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Cooperative models of dissolution of metal crystals

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ABSTRACT. The results of new approaches to the problem of dissolution of metal crystals in electrolytes are summarised and analysed. The analysis is based on consideration of a metal/electrolyte interface as a system of two coupled, structurally organised, condensed phases in which cooperative excitation processes take place. Excitation (suppression) of dissolution is discussed in terms of local initiation (inhibition) of surface linearly extended defects of the crystal structure. The ideas proposed are supported by experimental results.

The bibliography contains 63 references.

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I. Introduction

The study of the mechanism of dissolution of metals is a task with many practical applications (protection from corrosion, cementation, electrochemical technologies, etc.). In the last few years new models of dissolution of metals have been proposed[1–3] and in these models the dominant role is assigned to surface defects. The kinetics of dissolution of a metal depends on its crystallographic characteristics governed by the type of face. Different dissolution mechanisms are proposed for flat atomically smooth singular *F* faces and for rough *S* and *K* faces that have surface defects.

According to the Ising and/or cluster representations, the adsorption centres on the surface of a metal form structure elements which are short in one dimension ($\leqslant 10a$, where a is the lattice parameter). The structure motif in adsorbed films of inhibiting surfactants depends on predominance, on the surface of a dissolving crystal, of faces with a specific orientation (*hkl*). There is a considerable interest in the dissolution of rough *S* faces with linearly extended surface defects such as steps (ledges). In accordance with the terrace-step-kink (TSK) or terrace-ledge-kink (TLK) model, the terraces are closely packed, whereas extended defects (steps or ledges) carry highly active centres known as kinks, which represent projections of the step edge (Fig. 1).

The possibility of appearance of kinks on steps as a result of thermal fluctuations was first demonstrated by J Frenkel (1945). Heating of modified metal surfaces in vacuum gives rise to monatomic steps with a surface roughness (r). Formation of kinks increases greatly r. An estimate of the roughness of a step due to the formation of kinks (r_K) is important in estimates of corrosion and, if allowance is made only for the first coordination sphere (nearest neighbours), it depends nonlinearly on the metal–metal binding energy (E_{M-M}):

$$r_K = [\sinh(E_{M-M}/2k_BT)]^{-1}$$

where k_B is the Boltzmann constant and T is the absolute temperature.

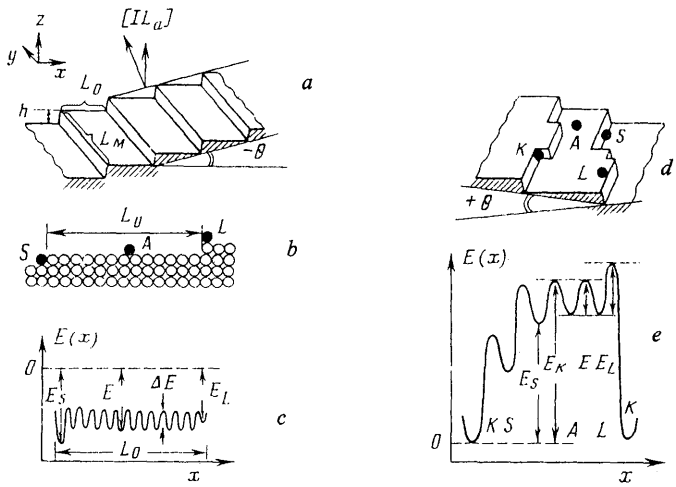


Figure 1. Energy diagram of adsorption of particles on *S* (*a*–*c*) and *K* (*d*, *e*) faces of a crystal. The diagrams show the binding energies of an adparticle on a terrace *A* (E), at the ledge of a step *L* (E_L), on the face of a step *S* (E_S), and in a kink *K* (E_K); the rest of the notation is explained in the text.

When a metal is in contact with an electrolyte, nonlinear wave processes occur on the surface of the metal crystal and they generate roughness of a dissolution step. Even if the description of dissolution is limited to a planar (two-dimensional) model, computer modelling of the displacement of dissolution steps $<IL_a>$ (L_a is a lattice step and I is the number of steps) on a cubic face of a Kossel crystal[4] shows—if allowance only for the interaction with the nearest neighbours is taken into account—that the process of dissolution does not reduce to the events of ionisation on a metal at specific active centres. The dissolution and growth of crystals is

modelled on the basis of ideas put forward by Gilmer.[5] It had become obvious that when the roughness is strong (i.e. when the Jackson–Temkin factor $E_{M-M}/2k_BT$ is small), the opposite to dissolution, i.e. crystallisation, involves cooperative attachment of chains of atoms and not consecutive growth of a new phase at an active centre.

From the thermodynamic point of view the appearance of roughness during the process of dissolution is the result of the 'fight of a crystal to ensure survival'. This should lower and then stabilise the rate of corrosion. However, when a metal/electrolyte system is acted upon by an external perturbation (for example, when an anodic potential is applied, a crystal is deformed in a solution, activating ions are introduced into an electrolyte, or when a metal is hydrogenated), linearly extended defects (waves) moving on the surface and characterised by a higher chemical activity may produce the opposite effect, i.e. they may prevent deceleration of the corrosion process with time.

It follows from the diagram demonstrating changes in the free energy of an adsorbed atom in the TLK model (Fig. 1) that an adsorbed surfactant particle experiencing a periodic field of the potential E on a terrace (position A) reaches states with higher coordination (K, S, L). The ease and strength of adsorption at a kink (position K) in the case of a low concentration of a surfactant in a solution ($C_{surf} = 10^{-4}-10^{-3}$ M) makes it possible to account for numerous observations of effective nonmonolayer ($\theta_{surf} < 1$ monolayer) inhibiting adsorption.

