

At low y, the following equation is obtained from (2):

$$N(t) = 2C_0\sqrt{\frac{Dt}{\pi}}, \tag{4}$$

which describes the passage of the negative component into solution under conditions of nonequilibrium diffusion, undistorted by the effect of displacement of the alloy/solution boundary. Differentiating (4) with respect to t and converting to electrical units, we obtain the well-known equation of nonequilibrium diffusion (1) [1]. From Eqs. (4) and (1) it follows that the presence of a linear portion on the curve of (N vs $\sqrt{t}$) and, consequently, on the curves of (i_i vs $1/\sqrt{t}$) is a characteristic of nonequilibrium diffusion. In the latter case, the linear portion, extrapolated to $t = \infty$, should pass through the origin. As can be seen from the expression for y, a low value of y can be obtained at very high D, while at a given D, y will be smaller, the lower t and V. In the case of small t, Eq. (4) is correct for any V. However, at sufficiently high V, the linear portion on the curves

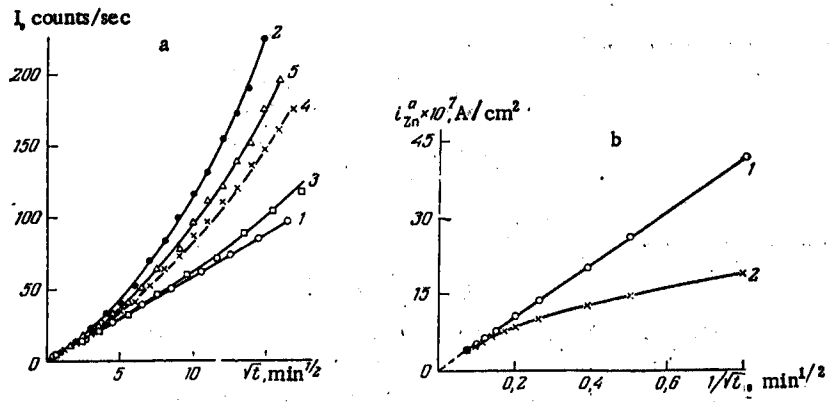

Fig. 2. Dependences: a) of the radioactivity of the solution on the time in cathodic polarization ($\Delta\varphi$ = 100 mV) (1) and in anodic polarization at i (A/cm^2): 2) $1 \cdot 10^{-3}$; 3) $1 \cdot 10^{-4}$; 4) $5 \cdot 10^{-4}$; 5) $7 \cdot 10^{-4}$; b) of the partial rate of dissolution of Zn from a Sn, Zn alloy during cathodic polarization ($\Delta\varphi$ = 100 mV) on the time on a cleaned sample (1) and on a sample subjected to preliminary anodic polarization at i = $1 \cdot 10^{-2}$ A/cm^2 for 1 h (2).

of (N vs $\sqrt{t}$) should be comparatively short, and at low V more extended. Thus, nonequilibrium diffusion of the negative component of the alloy will be described by Eqs. (1) and (4) at small t and low V for systems in which D has a comparatively high value.

In the case of large t, for any V differing from zero, Eq. (2) is simplified:

$$N(t) = \frac{DC_0}{V} + C_0 Vt. \tag{5}$$

The first term in Eq. (5) expresses the amount of the substance M (g/cm^2) that passed into solution from a depleted zone with surface equal to 1 cm^2:

$$M = \frac{DC_0}{V}. \tag{6}$$

The value of D can be calculated according to Eq. (2) from the slope of the curves of (N vs $\sqrt{t}$) at t and low V, while at large t, according to Eq. (6), it can be calculated from the value of M, determined by extrapolation of the linear portion of the curve of (N vs t), described by Eq. (5), to t = 0. In view of this, it is of interest to obtain the experimental curves of (N vs t), to describe them quantitatively using Eq. (2), and also to detect portions on these curves, described by Eqs. (4) and (5), and to use these portions for the calculation of D. When a radioactive label is used for the negative component, the radioactivity I (counts/sec) measured in solution will be proportional to N(t), and, consequently, the equations cited above for N(t) will also be correct for I(t).

It should be noted that functions (4) and (5) describe the process of SD not only in the case of anodic polarization, but also in the case of corrosion of an alloy, when displacement of the alloy/solution boundary occurs not on account of an external current, but as a result of the simultaneous occurrence of a coupled cathodic process of reduction of the depolarizer.

