Theoretical model of formation and growth of pitting

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ABSTRACT

The mechanism of origination, interaction, and growth of pits is discussed. The processes of dehydration of solution inside a pit, formation and performance of a resistive layer, and stabilization of pit growth are considered.

Key words: Pits, theoretical model.

INTRODUCTION

Pitting is an extremely hazardous corrosion type. While causing relatively low metal losses, it disables large metal structures and renders inoperative expensive constructions. Thus, great effort was always under- taken to control pitting. The problem of pitting theory may be divided into three interrelated but, nevertheless, autonomous parts:

´ origination of pits, i.e., their nucleation;

´ interaction of the pits formed, their competition and ''struggle for life'';

´ development of survived pits, i.e., the growth of the strongest. This work is devoted to the third problem. As regards the first two problems, the following should be mentioned.

The first problem, namely the mechanism of pit nucleation requires considering the local depassivation of small areas δS on the metal surface . Depending on the conditions (for example, the activity of δS), these bare areas can either heal or begin to grow. They may be called the pit nuclei.

The second problem that concerns the interaction of pits formed remains very poorly developed. To date, none of theoretical models of interaction are sufficiently complete.

The problem of local depassivation is $_S$ considered in detail in [1]; however, it is rather cumbersome, and we restrict ourselves to several remarks.

Many authors assume that pits are formed due to random defects of the passivating oxide layer (scratches, random micropores, etc). However, the attribution of pitting to pores and random defect is hardly consistent with the regular and reproducible dependence of the pitting potential on the solution concentration and the very fact of the existence of this potential. The idea of static defects as the cause of pitting also contradicts the fact that the passivating oxide has no stable structure and is thermodynamically non-equilibrium. It exists dynamically by constantly renewing its ionic composition and structure.

A principally different approach to the problem of pitting was put forward by Ya. M. Kolotyrkin[2]. He claimed that two factors are decisive during the pit nucleation. The first factor is the known presence of activating ions (Cl^-, Br^-, I^-) in the solution, and the second factor is the energetic inhomogeneity of the surface. This inhomogeneity entails the discreteness of the properties of the

whole passivating layer. It is also the reason for the discreteness of depassivation. Indeed, due to heterogeneity, the layer structure contains weak points, and the distribution of the dissolution current across the layer becomes non uniform. The energetic inhomogeneity of the surface is transmitted across the layer to the interface with electrolyte. In these ''weak points,'' pits form. Other conditions being equal, the pitting initiation –potential is a determinate function of the electrolyte composition and the energetic spectrum of the surface.

Aggressive anions A^{n-} involved in the acts of transfer of actions   to the electrolyte not only accelerate the metal depassivation but also make it irreversible.

This follows from the fact that pits formed at the pitting potential do not develop further in the absence of   . At the pitting potential, the anions   change the dissolution kinetics in such a way that it no longer corresponds to the extrapolation from the Tafel domain.

During the depasssivation of an area   , a local increase in the density of dissolution current *i* occurs, which represents a fluctuation   of the current density relative to the whole passivated surface   . This causes a corresponding increase in metal ion   concentration in the vicinity of and, hence, an increase in the supplied aggressive anions   , which compensate the positive charges of metal ions. The initial fluctuation of current generates a secondary fluctuation   of aggressive anions, that is   Inasmuch as the latter are involved in the elementary acts of the detachment of cations from the metal lattice (pit's bottom) and stimulate the acts, the origination of δC accelerates these acts still more. Hence, an increase in the current by   increases the overall concentration by   , which in turn increases by . Thus, the dissolution becomes not only irreversible but also self-accelerating. Hence, a growing pit represents an electrochemical system with a feedback .

The initial fluctuation can be expressed

via by using the common equations of diffusion kinetics

$$
\begin{cases}
\dfrac{\partial C}{\partial t} = D_{eff}\Delta C, \quad C = \dfrac{C_a}{Z_m} = \dfrac{C_m}{Z_a}, \\[2mm]
C_a = \left[A^{a-}\right], \quad C_m = \left[M^{a+}\right] \\[4mm]
D_{eff}\dfrac{\partial C_a}{\partial x} = \dfrac{i_\varphi - Z_m F\left(\dfrac{dN_a}{dt}\right)}{Z_a + Z_m}\dfrac{1}{Z_m F} \\[4mm]
i_\varphi = i_P + \delta\, i, \quad C = C_0 + \varphi, \quad \delta C = Z_a\varphi\left(r,x,t\right)
\end{cases}
$$

$$...(1)$$

Where   and C_m are the normalized concentration and those of anions and metal, respectively; N_a is the coverage of surface S by adsorbed anions; r_0 is the initial radius of the area δS with a center at   ; i_P is the mean current of passive dissolution; C_0 is the concentration in the solution bulk. The solution of this problem gives the maximum value of δC ,namely

$$
\left(\delta C\right)_{max} = Z_m\frac{r_0\delta\, i}{F D_{eff} Z_m\left(Z_a + Z_m\right)}. \qquad ...(2)
$$