Stepped surfaces (Fig. 1*a*) are described by the Miller indices of the terraces and steps; for example, in the case of the b.c.c. and f.c.c. crystals we have $[n(110)-(011)]$, $[n(110)-(001)]$, $[n(111)-(001)]$, etc. Some ('magic') vicinal stepped surfaces are stable because of reconstruction of the steps. The width (L_0) of a stabilised step is close to an integral multiple of a superstructure period.[6] In the course of dissolution of a polycrystalline solid its surface is bounded by stabilised grain faces with specific values of (hkl), which are the planes of b.c.c. crystals with the $[n(110)-(001)]$ steps. Less closely packed $[n(110)-(0\bar{1}\bar{1})]$ or $[n(110)-(011)]$ vicinal faces are more stable and carry less strongly bound adatoms. The rate of dissolution of a metal then decreases with time.

However, in spite of the physical attractiveness of the TLK model (ionisation of a metal is regarded as a system of consecutive transitions of metal ions M from the lattice into a solution: $M_L^{n+} \rightarrow M_S^{n+}$), it fails to describe satisfactorily the process of dissolution at high and/or very low corrosion rates. The first problem is the disagreement between the characteristic times of adsorption of the solution particles forming a surface intermediate layer and the characteristic times of elementary events of the ionisation of a metal. The second problem is related to high densities ($i_a \geqslant 10^4$ A/m^2) of anodic currents in the electrochemical process at defects on the K faces; such high local rates cannot be retained for a long ($>10 \times 10^3$ s) time. If the dissolution rate depends only on the local concentration of the electrolyte, then in the absence of diffusion limitations we can expect only spherical corrosion pits. The third problem is the delocalisation of atoms in the first layers of the crystals, which are in contact with a liquid phase, at sufficiently high anodic overvoltages ($\eta_a > 0.2$ V). A special structurally disordered state appears in such layers.

It is therefore necessary to consider alternative mechanisms of dissolution of a metal which allow for the cooperative ionisation events when the first surface layers of the atoms of the metal crystal go over to an excited state. Such resonant excitation creates a quasi-liquid (quasi-crystalline) state in a surface layer of a metal crystal and it is characterised by a short-range order typical of a two-dimensional ($2-D$) adsorption layer in an electrolyte. Concentration and deformation waves appear on the surface of a dissolving crystal as a result of collective excitations in the contact layers of the metal/electrolyte system. Resonant tunnelling of light chalcophilic particles near extended surface defects no longer occurs because of enhancement of the localisation of adsorbed solution particles. Therefore, the action of a corrosion inhibitor (when C_{surf} = const) is manifested more effectively on a stepped surface than on one which is atomically smooth.

This review summarises the results of theoretical investigations of dissolution of transition metals in electrolytes, which is treated by a new approach to the surface layers. A phase transition occurs in such contact layers by excitation of linear one-dimensional ($1-D$) surface defects.

II. Kinematic theories of dissolution

The first theoretical concepts allowing for cooperative effects during dissolution of crystals, known as kinematic theories, were proposed by Lighthill and Whitham[7] and by Frank,[8] and then extended by Hirth, Rouse, and Pound.[9] An analogue of such work in electrochemistry is the unusual approach of Hertz,[10] who considered collective effects of motion of electrolytes without recourse to the concepts of a 'charge' or 'electrochemical potential' and used only the equations for a nonlinear oscillator.

A microscopic approach to dissolution on singular and diffuse (nonsingular) faces of metal crystals shows that a morphological manifestation of a sequence of elementary events involved in the transfer of atoms from a crystal to a liquid phase involves formation of dissolution steps of different height h. The process of dissolution begins as a local form at a subsurface structure defect of a passive metal and rapidly changes to generation of dissolution steps (Fig. 2). Tunnelling electron microscopy has shown that local forms (0.4–0.6 mm) are observed on a passive surface of a crystal of stainless steel even as a result of brief (< 100 s) contact with a 3% aqueous solution of NaCl. The velocity of dissolution steps (V_S) increases on reduction of the density of these steps $\beta_0 = L_0^{-1}$ (which is the number of steps per unit length). In the case of a diffuse surface the height h and the flux of dissolution steps $J_S = f(\beta_0)$ depend strongly on the surface indices (hkl), on the degree of supersaturation of the solution $\Delta\gamma^*$, on the applied electrode potential E, and on the kinetics of diffusion processes at the phase boundary. An important experimental observation is that local dissolution nuclei, usually formed at a subsurface structure defect, grow quite independently and that dissolution steps propagate along the surface without 'noticing' one another.