In the anodic polarization of an alloy, if the position of the interface is practically unchanged, i. e., V $\approx$ 0 (and at a low content of the negative component this is so), the general expression (2) is simplified, and the process of SD for any t is described by the equation of nonequilibrium diffusion with a stationary boundary [Eq. (4)] [5], which also follows from (2). Therefore, the presence of a process of SD during cathodic polarization is of interest from the standpoint of obtaining data on nonequilibrium diffusion of the negative component in an alloy, undistorted by displacement of the interface as a result of dissolution of the alloy.

The purpose of this work was to study the principles of the removal of zinc from a Sn, Zn alloy in anodic and cathodic polarization, as well as in the absence of external current.

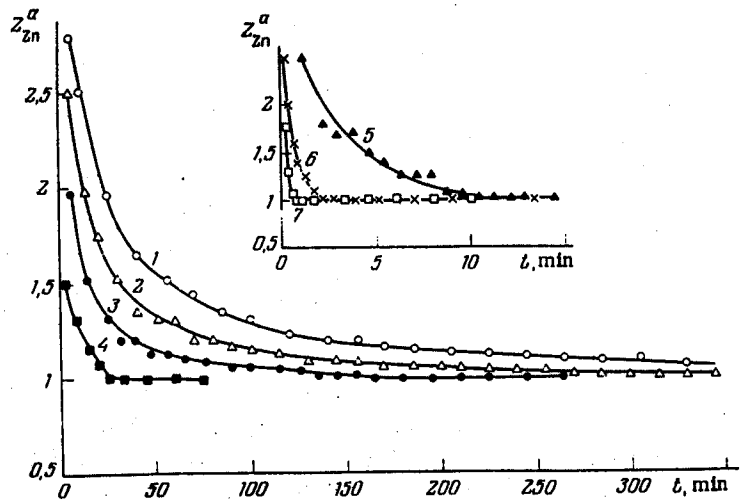

Fig. 3. Dependence of Z_{Zn}^a on the time in the dissolution of alloy at i (A/cm^2): 1) $5 \cdot 10^{-4}$; 2) $7 \cdot 10^{-4}$; 3) $1 \cdot 10^{-3}$; 4) $2 \cdot 10^{-3}$; 5) $5 \cdot 10^{-3}$; 6) $1 \cdot 10^{-2}$; 7) $2 \cdot 10^{-2}$.

Experimental Section and Discussion of Results

The Sn, Zn (0.1 at. %) alloy was investigated in a solution of 3 M NH_4Cl + 0.01 M HCl in an atmosphere of N_2, combining electrochemical and radiochemical measurements. The Zn in the alloy was labeled with the radioactive isotope ^{65}Zn, while melting the components at 250°C. The alloy was cooled at a rate of 1 deg/min, rolled out, and exposed at room temperature before the experiment for no less than 24 h to remove cold hardening. The rate of passage of Zn into solution was determined according to the slope of the curves of I vs t, obtained by continuous recording of the radioactivity I of the solution during the dissolution of the alloy [6]. As was established by special experiments, in air there is a predominant oxidation of Zn on the surface of the alloy, leading to a depletion of zinc in the surface layers. In view of this, directly before the experiment, oxides and the zinc-depleted surface layer were removed by mechanical cleaning. Cathodic polarization was conducted in a potentiostatic system, and anodic polarization in a galvanostatic system. In anodic polarization, the potential varied slightly with time. A stable value of the potential was achieved after ≈ 5 min.

Figure 1 shows a gradual decrease in the slope of the curve of I vs t, obtained in cathodic polarization ($\Delta\varphi$ = 100 mV). Consequently, the partial rate of dissolution of Zn (i_{Zn}^a), proportional to this slope [3], also decreases with time. The linearization of the curve of I vs t in a plot of I vs $\sqrt{t}$ (Fig. 2a, curve 1) is characteristic of the case of nonequilibrium diffusion [Eq. (4)]. The experimental data obtained at other values of the cathodic polarization ($\Delta\varphi$ = 200 and 300 mV), in corrosion of the alloy with hydrogen depolarization, as well as low anodic current densities ($i < 1 \cdot 10^{-4}$ A/cm^2), lie on the same curve. From the results cited in it follows that, both in the absence of displacement of the alloy/solution boundary and at a comparatively low rate of displacement of this boundary, the kinetics of zinc removal remains unchanged.