On each   of the surface S , depending on its energetic spectrum and other factors, a multitude of pit nuclei arises, which divide the near–electrode layer into areas δV with mobile boundaries. These areas are the source of aggressive anions   and water molecules necessary for the growth of pit, i.e., represent their "life spans". For each area δS depending on the parameters   and C , a critical value δV_{cr} sufficient for the growth of a pit exists. It is determined by the growth rate, the diffusion rates of solution components, etc. If $\delta V \langle \delta V_{cr}$ then pits start to interact and compete with one another, and, as a result, only the strongest of them survive. According to Fig. 1, the neighboring fluctuations of current δi each of a radius   do not interact if the radii R of the corresponding cylindrical solution volumes at least twice exceed.

The pitting potential is determined by the expression (3) at [1]

$$\varphi_{pit} = \varphi_{eq} + \frac{\delta_{Pl} A \ln\left\{\left(\frac{i_p z_{max}}{i_0 A}\right) + \frac{C_a}{a}\right\}}{\beta z_{max}\left[1 + \frac{C_a}{a}\right]}, \quad ...(3)$$

where φ_{eq} is the potential of oxygen equilibrium [3], and δ_{Pl} is the average thickness of passive layer. Thus, in each case, all other factors being equal, the potential of pit formation is a function of two parameters: the concentration of the aggressive medium　　and the heterogeneity parameter $z_{max} = exp\left[(W_M - W_m)/KT\right]$.

Figure 2 shows the $\varphi_{pit}\ vs. C_a$ dependence for an iron electrode in　　solution. It illustrates the agreement between the discussed theory and experimental results (in Fig. 2, the function $\eta = \varphi_{tp} - \varphi_{pit}, \varphi_{pit} = \varphi_{pit}(C_a), A \sim 1, \varphi_{tp}$ is the transpassivation potential), and $z_{max} = \exp\left(\frac{\Delta W}{KT}\right) \sim 10$.

Thus, only a part of N nuclei develops into pits. The interaction between them suppresses weak pits and, concurrently, affects the activation of nucleation, which is decisively dependent on solution anions. The anions participate in elementary acts of the processes on the metal surface S. Schemes of these processes are shown in Figs. 3-5. In the range from φ to　　, the presence of　　ions, which strongly interact with the surface S, changes the situation shown in Fig. 4. Being locally bared, the most active areas　are covered by chloride complexes, which arise via the reaction

$$M + \rho Cl^{-1} \rightarrow (M\rho Cl)^{-\rho+\sigma} + \sigma e,$$
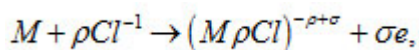
and displace water molecules.

Because Cl^{-1} ions are weakly hydrated, the adsorption complexes $(M\rho Cl)^{-\rho+\sigma}$ do not leave the surface themselves. However, by interacting with water dipoles, they apparently form the bonds giving rise to mixed surface complexes of a type of $(M\rho Cl.nH_2O)^{-\rho+\sigma}$, which can pass to solution via the scheme of Fig. 5. According to this figure, those metal atoms pass to solution that, firstly, are bound

with ρCl^{-1} and, secondly, interact with n oriented water molecules. When, during their dissolution, the mixed complexes rapidly dissociate, the anions are recovered and can again take part in the elementary act. The liberated　　ions acquire hydrate shells and are removed to the periphery.

Pit Development

The mechanism of pit growth can be understood on the basis of model experiments [4] with two groups of measurements.