Even the early kinematic theories of dissolution of ionic crystals deal with systems of $1-D$ (steps) and $2-D$ (terraces) regions with a low step concentration β_0, when the boundary effects can be ignored. Enhancement of dissolution of ionic crystals at steps is attributed to breakdown of the electrical neutrality at a phase boundary and to the long-range effects of steps in the process of their decoration with impurities from the solution. The steps on nonsingular faces of metal crystals have a considerable influence on surface reconstruction in the course of adsorption of the solution particles. A theoretical description of the reconstruction process is based on the theory of phase transitions. This process always occurs on the surface of a metal considered as the main defect of a solid.[11] Adsorption of the solution particles changes the kinetics and

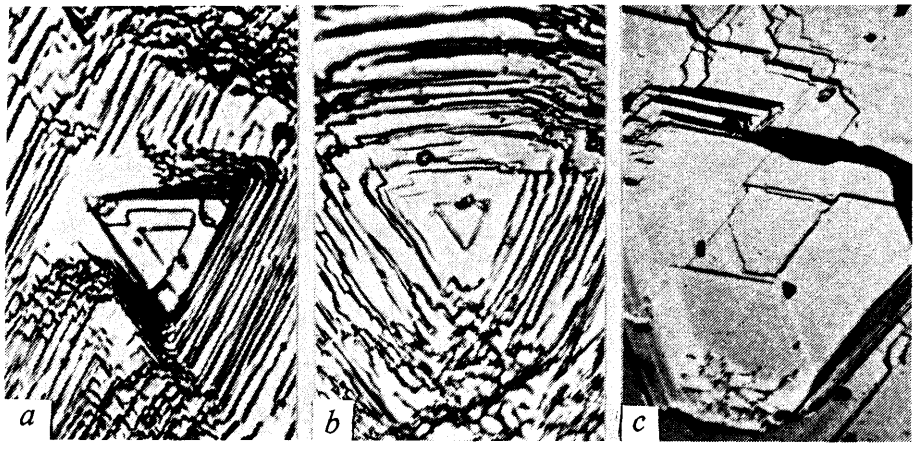


Figure 2. Evolution of dissolution steps beginning from a single subsurface defect in a system formed by (111)Ni and 1 M HNO_3 solution, obtained using an anodic current of density i_a = 50 A/m^2; 298 K; magnification 960. Time t (s): *a*, 20; *b*, 40; *c*, 60.

sometimes even the phase diagram because of reconstruction. The rate of dissolution i of a crystal in an electrolyte is largely determined by supersaturation with metal ions $\Delta\gamma^*_{M^{n+}}$ and with a surfactant $\Delta\gamma^*_{surf}$ at the phase boundary, and by the diffusion of M^{n+} in the bulk of the solution.

III. Dissolution in the form of a monatomic step

An ideally atomically smooth singular low-index F face should form a monatomic step during dissolution and the step should move from the extreme positions on a crystal. Experiments[12] have shown that such monatomic steps appear when the electrode potential is 'cycled' and a surface is prepared carefully under near-equilibrium conditions from a high-purity single crystal.

The shape of monatomic steps, which represent Frenkel–Kontorova surface dislocations, can be described at a given moment t by a wave function

$$\varphi(x, t) = \pi - 4\arctan\{\exp[-(x_i - V_i t)/kD_V]\} \quad (1)$$

where kD_V is the half-width (size) of the Frenkel–Kontorova dislocations; D_V is the diffusion coefficient (viscous); V_i is the velocity of an i-th atom of size a moving from one cell to another; $x_i = ika$ is the diplacement. The mathematical solution given by Eqn. (1) represents a domain wall with a kink; it is obtained by solving the nonlinear differential equation of the sine–Gordon type

$$\varphi_{tt} - \varphi_{xx} + \sin\varphi = 0, \quad (2)$$

where $\varphi = \Phi(X)$ and $X = x_i - V_i t$. The master equation for $\Phi(X)$ is

$$\tfrac{1}{2}\left(V_i^2 - 1\right)\Phi_x^2 + 2\sin^2 \tfrac{1}{2}\Phi = A,$$

where A is a constant of integration related to the wave amplitude.

It follows from an investigation of Eqn. (2) that the appearance of a dissolution step and its subsequent behaviour (including the stability of a step wave against external perturbations by an electrolyte) depends on the initial velocity and the initial amplitude of the wave.[13] Dissolution steps stable in the presence of such perturbations form in at least two cases. The first is represented by $A < 0$ and $V_i^2 - 1 < 0$, when helical waves obeying the following relationships are observed

$$\Phi_x = \pm\left[\frac{2}{1 - V_i^2}\left(|A| + 2\sin^2 \tfrac{1}{2}\Phi\right)\right]^{1/2}, \quad (3a)$$

where Φ_x may increase or decrease. In the second case we have $A > 2$ and $V_i^2 - 1 > 0$, when helical waves obeying the following relationship appear:

$$\Phi_x = \pm\left[\frac{2}{V_i^2 - 1}\left(|A| + 2\sin^2 \tfrac{1}{2}\Phi\right)\right]^{1/2}. \quad (3b)$$

The source of the Frenkel–Kontorova dislocations may be the edges of a crystal, where the characteristics of the displacement processes reach their critical values, or the numerous subsurface defects. When the solution particles are adsorbed, the local positions of a strong disturbance of the translational invariance of a crystal stimulate the motion of a step wave.

In the case of a monatomic dissolution step (a Frenkel–Kontorova dislocation) on a metal crystal the velocity of its propagation in a surface layer is governed primarily by the density ρ of the metal and by the surface tension of stress γ_S:

$$V_S = \left(2\pi\gamma_S/\rho b\right)^{1/2} \sin\left(\frac{\pi a}{b}\right) \Big/ \left(\frac{\pi a}{b}\right). \quad (4)$$

If the distance between the atoms is $b \gg a$ (where a is the lattice parameter), then bearing in mind that $\sin x \approx x - x^3/3!$, we find that Eqn. (4) can be reduced to

$$V_S = (2\pi\gamma_3/\rho b)^{1/2}\left(1 - \frac{\pi^2 a^2}{6b^2}\right). \quad (5)$$

Eqn. (5) is used to describe dissolution of f.c.c. and h.c.p. crystals in view of the anisotropic dependence of the corrosion rate on (hkl).