In Fig. 2b, the curve of i_{Zn}^a vs $1/\sqrt{t}$ was constructed using the same data as curve 1 (Fig. 2a), corresponding to cathodic polarization. As can be seen, this dependence is linear; moreover, in the case of extrapolation of the straight line obtained, it passes through the origin, i. e., the dissolution of Zn from the alloy during cathodic polarization is described by the equation of nonequilibrium diffusion (1) [3]. The same is correct for the process of zinc removal during corrosion and during anodic polarization at low i, since the kinetics of zinc removal under these conditions is the same as in cathodic polarization. As a result, all the curves for these conditions merge with the curve 1 cited in Fig. 2b, obtained for the case of cathodic polarization.

Thus, the process of zinc removal at $i < 1 \cdot 10^{-4}$ A/cm^2, as well as in cathodic polarization, is entirely described by Eq. (4), and, consequently, for this system at low V, at all the t studied, movement of the alloy/solution boundary has no appreciable influence on the process of zinc removal.

It should be emphasized that the results described above are obtained only under the condition of a uniform distribution of both components in the initial alloy. If, however, we use samples, on the surface of which there is a zinc-depleted zone as a result of oxidation in air or preliminary anodic polarization, then the

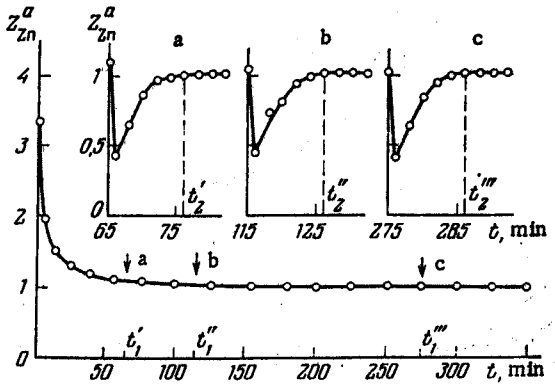

Fig. 4. Change in Z_{Zn}^a with time in the dissolution of the alloy at $i = 1 \cdot 10^{-3}$ A/cm² and periodic turn-on (arrows) of a higher current density ($i = 1 \cdot 10^{-2}$ A/cm²) at different moments of time after the establishment of an equilibrium state at $i = 1 \cdot 10^{-3}$ A/cm²: a) 65; b) 115; c) 285 min.

initial portion of the curve of i_{Zn}^a vs $1/\sqrt{t}$ has a reduced slope, and in extrapolation does not pass through the origin (Fig. 2b, curve 2). As can be seen, in the case of sufficiently large t, a break appears on curve 2, and subsequently it merges with curve 1, recorded on a cleaned sample. Consequently, the nonlinear character of the curves of i_{Zn}^a vs $1/\sqrt{t}$ and the presence of such breaks on them are evidence of the existence of a zinc-depleted zone on the surface of the initial sample.

In the case of higher V, e.g., when $i = 1 \cdot 10^{-3}$ A/cm² (Fig. 1, curve 2), the slope of the curve of I vs t (and, consequently, the value of i_{Zn}^a) decreases with time only at the very initial period of dissolution, and then becomes constant. In this case, on the corresponding curve of I vs $\sqrt{t}$ (Fig. 2a, curve 2), the linear portion corresponding to nonequilibrium diffusion is observed only for the initial time interval. Analogous curves were obtained for other i. From a comparison of the curves of I vs $\sqrt{t}$, taken at $i \geq 1 \cdot 10^{-4}$ A/cm² (Fig. 2a, curves 3-5), it can be seen that the extent of the linear portion is decreased with increasing i, in view of which the quantitative treatment of these portions becomes difficult. The deviation from linearity on curves of I vs $\sqrt{t}$ at high i shows that in this case the patterns of nonequilibrium diffusion described by Eq. (4) and function (1) are disrupted.