The first group represent galvanostatic measurements on Ni and Fe by a polarizing–current density I_g from 5 to100 A/cm^2. A cylindrical sample of a radius $r \sim 0.1cm$, in armored Teflon casing, was exposed to concentrated aqueous solution of $1-3M$ KCl and　　, and, upon a corresponding treatment dissolved uniformly. At $I_g \rangle 1 A/cm^2$, the samples surface was cleaned and operated as a large pit. Then, the φ vs. t curves were measured, which are shown in figs. 6a and 6b. Each curve demonstrates two time intervals　　and $t \rangle T$, which correspond to two successive stages of the pit growth mechanism. In both cases, the time of the first stage turns out to be

$$T \sim \left(\frac{1}{I_g}\right)^2 s$$

The second group includes potentiostatic measurements on the same samples in a　　aqueous solution at potentials of $1.5-2$ V (n.h.e). In this case, the current densities　　range from 5 to 100 A/cm^2. The results of both groups are well reproducible and inter-consistent.

The mentioned high current densities I_g and i_a determine the kinetics of pit growth. They correspond to the number of atomic layers $n \sim \left(\frac{i_a}{Z_m e\Gamma}\right)$, which every second pass to the solution from $1cm^2$ of pit's bottom, where $Z_m e$ is the charge of metal ions and $\Gamma \sim 10^5$ is their number on a cm^2 of the surface. Hence, it follows that $n \sim 3(10^3 - 10^4)$, the rate of pit deepening $\left(\frac{dl}{dt}\right) \sim 10^{-4} cm/s$, and the flow of species to the solution $j \sim 3 \times 10^{19}$ species $/(cm^2 s)$. With the mentioned orders of magnitudes, the solution properties should

substantially change in the vicinity of a pit. Thus, when $I_\varepsilon \sim 10.4\,A/(cm^2 s)$, the increment of the normalized concentration ΔC at the pit's bottom, in a layer of a thickness of $\delta \sim \sqrt{DT} \sim 10^{-4} cm$ that is equal to the depth of diffusion penetration for the characteristic time of the first stage   , is

$$\Delta C \sim \frac{I_\varepsilon TS_p}{Z_m F\left(\delta S_p\right)} = \frac{I_\varepsilon}{Z_m F}\sqrt{\frac{T}{D}} \sim 6\,mol/l, \quad ...(4)$$

that is, the solution concentration approaches a complete salvation limit C_t, where all water molecules find themselves in hydrate shells of metals ions M^{z+}. Correspondingly, by the end of the first stage at $t \sim T$, the solution at the pit's bottom is virtually "deprived" of free water, which transfers, from the free state into the bonded one. At the same time, the average change of concentration $\overline{\Delta C}$ in the whole cell volume $V \sim 1cm^3$ is small.

$$\overline{\Delta C} \sim \frac{I_\varepsilon TS_p}{Z_m FV} \sim 10^{-6}\,mol/l. \quad ...(5)$$

For convenience sake, the appeared layer $\delta \sim \sqrt{DT}$ of "dehydrous" solution is called the resistive layer. By its structure, the resistive layer is intermediate between solutions and crystal hydrates (with high coordination numbers). Apparently, it can be represented as a combination of two ionic subsystem (sublattices): firstly, a sublattice of chloride ions and, secondly, a cationic lattice of dissolving metal. Water molecules that enter into hydrate shells, and, hence, are oriented in a certain way, are located between the opposite charges of these subsystems. Under the effect of electric field, vacancies and the ionic current arise in the positive subsystem. Ions move by successive jumps from there own hydrate shells to vacant neighboring shells. The electric field is the driving force of these relay-race transitions. When an ion is transferred, its hydrate water is freed for a while. This should prevent the possible salt crystallization in the resistive layer and the formation of salt plugs. Immediately at the pit's bottom, this process produces a corresponding amount of free water capable of participating in the further acts of dissolution via the scheme in Fig. 5. Hence, the dissolution kinetics is limited by the liberation of hydrating water, which depends on the polarizing current or the external potential.
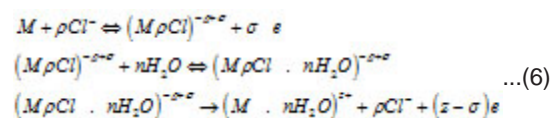
Thus, by the end of the first stage, the electrolyte solution at the pit's bottom is "dehydrated" and the concentration of ions reaches its maximum possible value C_t. However, the sample continues to dissolve, and the arising metal ions M^{z+} acquire hydrate shells. Hence, the processes of water binding and solution dehydration go on. The resistive layer becomes thicker and, in the general case, at sufficiently great currents I_g, can fill the whole pit's cavity and come out to the periphery (Fig.7).