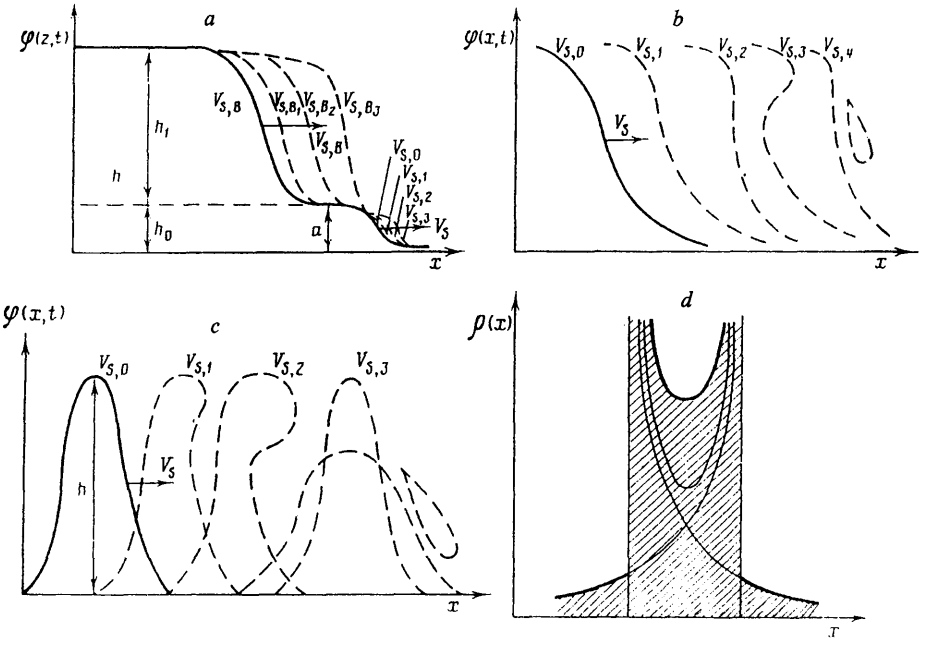


Figure 3. Changes in the surface profile of a dissolving crystal in the case of a shock wave (*a*), a kink (*b*), and a solitary wave (*c*), and characteristic features of the density of a crystal in the course of evolution of a kink (*d*).

Such an integral characteristic as the density $\rho = f(S_{hkl})$, where S_{hkl} is the reticular density of a crystal face, may be modified anisotropically on adsorption of the solution particles (reconstruction of the surface layer). The distance between the first and second (Δa_{12}) layers along the normal to the surface is less than the corresponding distance in the bulk. The changes in Δa_{12} appear under the action of unidirectional mechanical surface tension forces and the stimulus for the reconstruction is provided by the energy gained by the electron states as a result of a small deformation of the surface structure. The appearance of a monoatomic step is usually analysed in terms of the surface stresses γ_S, directional strains $\vec{\varepsilon}$, displacements x_i, and the elastic energy $E_{L,a}$ of a step of atomic length. The energy of appearance of a Frenkel–Kontorova dislocation E_{FK} originates mainly from perturbations of the electron and phonon subsystems, and it has two components: an elastic energy E_{La}, associated with directional strains $\vec{\varepsilon}$ in the course of phase modification of the surface layer, and a linear energy E_K, localised at distances $<k$ (Burgers vector) and estimated in terms of the free energy of an outer face of the step.

A strong reduction in γ_S as a result of adsorption of nucleophilic surfactants (such as halogen ions, OH^-, H^-, etc.) on a hydrophilic surface of a *d*-metal reduces V_S and slows down correspondingly the dissolution rate. An adsorbed surfactant quenches vibrations (reduces the vibration amplitude Φ) in the surface layer of atoms and in the final analysis destroys the resultant surface Frenkel–Kontorova dislocation.

These ideas are based on a Kossel–Stranski model of a defect-free crystal on the surface of which a particle may be in various energy states (Fig. 1*d*). A description of a model of monatomic parts of the first surface layer can be given in two variants: as a shock wave (kink) and as a solitary wave ('rolled-up carpet'). In the former case (*i*) a nonlinear diffusion equation of the Burgers type is considered:

$$\varphi_t + \varphi\varphi_x = D_V\varphi_{xx}, \qquad (6)$$

where D_V is the viscosity of a concentration wave $C(z, t) = C(t)\exp(ikz)$, in which the dependence of the particle concentration C on time t along the coordinate z, directed into a solution, obeys the second Fick law $dC/dt = D_V(\partial^2 C/\partial z^2)$ in the electrode layer (Fig. 3*a*). The amplitude of a concentration wave in a solution is h_1 and the velocity of its motion $V_{S,B}$ is higher than the velocity of a kink V_S in the first surface layers of a crystal of thickness a ($V_{S,B} \gg V_s$, $h_1 \gg a$). The profile of a kink (Fig. 3*b*) corresponding to Eqn. (1) changes in the course of dissolution. In the case of the curves representing the dependence of $\varphi(x, t)$ on x there are regions with a negative slope [$d\varphi(x, t)/dx < 0$, represented by the curve $V_{S,3}$]. From this moment we can expect resonant excitation of a surface layer of a metal and a phase transition $M_L^{n+} \rightarrow M_S^{n+}$, corresponding to the position $V_{S,4}$. The amplitude does not change in the course of the subsequent nondissipative development of the process.