Thus, in the dissolution of a Sn, Zn alloy, several portions may be observed on curves I vs t, corresponding to different patterns of passage of Zn into solution. In the case of small t (first portion), even at high i (Fig. 1, curves 2 and 3), the curves of I vs t coincide with the analogous curve (Fig. 1, curve 1) obtained in cathodic polarization and corresponding to the case of nonequilibrium diffusion of Zn from the depth of the alloy to the surface of the electrode. In the case of large t (second portion), a linear portion appears on curves of I vs t (Fig. 1, curves 2 and 3). In this case i_{Zn}^a depends only on i (or V), and, consequently, the curve of I vs t is described by Eq. (5). As will be shown below, this equilibrium portion of the curve of I vs t corresponds to uniform dissolution of the alloy. In the region of transition between the first and second portions, there is also SD of zinc; in this case i_{Zn}^a depends both on t and on i. From a comparison of curves 2 and 3 (Fig. 1), it follows that the transition from conditions of nonequilibrium diffusion to uniform dissolution occurs earlier, the higher i.

Hence, the experimental results confirm the conclusion drawn on the basis of an analysis of expression (2), that nonequilibrium diffusion of the negative component can be observed at low V and small t.

Using equations describing different portions on the curves of I vs t, we can calculate D by two methods. When the first portion appears on the curve of I vs t, while the process of SD is described by Eq. (4), D is determined from the slope of the curves of I vs $\sqrt{t}$. This method was used in cathodic polarization, in anodic polarization at low i, and in the case of corrosion of the alloy. At high i, for the calculation of D according to Eq. (6), we determined M according to the radioactivity, obtained by extrapolating the linear portion of the curve of I vs t, the slope of which corresponds to uniform dissolution of the alloy at set i, to t = 0 (Fig. 1, curves 2 and 3).

TABLE 1. Dependence of the Values of D for Zn in a Sn, Zn (0.1 at. %) Alloy and δ_{eff} on the Conditions of Polarization

Exptl. conditions	φ, V (normal hydrogen electrode)	i, A/cm^2	D (10^{11} cm^2/sec), calculated		$\delta_{ef} \cdot 10^4$, cm
			according to Eq. (4)	according to Eq. (5)	
Cathodic polarization	−0,670		1,6		
	−0,570		1,6		
	−0,470		1,5		
Conditions of self-dissolution	−0,370		1,7		
Anodic polarization	−0,355	$3 \cdot 10^{-5}$	1,6		
	−0,340	$1 \cdot 10^{-4}$	1,6		
	−0,328	$3 \cdot 10^{-4}$	1,8	1,9	76
	−0,320	$5 \cdot 10^{-4}$	1,5	1,6	39
	−0,315	$7 \cdot 10^{-4}$	1,9	1,65	28
	−0,312	$1 \cdot 10^{-3}$		1,7	21
	−0,305	$2 \cdot 10^{-3}$		2,8	17
	−0,295	$5 \cdot 10^{-3}$		3,6	8,7
	−0,280	$1 \cdot 10^{-2}$		3,6	4,3
	−0,250	$2 \cdot 10^{-2}$		3,3	2

The values of D calculated by the indicated methods are cited in Table 1. As can be seen, both methods of calculation, corresponding to the two limiting cases [Eqs. (4) and (5)] of the general equation (2), give practically coinciding values of D. Moreover, the values of D found from experiments with cathodic polarization at $\Delta\varphi$ = 100-300 mV do not depend on the value and duration of the polarization (Fig. 2a, curve 1); in this case the average value of D ($\bar{D}$) is $(1.57 \pm 0.05) \cdot 10^{-11}$ cm^2/sec. The values of D obtained from experiments under conditions of corrosion, as well as in the case of an anodic current density all the way up to i = $1 \cdot 10^{-3}$ A/cm^2, differ little from $\bar{D}$. As can be seen from these results, D does not depend on the conditions of polarization. In the case of higher i, an increase in D is noted, evidently due to an increase in the roughness of the surface of the alloy.

Equations (4) and (5) describe only the limiting cases of the process of SD of the negative component, corresponding to relatively small and large t. It is of interest to describe the experimental curves of I vs t using Eq. (2) within a broad range of values of t at various i (or V). Using the value of $\bar{D}$ obtained in cathodic polarization, we calculated the theoretical curves of I vs t at i = $5 \cdot 10^{-4}$ and $1 \cdot 10^{-3}$ A/cm^2 (Fig. 1). As can be seen, good agreement of these curves with the experimental points is observed. An analogous coincidence was obtained for lower i.

Thus, Eq. (2) entirely describes the process of zinc removal both during anodic and during cathodic polarization of the alloy, as well as in the case of its corrosion.