At the resistive-layer boundary $x = \xi(t)$, the flow of metal ions M^{z+} splits into tow. The first part consists of ions going to solution and the second builds up the layer. That's why, at the observed currents I_g, the boundary $\xi(t)$ moves, approaching the mouth of the pit. In doing so, the solution near the boundary $\xi(t)$ is apparently dehydrated, and the motion of ions to solution is impeded due to their low mobility and, probably the exhanced interaction of incompletely hydrated ions. We can assume that, at the boundary , the free and bound water molecules form opposite flows, and, at sufficiently high currents , the boundary reaches the pit's mouth.

Then, in the general case, the resistive layer comes out of the pit's cavity and begins to develop into a hemisphere (Fig. 8). Its radius constantly grows, and the situation changes, because the initial flow of metal ions   from the pit's bottom through the resistive layer now comes to the growing hemispherical surface $\Sigma = 2\pi r^2(t)$, i. e., the current density of ions decreases and the water deficiency disappears . the pit is stable now.

Thus, in its development, a pit passes three stages: (1) the solution at the pits bottom is ''dehydrated''; (2) the pits cavity is the filled with the resistive layer and the latter comes out to the periphery; (3) the pit becomes stable.

At the first stage, the kinetics of processes occurring at the pit bottom, which are shown by a scheme in fig .5 , is of prime importance
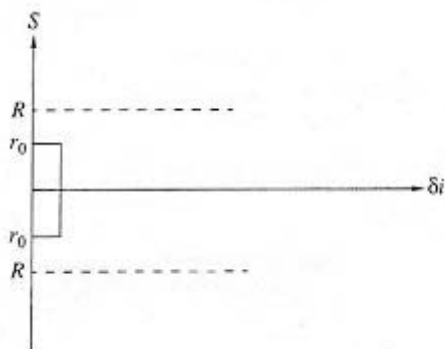
$$M + \rho Cl^- \Leftrightarrow (M\rho Cl)^{-\rho + \sigma} + \sigma\ e$$
$$(M\rho Cl)^{-\rho + \sigma} + nH_2O \Leftrightarrow (M\rho Cl \cdot nH_2O)^{-\rho + \sigma}$$
$$(M\rho Cl \cdot nH_2O)^{-\rho + \sigma} \rightarrow (M \cdot nH_2O)^{z+} + \rho Cl^- + (z-\sigma)e \quad ...(6)$$

Fig. 1: A scheme of fluctuations δi of the dissolution current density of a passive metal

$$M + nH_2O \rightarrow M(O^{2-}\langle{}^{H^+}_{H^+}\rangle)_n \rightarrow (M \cdot nH_2O)^{z+} + ze^-$$
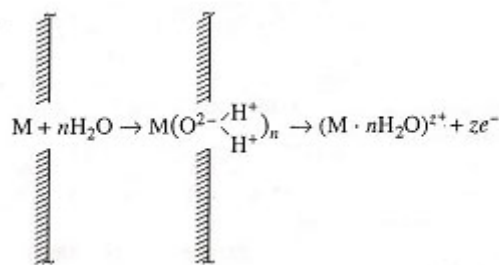
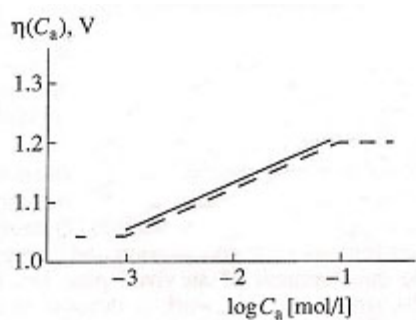**Fig. 4: A scheme of passivation (φ, (φ_a, φ_a and in Fig. 3)**

Fig. 2: Department $\eta(C_a) = \varphi_g - \varphi_{pa}(C_a)$. The solid curve demotes experimental data for Fe in KCl, pH 5 [4];in the dashed curve demotes theoretical data [1]; $z_{max} = 8$, $a = 0.33 \times 10^{-2}$, $\varphi_{pa}(C_a)$ is determined by Eq (3) and φ_{tp} is the end potential of passive rage at $C_a = 0$

$$M + pCl^- \rightarrow [MCl_p]^{-p+\sigma} + nH_2O \rightarrow [MCl_p(\langle{}^{H^+}_{H^+}\rangle O^2)_n]^{-p+\sigma}$$