In the phase space on a rolled-up surface, when the projection ($0z$, $0x$) is nonmonotonic — $dx/dt > 0$ above the $dx/dt < 0$ below — the path of a particle in the course of the $M_L^{n+} \rightarrow M_S^{n+}$ transition is such that the motion is slow on the upper and lower planes, but it is catastrophic at the fold.

We shall now analyse the process. It is known[14] that a mathematical description of a quantum-mechanical potential differs from the expression for the potential energy by a multiplicative constant. Any system tends to assume a position which minimises its energy and, if there are several minima, these minima can be identified with different phase states. The minima of the relevant

potential reflect the phase states. The catastrophe theory[15] shows that if a function depends on parameters, then there are such zones or such states that—depending on the set of parameters—a smallest deviation results in a transition from one phase state to another.

We shall consider a potential of the type

$$E(x) = E_0 - a_0 \frac{e^2}{\Omega^{1/3}} x + b \frac{e^2}{\Omega^{2/3}} x + c \frac{e^2}{\Omega} x^3 + d \frac{e^2}{\Omega^{4/3}} x^4,$$

where Ω is the atomic volume; $a_0 = 6 - 12/\sqrt{2} + 8/\sqrt{3} - \ldots$ is the Madelung parameter which depends on the geometry of the metal crystal lattice; b, c, and d are constants that determine the properties of the metal.

We shall find the surface of the minimal potential

$$a_0 \frac{e^2}{\Omega^{1/3}} + 2b \frac{e^2}{\Omega^{2/3}} x + 3c \frac{e^2}{\Omega} x^2 + 4d \frac{e}{\Omega^{4/3}} x^3 = 0$$

and reduce it to the form

$$x^3 + rx^2 + sx + t = 0,$$

where

$$r = \frac{3c}{4d} \Omega^{1/3}, \quad s = \frac{2b}{4d} \Omega^{2/3}, \quad t = \frac{a_0}{4d} \Omega.$$

The boundary of a catastrophic phase transition lies on a surface described by the equation

$$\left(\frac{P_L^3}{3}\right)^3 + \left(\frac{Q_L}{2}\right)^2 = 0, \tag{7}$$

where

$$P_L = \frac{3s - r^2}{3}, \quad Q_L = \frac{3r^3}{27} - \frac{rs}{3} + t.$$

The resultant fold-type singularity is a V-shaped curve with a kink in the space of the parameters. Inside the region bounded by this curve the system is stable. At the boundary of the region the above function has three roots, two of which are identical. Consequently, in the case of the inner part of the region there are three real but different roots. A slight 'tremor' may displace a point from the boundary into the region in question, giving rise to a multisheet surface of a metal and a phase transition at the metal/electrolyte boundary between the condensed media. An analysis of Eqn. (7) shows that the occurrence of a catastrophe does not depend on E_0, e, or Ω: it is related only to the constants a_0, b, c, and d.

What is the process that gives rise to a concentration wave? In a general model of dissolution this is very important, since a nondissipative process of propagation of a dissolution step in a surface layer of a crystal may become a resonant effect on interaction with a concentration wave that appears in the adjoining electrolyte. The functional relationship between $V_{S,B}$ and V_S is manifested by a monotonic increase in V_S on increase in $V_{S,B}$. If $h_0 \gg a$ (where a is the lattice parameter) and the front of a concentration wave overtakes the front of a kink in the metal investigated, a solitary wave (soliton) appears (Fig. 3*c*) and its evolution in a nondissipative scenario involves either conservation of its amplitude or a reduction in the amplitude accompanied by a simultaneous broadening of the face of the wave. In time such a solitary wave may degenerate into a 'rolled-up carpet',

Dissolution differs from crystallisation of a metal because the motion of the M^{n+} ions is in the former case to a condensed medium with an undersaturation of M^{n+}, whereas in the latter case the motion of M^{n+} occurs from a supersaturated state. In the course of dissolution the M^{n+} particles may not 'notice' one another. However, the ionisation occurs at inequivalent positions on the crystal surface and, therefore, after a time t the fast particles (from defects) will overtake the slowly moving ones.[15] The velocity field V_S becomes triple-valued: three fluxes of particles may cross the same point in space (Fig. 3*b*) and their velocities at each point are different. If initially the density of the medium at a point x_0 is $\rho_0(x_0)$, it changes with time giving rise to a density singularity: at a distance x from the point on the fold the density is of the order of $(I\Omega)^{-1/2}$ (Fig. 3*d*). After a sufficiently long time t at the points with an infinitely high density of the medium we can expect formation of particle clusters, i.e. the $M_L^{n+} \rightarrow M_S^{n+}$ transition takes place. This conclusion applies also to a multidimensional space. Therefore, a concentration wave is excited in a surface layer of the electrolyte adjoining a metal because of inequivalence of the active points on the surface of the metal. Such a wave is coupled resonantly to a surface layer of the metal and excites there a kink (Fig. 3*b*) or a solitary wave (Fig. 3*c*).