A graphic idea of the nature of SD during anodic polarization and corrosion* of the alloy can be obtained by studying the dependence of Z_{Zn}^a on the time [3, 7, 8]. The differential value of Z_{Zn}^a determined in our experiments was calculated according to the Eq. (3)

$$Z_{Zn^a} = \frac{(\partial C_{Zn}/\partial t)_{soln}}{(\partial C_{Sn}/\partial t)_{soln}} : \left(\frac{C_{Zn}}{C_{Sn}}\right)_{al} = \frac{i_{Zn^a} n_{Sn}}{i_{Sn^a} n_{Zn}} : \left(\frac{C_{Zn}}{C_{Sn}}\right)_{al}, \quad (7)$$

where

$$i_{Zn^a} = \left(\frac{\partial C_{Zn}}{\partial t}\right)_{soln} \cdot \frac{n_{Zn}F}{s} \text{ and } i_{Sn^a} = \left(\frac{\partial C_{Sn}}{\partial t}\right)_{soln} \cdot \frac{n_{Sn}F}{s}$$

i_{Zn}^a and i_{Sn}^a are the anodic partial rates of dissolution of Zn and Sn at the moment of time t; n_{Zn} and n_{Sn} are the valences of Zn and Sn ions passing into solution; C_{Zn} and C_{Sn} are the concentrations of the components of the alloy, expressed for the solution in M and for the alloy in at. %; S is the area of the electrode, cm^2; and F is the Faraday number. The value of i_{Sn}^a in Eq. (7) was determined from the function

$$i_{Sn^a} = i - i_{Zn^a}. \quad (8)$$

Figure 3 presents the experimental dependences of Z_{Zn}^a on t (points), obtained at various i and the corresponding curves for i = $5 \cdot 10^{-4}$, $7 \cdot 10^{-4}$, and $1 \cdot 10^{-3}$ A/cm^2, calculated according to Eq. (3) (solid lines).

* To obtain curves of Z_{Zn}^a vs t in the corrosion of a Sn, Zn alloy, it is necessary to label both components with the corresponding radioactive isotopes and use continuous recording of the I vs t curves of both isotopes simultaneously.

The values of $\bar{D}$ were used for the calculation. As can be seen, the experimental data fit well on the calculated curves. Moreover, in the initial period of dissolution, at all i up to $i = 2 \cdot 10^{-2}$ A/cm^2, Z_{Zn}^a appreciably exceeds 1, which is evidence of the presence of SD of zinc from the alloy even at a high rate of displacement of the alloy/solution boundary. After some time interval, at all i, $Z_{Zn}^a = 1$ is reached, i.e., an equilibrium state with uniform passage of the components of the alloy into solution is established. * This result agrees with Eq. (3), from which it follows that in the dissolution of the alloy, Z_{Zn}^a decreases monotonically and approaches 1 at large t. As can be seen from Fig. 3, an equilibrium state is reached more rapidly, the higher i.

The establishment of an equilibrium in the process of dissolution of an alloy may be represented as follows. In the initial period of dissolution, the rate of movement of the diffusion front V_1 exceeds the rate of displacement of the alloy/solution boundary V. In this case $Z_{Zn}^a > 1$. However, since the thickness of the zinc-depleted zone, according to the principles of nonequilibrium diffusion, is proportional to $\sqrt{t}$, and the value of the displacement of the alloy/solution boundary is proportional to t, in time the condition $V = V_1$, corresponding to the equilibrium state, will be reached [3, 9]. According to Eq. (7), the presence of a relationship $Z_{Zn}^a > 1$ is an indication of SD of zinc. Therefore, observance of this ratio in the initial period of dissolution at all i (Fig. 3) indicates that by the time of establishment of the equilibrium state, a zinc-depleted zone should be established on the surface of the electrode. The conservation of a ratio $Z_{Zn}^a = 1$ for a long period of time is a sign that the thickness of this zone should not change with time, and, consequently, the dissolution of Zn in the equilibrium state will be described by the principles of equilibrium diffusion.