$$pCl^- + nH_2O + M^{2+} + ze$$
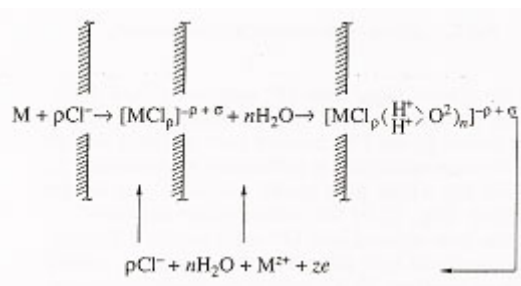
Fig. 5: A scheme of the formation of mixed surface complexes

$$M + \tfrac{z}{2}H_2O \rightarrow M(O^{2-}\langle{}^{H^+}_{H^+})_{z/2} \rightarrow MO_{z/2} + zH^+ + ze^-$$
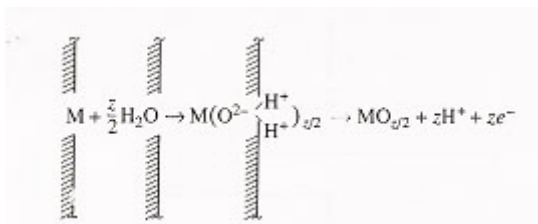
Fig. 3: A scheme of metal dissolution involving water molecules (φ, (φ_a, φ_a is the initial potential of the passive range)
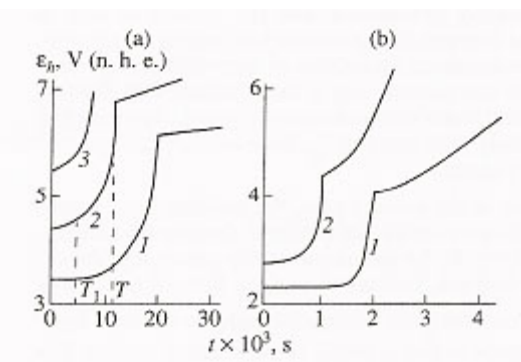

Fig. 6: The dependence of is $\varepsilon_k = \varphi + \Delta\varphi_{ohm}$ [4], $\Delta\varphi_{ohm}$ ohmiclosses in the bulk of solution I_g, $\dfrac{A}{cm^2}$,

(3) 52,6; (b) Ni in 4 M KCl: (1) 72, (2) 90.
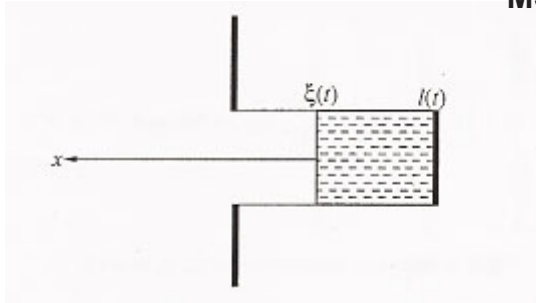
MSRIVol07N1

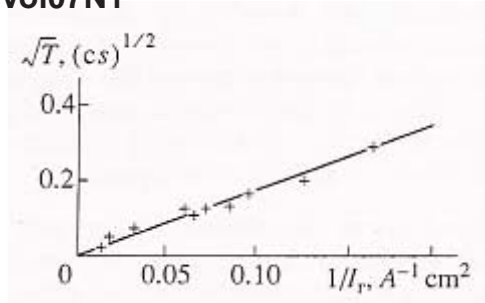**Fig. 7: A scheme of the resisteve layer in a pit cavity**

Fig. 10: Dependence of T on I_s for Ni in a 3M NICl2, Ph5. Point s are experimental data (4)
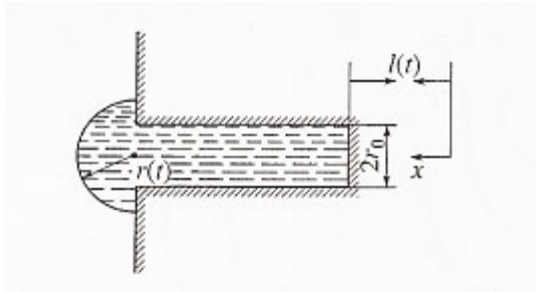