The concentration wave penetrates the electrolyte when the matching of the solid (crystal) to the electrolyte supersaturated with M^{n+} is coherent. A combination of the equations for the dissolution rate (representing the density of the flux of the M^{n+} particles) $i = i_0 \sin V_j t$ (i_0 is the exchange current density) with the second Fick law leads to an equation describing a concentration wave with an amplitude that decays with depth (along the coodinate z) in the solution[16]

$$C(z,t) = C_0 + \Phi \exp\left(-\sqrt{\frac{V_j}{2D_i}} z\right) \sin\left(V_j t - \sqrt{\frac{V_j}{2D_V}} z - \frac{\pi}{4}\right), \tag{8}$$

where Φ is the amplitude, which is proportional to i_0, and V_j is the velocity of the wave (its angular frequency).

It follows from Eqn. (8) that

$$\frac{\partial C(z,t)}{\partial z} = -\Phi \sqrt{\frac{V_j}{D_V}} \exp\left(-\sqrt{\frac{V_j}{2D_V}} z\right) \sin\left(V_j t - \sqrt{\frac{V_j}{2D_V}} z\right). \tag{9}$$

The amplitude Φ of the concentration wave in the electrolyte and the depth of its penetration z_0 into the electrolyte fall proportionally to $V_j^{1/2}$.

When a kink or a solitary wave propagates in a metal, the value of the viscosity coefficient D_V depends on the action of periodic forces in a regular lattice, when

$$D_V \simeq \nu_L^{-1} \simeq 1 \text{ P}^{-1},$$

where ν_L is the viscosity of a crystal (sound attenuation coefficient), or in the absence of a periodic short-range of a crystal when

$$D_V \simeq D_F / K_C a^2 \simeq 10^{-8} \text{ P}^{-1},$$

D_F is the diffusion coefficient of phasons and K_C is the elastic (Young's) modulus of a crystal.[17] If D_F is small, the solution of Eqn. (6) differs from Eqn. (1) and corresponds to a shock wave (kink) of the type

$$\varphi(x, t) = kD_V[1 - \tanh^{1/2}(kz - D_V k^2 t)], \tag{10}$$

which obviously appears when filamentary single crystals of metals with perfect singular surfaces are dissolved (Fig. 3*b*). In the limit

$z \to \infty$, we have $(x, t) \to 0$, whereas for $z \to -\infty$, we have $(x, t) \to 2kD_V$. The approach of a shock wave to the edge of a crystal results in an abrupt fall in the concentration and excitation of a new concentration wave

$$C(t) = C(t_0) \exp[-\alpha(k)t], \alpha(k) = D_V k^2, \quad \text{(I)}$$

which moves in the opposite direction. Near the edge the properties of a crystal are unusual: the Gaussian curvature ($R_G = r_1 r_2$, where r_1 is the largest and r_2 is the smallest curvature) has a finite discontinuity of universal amplitude; the fall of the transverse curvature is described by an universal exponent.

In the second case (*ii*) an allowance is made for the fact that crystals very rarely have singular faces and that diffuse (nonsingular) faces have a ready-made step right from the beginning. The subsequent development in the kinematic theories of dissolution of diffuse K faces is due to Lighthill and Whitham[7,13] who based their ideas on the models of dissolution of the surfaces of a crystal which have terraces, steps and kinks on the steps (TLK model). The steady-state velocity of linear steps in accordance with the 'rolled-up carpet' mechanism, representing consecutive detachment of a semi-infinite chain of atoms in the upper layer from atoms in the lower layer, can be described by the following nonlinear relationship containing parameters which can be determined experimentally:

$$V_S = 2K\bar{x}_S \tanh(L_0/2\bar{x}_S) D_V \Omega (C_0 - C_0')/(h\delta), \quad (11)$$

where $\bar{x}_S$ is the mean free path in the diffusion of the M^{n+} ions on a step; $\delta = 4.5(D_V/\nu_c)^{1/3} (\nu_c \bar{x}_S / V_L)^{1/2}$ is the thickness of the Nernst diffusion layer (in aqueous solutions this thickness is $\delta \approx 10^{-5}$ monolayer); ν_c is the kinematic viscosity of the solution; V_L is the velocity at which the solution moves away from the steps; $K = f(\tan\theta) \equiv f(P)$ is a kinetic coefficient; C_0 is the equilibrium concentration of the M^{n+} ions in the solutions; C_0' is the concentration of the M^{n+} ions in the metal near the phase boundary. The passage of a dissolution step along the surface of a crystal at a velocity V_S is determined by the relationships between the constants in Eqn. (11). The kinetic coefficient, depending functionally on a slope θ of a given face relative to a singular face (Fig. 1), is governed by the process of incorporation of atoms at the steps[18]

$$K(P) \simeq a\nu_D (a/\bar{L}_K) \exp(-E_{M-M}/k_B T),$$

where $\bar{L}_K$ is the average distance between the kinks on the steps and $\nu_D \approx 10^{13}$ s^{-1} is the Debye frequency of vibrations of the surface atoms.

The velocity of translational motion of a step reaches its limiting value $V_{S,\infty}$ when the hyperbolic tangent with the argument $\bar{x}_S \approx L_0/6$ or $L_0/2\bar{x}_S \approx 3$ in the relationship (11) becomes equal to 1:

$$V_{S,\infty} \simeq D_V \Omega (C_0' - C_0) L_0 / 3\delta h. \quad (12)$$

An analysis of Eqn. (12) shows that if $C_0 \to C_0'$ or, more accurately when the activities of the M_S^{n+} ions in the solution in the surface of the investigated crystal and of the M_L^{n+} ions in the metal are equal, the velocity of a dissolution step falls to zero. The size of the active surface which appears as a result of the passage of dissolution steps is determined by their density $\beta_0 \equiv L^{-1}$ and their height h:

$$L_0 h \equiv h/\beta_0 \simeq (hk_B T/19\Omega E_M) \ln(C_0' - C_0). \quad (13)$$

The relationship (13) includes the free surface enegy E_M, which rises and thus reduces the active surface of a metal. The difference between the concentrations $C_0' - C_0$ determines the supersaturation $\Delta\gamma^*$ at the phase boundary. In other words, we have

$$V_S \sim \Delta\mu = \mu_K - \mu_L = k_B T \ln(C_0'/C_0) \simeq -k_B T \Delta\gamma^*,$$

i.e. the velocity of a dissolution step is proportional to the difference between the chemical potentials of the M^{n+} ions in the solution and of the metal lattice.