To characterize the depleted zone, it is convenient to use its effective thickness δ_{eff}. The quantity δ_{eff} is defined as the thickness of the imaginary layer of the alloy, in the case of complete removal of the negative component from which the same amount of this component Δp (g/cm^2) passes into solution as from the real depleted zone [1]:

$$\delta_{eff} = \frac{\Delta p}{C_0}. \tag{9}$$

Considering $C_0 = N_0^{Zn} A_{Zn} / v_m^{al}$, where N_0^{Zn} is the mole fraction of Zn in the alloy; A_{Zn} is the atomic weight of Zn; v_m^{al} is the molar volume of the alloy (cm^3), which differs negligibly from the molar volume of Sn (v_m^{Sn}) at a low content of zinc in the alloy, it is easy to calculate δ_{eff} from radiochemical data [3]:

$$\delta_{eff} = \frac{v_m^{Sn} p_0 v \Delta I_{av}}{s A_{Zn} N_0^{Zn} v_0 I_0}, \tag{10}$$

where p_0 and I_0 are the mass (g) and radioactivity (counts/sec) of the calibration solution for Zn, respectively; v_0 and v are the volume (ml) of the corresponding calibration solution and that of the solution in the cell; ΔI_{av} is the excess amount of radioactivity of the negative component that passed into solution from the depleted zone, related to the total amount of radioactivity of this component that passed into solution, ΔI, by the function $\Delta I_{av} = \Delta I - \Delta I_{ud}$, in which ΔI_{ud} is the amount of radioactivity of the negative component that should have passed into solution in the same time in the case of uniform dissolution of the alloy.† It should be noted that in the case of cathodic polarization, $\Delta I_{av} = \Delta I$. Under equilibrium conditions of dissolution, ΔI_{av} becomes constant, and, consequently, δ_{eff} does not change with time.

Table 1 presents the values of δ_{eff} for various i, calculated for equilibrium conditions of dissolution. As can be seen, the value of δ_{eff} decreases with increasing i, which agrees with Eq. (6).

For the detection of a zinc-depleted zone in the equilibrium state, we conducted the following experiment. At various time intervals after the reaching of an equilibrium state at $i = 1 \cdot 10^{-3}$ A/cm^2, a higher i ($1 \cdot 10^{-2}$ A/cm^2, Fig. 4) was periodically imposed upon the electrode. In this case, immediately after the imposition of a higher i, the value of Z_{Zn}^a drops sharply to 0.4; this is evidence of the presence of a zinc-depleted zone in the equilibrium state at $i = 1 \cdot 10^{-3}$ A/cm^2. When the thickness of this zone is reduced, as a result of the imposition of a higher i, Z_{Zn}^a subsequently rises to $Z_{Zn}^a = 1$, which provides for the establishment of a new equilibrium state and a decrease in the thickness of the zinc-depleted zone to a value corresponding to this equilibrium state. Moreover, it follows from Fig. 4 that the time interval from the moment of application of $i = 1 \cdot 10^{-2}$ A/cm^2 (t_1^q) until the establishment of a new equilibrium state (t_2^q), in this case i does

* Let us consider that the equilibrium state is reached when the value of Z_{Zn}^a differs from 1 by not more than 10%.

† In [3] φ_{eff} was calculated according to a somewhat different formula, using ΔI and the anodic current density.

not depend on the time of exposure of the alloy in the equilibrium state at $i = 1 \cdot 10^{-3}$ A/cm^2. This result indicates that the thickness of the layer removed from the electrode during the establishment of the new equilibrium state does not depend on the time of stay of the alloy in the equilibrium state, $i = 1 \cdot 10^{-3}$ A/cm^2, and, consequently, the quantity δ_{eff} actually is unchanged with time, which is a characteristic of equilibrium diffusion of the negative components in the alloy.

The results cited are evidence that the process of dissolution of a solid solution of Sn—Zn is accompanied by a substantial change in the composition of its surface.

CONCLUSIONS

1. The principles of the removal of zinc from a Sn, Zn (0.1 at. %) alloy in a solution of 3 M NH_4Cl + 0.01 M HCl were studied. It was shown that in the case of anodic polarization at $i \leq 1 \cdot 10^{-4}$ A/cm^2, in the case of cathodic polarization ($\Delta\varphi$ = 200 and 300 mV), as well as in the case of corrosion with hydrogen depolarization, the kinetics of the dissolution of Zn remains unchanged and is described by the principles of nonequilibrium diffusion of Zn in the alloy. In the case of higher i, a disruption of this pattern is noted, followed by transition to an equilibrium state providing for uniform dissolution of the alloy.

2. In the equilibrium state, a zinc-depleted zone was detected directly.

3. The diffusion coefficient of Zn in the alloy was calculated.

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