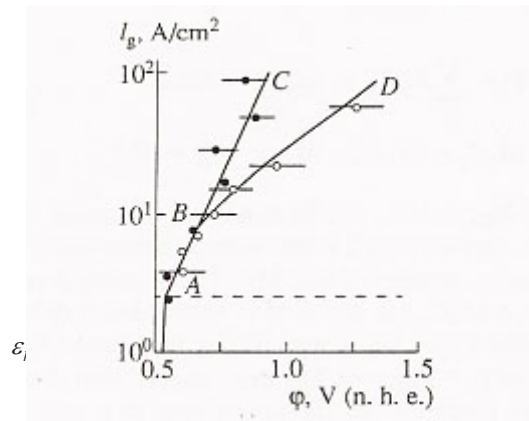**Fig. 8: Resistitive layer above the pit**

Fig. 11: Current dependence on potential for Ni in a KCl solution, pH 5[1], Point s are experimental data [4], concentration of KCl, mol/l: in ABC segment, 4; in ABD segment
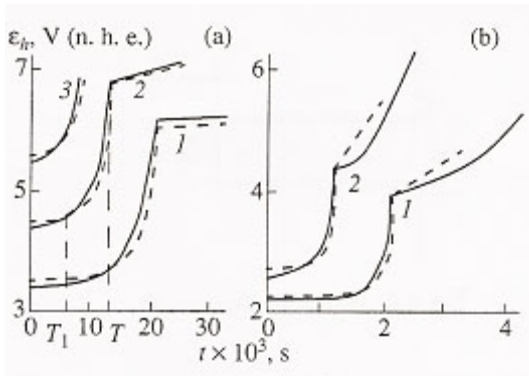

Fig. 9: The dependence of is

ohmiclosses in the

bulk of solution I_g, $\dfrac{A}{cm^2}$,

(*a*) *Fe in* 1 *M KCl*: (1) 31.6, (2) 42, (3) 52,6;

(*b*) *Ni in* 4 *M KCl*: **(1) 72, (2) 90 solid and dashed curves represent experimental [4], and calculated [1] data, respective ly**
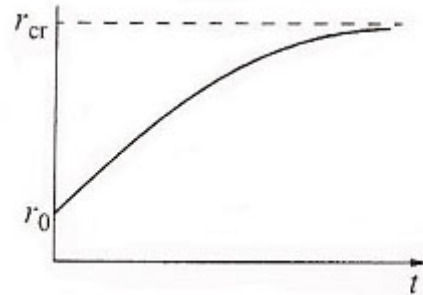

Fig. 12: Time dependence of the radius of a hemispherical resistive layer [1]

At this stage, due to their strong (at the pitting potential) interaction with the metal surface , the activating anions force out water molecules so that the latter can no longer play the role of a passivator according to Fig. 4. The surface S is occupied by adsorption complexes. However, Cl^- ions are not hydrated, and the formation of complexes $(M\rho Cl)^{-\rho+\sigma}$ is yet insufficient for the metal to dissolve. For this to happen, the second stage of (6), which results in the formation of a resistive layer, is essential. As this layer is formed and the solution is dehydrated, the kinetics of dissolution (6) becomes directly related to the
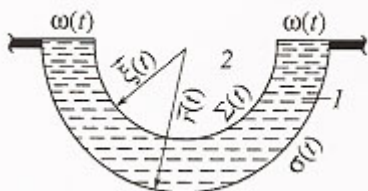

Fig. 13: A model of a hemispherical pit: (1) resistive layer, (2) a part of pit's scavity filled with aqueous solution [1],

current i. As was noted above, the foregoing factors suppress the dissolution, because the function of free water is now performed solely by water molecules of interfacial hydrate shells in as much as the latter remain unoccupied.

The mechanisms of the elementary act and ionic conduction, as well as the ohmic losses in the near electrode layer, change correspondingly. This is reflected in the break in   curves of Fig. 6. The solution density   , which is determined by the concentration   of all components, also changes

$$\rho = \sum_i M_i C_i = M_w C_w + MC,$$
$$M = M_1 Z_2 + M_2 Z_1, \qquad M_1 = M_{10} + RM_w, \qquad ...(7)$$

Where M_1, M_2, and M_w, are the masses of the metal, the counterion, and water; C_w is the water concentration; R is the hydration number of ions M^{z+}. The quantity ρ varies from

to   in a completely dehydrated solution (for $FeCl_2$ and $NiCl_2$, it is found that $C_t \sim 5.85$, and $\rho_t \sim 2\,g/cm^2$). The mass distribution along the pit axis gives rise to the convection at a rate v. Therefore, the full flow of each component is combined of diffusion, migration, and convection components.