The growth (dissolution) rate of a crystal normal to a singular F face in electrolytes can be estimated from a relationship similar to Eqn. (11):

$$V_{S,\perp} = K\Omega C_0 (\Delta\gamma * - \Delta\gamma_{cr}^*), \quad (14)$$

where $\Delta\gamma_{cr}^*$ is a critical supersaturation governed by the mechanism of growth (dissolution) of a step, which may be two-dimensional nucleation or a dislocation mechanism. The critical supersaturation $\Delta\gamma_{cr}^*$ is different near the surfaces of large and small crystals and it depends strongly on the index (*hkl*) of the surface.

The undersaturation near the surface of a small crystal results in its faster dissolution; in the case of a polycrystalline aggregate the smaller crystallites (grains) with the orientations of the faces characterised by smaller values of E_M disappear first.

Slowing down of the tangential motion of the dissolution steps may be the result not only of lowering of E_M, but also of crystallographic features of vicinal faces. It had been mentioned earlier[6] that specific 'magic' vicinal surfaces are stabilised by reconstruction. An investigation of the surface structure and of the energetics of the (100)Au and (111)Au vicinal faces by the model of multiparticle forces and molecular dynamics has shown that in the case of surfaces of the (K11)Au(100) type, where $K = 3-45$, the 'magic' orientations correspond to the (111) and (511) faces. These surfaces are characterised by local surface energy minima ($E_M = 1.06 \times 10^4$ and 1.04×10^4 meV/nm^2, respectively) of the dependences of the surface energy on $P \equiv \tan\theta$ [where the tilt angle is $\theta = 0-0.5$ rad, defined by $\theta = \tan^{-1}(h/L_0) = \tan^{-1}(h\Delta\mu/19\Omega E_M)$]. Stabilisation of other vicinal faces occurs as a result of formation of a set of these 'magic' orientations for surfaces tilted slightly from (100)Au. In the case of the surfaces ($H + 1$, $M - 1$, H) close to (111)Au, the 'magic' vicinal faces are different: they correspond to minimisation of the energy for $H = 11, 22, \ldots$, when the step with L_0 is a multiple of the superstructure period.[19] Therefore, faceting of the surface by the motion of monatomic steps and formation of 'magic' orientations may reduce the rate of dissolution of the metal to zero. This unexpected result of recent experimental investigations has not yet been considered properly from the practical point of view.

It also follows from Eqn. (11) that an increase in the height h of the steps should slow down the velocity of their motion. A kinetic and morphological analysis of a metal/electrolyte contact between condensed phases, based on the experimental results, demonstrates the opposite: the value of V_S increases on increase in h. This conflict is implicit in the very 'rolled-up carpet' model, which has been applied successfully to monatomic spallation when $h \approx a$. If $h \gg a$, a solitary wave 'collapses' (see curve $V_{S,2}$ in Fig. 3*c*) and the velocity of this wave falls strongly.

Determination of the rate of growth of crystal faces in accordance with the $2-D$ nucleation mechanism,[20] shows that difficulties associated with the relationship between V_S and h can be overcome. The rate of normal growth of a crystal face due to the motion of a growth step is

$$V_{S,\perp} = hi_n S \Big/ \left[1 + \left(S/\beta b_n^{1/3}\right)\left(i_n/V_S\right)^{2/3}\right], \quad (15)$$

where $i_n = f(\Delta\gamma^*_{cr})$ is the nucleation rate; S is the area of the growing face; $\beta \approx 1$; b_n is the shape factor (in the case of dome-shaped nuclei, we have $b_n = \pi$). Eqn. (15) had been checked by computer modelling using the Monte Carlo methods and by experimental studies of electrochemical nucleation.

In Eqn. (11) the quantity $\bar{x}_S$ for one dimensional diffusion-like random motion is

$$\bar{x}_S \equiv \left\langle U_x^2 \right\rangle^{1/2} = \left(2D_V t\right)^{1/2},$$

whereas in the case of two-dimensional and three-dimensional motion, we have, respectively,

$$\bar{x}_S = 2(D_V t)^{1/2} \text{ and } \bar{x}_S = (6D_V t)^{1/2}.$$

In a surface nonisotropic layer of a crystal the rate V_S must be regarded as dependent on the action of directional forces $\vec{\varepsilon}$ (for example, a gradient of particle concentrations in the regions between the phases). We then have

$$\vec{\varepsilon} = -\frac{\partial}{\partial x} k_B T \ln \frac{C'_0}{C_0} = -\frac{k_B T}{C'_0} \frac{\partial C'_0}{\partial x}. \quad (16)$$