Equations [1] that describe the growth of a pit pertain to the Onsager general theory of transport processes in concentrated solution, where the concentrations of ionic components are commensurable with that of solvent. Hence, one must not consider them independently, neither assume that the motion of ionic components does not affect the equilibrium states of the solvent. Actually, the latter is involved in the transport processes. This theory is known as a hydrodynamic view on diffusion. Onsager equations used in this work determine the mean statistical rates of species   of the   component, which are involved in the expressions for the density $\vec{I}_i$ of the full mass flow

$$
\begin{aligned}
&\vec{I}_i = M_i C_i \vec{v}_i \\
&\vec{j}_i = \vec{I}_i - MC\vec{v}, \qquad \rho\vec{v} = \sum_i \vec{I}_i, \\
&\rho = \sum_i M_i C_i, \qquad \sum_i \vec{j}_i = 0 \\
&\rho\vec{v} = \sum_i \vec{I}_i, \qquad \rho = \sum_i M_i C_i
\end{aligned}
\qquad ...(8)
$$

Where   , and $\vec{j}_i$, are the molar mass, concentration, and diffusion flow of the   component, respectively; this automatically means that $\sum_i \vec{j}_i = 0$. The mean statistical rates   are related to the gradients of chemical potentials   of an m-component mixture by the Onsager equation

$$
\left(\frac{\bar{C}}{RT}\right)\nabla\mu_i = \sum_k^m \left(\frac{C_k}{D_k}\right)(\vec{v}_k - \vec{v}_i), \qquad \sum_i C_i\mu_i = 0
$$
$$
\mu_i = \mu_i^0 + z_i F\varphi + RT\ln\left(\frac{\gamma_i C_i}{C_0}\right), \qquad \bar{C} = \sum_k^m C_k
\qquad ...(9)
$$

Where D_{ik} are the diffusivities in the corresponding binary mixtures, which are related

to Onsager coefficients. From this expression, at small concentrations, i.e., in a linear approximation, we can obtain usual expressions for the current density, which involve diffusion, migration, and convection components. From (9), the explicit equations for mass flows $\vec{j}_i$ follow

$$\sum_k \left[M_i C_i C_k \nabla \mu_k + \left(\frac{RT}{M_i D_{ik}} (M_i C_k \vec{j}_i - M_k C_i \vec{j}_k) \right) \right] = 0, \quad i, k = 1, 2, 3, \dots, m,$$
...(10)

and

$$\frac{\partial C_i}{\partial t} + div \left(\frac{\vec{j}_i}{M_i} + C_i \vec{v} \right) = 0. \qquad ...(11)$$

From Eqs (10) and (11), one can determine the sought concentrations , and C_w of solution components in the pit and also their flows $\vec{j}_1, \vec{j}_2$, and [1] as the functions of and other parameters. More over, due to the presence of the factors , and ρ specified below, the expressions (8)-(10) take into account the effects of ionic interaction, electrical field, and changes in the solvent concentration

$$\left. \begin{array}{l} \ln \gamma_i = -z_i^2 \left(\dfrac{1.12\sqrt{\Gamma}}{1+\sqrt{\Gamma}} - 0.1\Gamma \right), \\[2mm] \Gamma = \dfrac{1}{2} \sum_k z_k^2 C_k \quad (C_k, \; mol/l), \\[2mm] k = -D_{13} D_{23} \left(z_2 D_{23} + z_1 D_{13} \right) \\[2mm] \rho = \sum_i M_i C_i = MC + M_w C_w \\[2mm] M = M_1 z_1 + M_2 z_2, \quad M_1 = M_{10} + R M_w \end{array} \right\} \quad ...(13)$$

The normalized concentration of ionic components and solvent at the pits bottom are as follows [1] :

$$C_{w,i}(t) = C_{w0} \left(1 - \sqrt{\frac{t}{T}} \right), \quad C = \frac{C_1}{z_2} = \frac{C_2}{z_1},$$

$$C_i(t) = C_0 + (C_T - C_0) \sqrt{\frac{t}{T}}, \quad C_T \sim 6 \;\; (mol/l), \quad ...(14)$$

$$I_g \sqrt{T} = A, \quad A = const.$$

By using the shown expressions, one can calculate curves in a galvanostatic mode and the dependence of the first stage time on the galvanostatic current I_g (Figs. 9-11).

Below, the formulas for the resistive layer in the pit are shown. The equations [1] for the movement of its boundary $\xi(t)$ are as follows:

$$\frac{d\xi}{dt} = \frac{1}{z_2 C_t} \left(\frac{I_g}{z_2 F} - \frac{I_{1\xi}}{M_{11}} \right),$$

$$M_{11} = M_{10} + R_1 M_w \qquad ...(14)$$

$$I_{1\xi} = j_{1\xi} + \alpha C_t v_\xi M_{11} z_2, \quad \alpha \le 1,$$

Where $I_{1\xi}$ is the flow of cations that depart from the resistive layer to solution. The equation for the shift of the pits bottom $l(t)$, i. e. its deepening is as follows:

$$-\frac{dl}{dt} = \frac{M_{10}}{\rho} \frac{I_g}{z_1 F} \sim 0.36 \times 10^{-4} I_g \;\; (cm/s) ...(15)$$

As was mentioned above, for sufficiently great currents I_g, the resistive layer fills the pits cavity and, having come out to the periphery, develops into a hemisphere. Therefore, the former current $\pi r_0^2 I_g$ of metal ions is fed to the growing hemispherical interface $2\pi r_1^2(t)$. Consequently, the current is dissipated, and the pit is stabilized. The equation describing the shift of this surface [1] is as follows (Fig .12):

$$\frac{dr_1(t)}{dt} = \frac{1}{C_t} \left(\frac{\alpha_1}{r_1^2} - \frac{\alpha_2}{r_1} \right),$$

$$\alpha_1 = 3.86 \; r_0^2 \left(\frac{I_g}{z_1 F} \right), \quad \alpha_2 = 12.66 \; D_t \left(C_t - C_0 \right). \quad ...(16)$$

A stable (maximum) value of the radius r_{cr} is

$$r_{cr} = \frac{\alpha_1}{\alpha_2} = \frac{0.3 r_0^2 I_g}{D_t F \left(C_t - C_0 \right)}. \qquad ...(17)$$

By integrating Eq. (16) for and taking into account Eq. (17), we obtain for $k(t) = \frac{r_1}{r_{cr}}$

$$\frac{\left(1-k^2 q^2 r_0^2 I_g^2\right) r_0^2}{2}+\left(1-kqr_0 I_g\right)qr_0^2 I_g -q^2 r_0^4 I_g^2 \ln\left|\frac{1-k}{1-\frac{r_0}{r_{cr}}}\right|=\frac{\alpha_2}{C_z}t_z,$$

$$\alpha_2 = 12.66 D_z\left(C_z - C_0\right),$$

$$k(t)=\frac{r_1}{r_{cr}}, \quad r_{cr}=qr_0^2 I_g,$$

$$q=\frac{\left(1+z_2 Q_2\right)}{\left[2z_1 z_2 Q_1 D_1 F\left(C_z - C_0\right)\right]}.$$

The table shows a numerical dependence of the   value on   and estimates the time of pit stabilization;

$$k(t)=\frac{r_1(t)}{r_{cr}}, \quad t=t_z.$$

Values of t_k and $r_{cr}=qr_0^2 I_g$ for the resistive layer of a pit at different $k(t)$ and currents I_g $\left(Fe,\ 3\ M\ \ NiCl_2,\ r_0 = 0.07\right)$

I_g, A/cm^2	t_k, s			r_{cr}, cm
	$k=0.6$	$k=0.8$	$k=0.9$	
1	6×10^2	2.2×10^3	4.4×10^3	0.48
2	2.4×10^3	8.7×10^4	1.75×10^4	0.836
5	1.5×10^4	5.5×10^4	11×10^4	2.1
10	6.1×10^4	2.2×10^5	4.4×10^5	4.18
100	6.1×10^6	2.2×10^7	4.4×10^7	41.8

$\sigma(t)$

The problem of a hemispherical pit (Fig. 13) also deserves attention. In this case, the distribution of the potential φ in the resistive layer is determined by the Laplace equation

$$\Delta\varphi=0, \quad -k\frac{\partial\varphi}{\partial r}\Big|_{\sigma(t)}=i_z\left(\sigma\right), \quad -k\frac{\partial\varphi}{\partial\xi}\Big|_{z(t)}=zFj\left(\Sigma\right).$$

These expressions represent a principle formulation of the problem of the dissolution of bottom surface   of a pit. They correlate the kinetics of this process and the shape of the pit. This problem is considered in [1].

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