Eqn. (16) follows from generalisation of the Fermi–Dirac distribution to the case of a transition between two phases of any charged particle. In the case of directional (drift) velocity of motion of a dissolution step, we can write down[21]

$$V_S = (D_V / k_B T)\vec{\varepsilon}, \quad (17)$$

where ε is proportional to the displacement Δa and to the step height h, and is governed by directional tangential displacements of atoms in a surface layer $< U_x^2 >$:

$$\vec{\varepsilon} = \Delta a \left\langle U_x^2 \right\rangle h. \quad (18)$$

It follows from Eqns. (17) and (18) that the step velocity V_S is proportional to the step height h at low stresses in the surface layer which set the dissociation steps in motion:

$$V_S = D_V \left(\Delta a \left\langle U_x^2 \right\rangle h\right) / k_B T. \quad (19)$$

The differences in the kinetic situation in respect of the step height h appear not only because of the differences between the drift and diffusion of steps, but also largely as a result of nonuniform adsorption blocking of steps with smaller or larger height h by a surfactant.

IV. Multilayer dissolution steps

At high dissolution rates (anodic process) it is usual to find high steps ($h \geqslant 0.1$ μm) on the S faces; the value of h depends on (hkl) indices of the surface: the greater the deviation from singularity, the higher the step. High-index nonsingular faces of transition metals dissolved in electrolytes form the highest dissolution steps the heights of which are considerably higher than those of monatomic layers and they are quite readily distinguishable when examined in an electron microscope (with a resolution of 0.2–0.3 nm).

The height of a step h, multiplied by its length L_M, provides an estimate of an active surface which, combined with the density of steps β_0 given by Eqn. (13), can be used to obtain a preliminary value of the rate of dissolution of individual crystallites in a surface layer of a metal. For example, Fig. 4*a* illustrates dissolution in a galvanostatic anodic process ($i_a = 5 \times 10^2$ A/m^2, 295 K, $t = 120$ s) of a nickel single crystal with a nonsingular stepped surface close to (111)Ni when immersed in a 5% ethanol solution of HNO_3. The degree of deviation of the close-packed singular (111)Ni surface, deduced from $\gamma' = h\beta_0$, is $\gamma' = 0.4$, and we then have $\theta = \tan^{-1}(\gamma') = 15°$. Differences between the rates of dissolution of the individual crystallites of annealed polycrystalline samples of high-purity metals can also be seen quite clearly (Figs. 4*b* and 4*c*). The experimental data reported in Refs. 22 and 23 demonstrate that in the case of b.c.c. structures a higher rate of dissolution is exhibited by the {111} faces which are those with the 'loosest' packing.

It should be pointed out that already in the early kinematic theories[24] it has been assumed that a stepped surface of a metal has a discrete nature and the velocity of the steps depends on β_0. A change in the separation between the steps L_0 results in a discontinuity of the density of the steps; such an effect is observed readily in the case of polycrystalline samples near crystallite boundaries (Fig. 4*d*). Branching of the steps and a discontinuity of their density gives rise to shock waves [see Eqns. (1) and (10) and Fig. 3]. According to the kinematic theory of dissolution the velocity of a single monolayer microscopic step is higher than the velocity of a multilayer shock wave (Ref. 24), which depends directly on the diffuseness of a face

$$V_S = \left(V_0 - V_1\right) / \left(\gamma'_0 - \gamma'_1\right), \quad (20)$$

where the rate of sinking of the metal is $V = (dz / dt) = \beta_0 h V_S$ and the diffuseness if $\gamma' = h\beta_0$, and the subscripts in the above equation correspond to the times t_0 and t_1 ($t_1 > t_0$). Hence it follows that for a fixed density of steps $\beta_0 = \text{const}$ an increase in the height of a step h tends to increase the velocity of a multilayer step V_S. This conclusion is in agreement with an analysis made above [see Eqn. (19)]

Microscopic steps are crystallographic planes[18] with the orientation P which can be determined from

$$P \equiv \left(dz/dx\right) = h\gamma' + hJ_S\left(dx/dt\right), \quad (21)$$

where x is the direction of motion of the steps, z is the direction perpendicular to such motion, and $J_S = V_S h^{-1}$ is the flux of steps at a given point. It follows from Eqn. (21) that in the case (*i*) when the density of steps β_0 is fixed, the orientation of the surface remains the same during dissolution ($P = \text{const}$), whereas in the case (*ii*) for a specific crystallographic orientation, when $P = \text{const}$, the dissolution occurs where

$$(dx / dt) = dJ_S / d\gamma'. \quad (22)$$

In the case (*ii*) the condition of conservation of the steps should be observed. In the absence of external perturbations, Eqn. (22) for a metal/solution system transforms to

$$\frac{dV}{d\beta_0} \frac{\partial \beta_0}{\partial x} + \frac{\partial \beta_0}{\partial t} = 0$$

or

$$\frac{\partial \beta_0}{\partial t} + V_c \frac{\partial \beta_0}{\partial x} = 0,$$

where $V_s(\beta_0) = dV/d\beta_0$. If $\beta_0 = \text{const}$, we have

$$\Delta\beta_0 = \frac{\partial \beta_0}{\Delta x} \Delta x + \frac{\partial \beta_0}{\partial t} \Delta t = 0$$

or

$$\frac{\Delta x}{\Delta t} = -\left(\frac{\partial \beta_0}{\partial t}\right) \Big/ \left(\frac{\partial \beta_0}{\partial x}\right) = V_S.$$

The regions of constant tilt characterised by P = const (kinematic waves) have the same dissolution rates, which agrees with Eqn. (20).

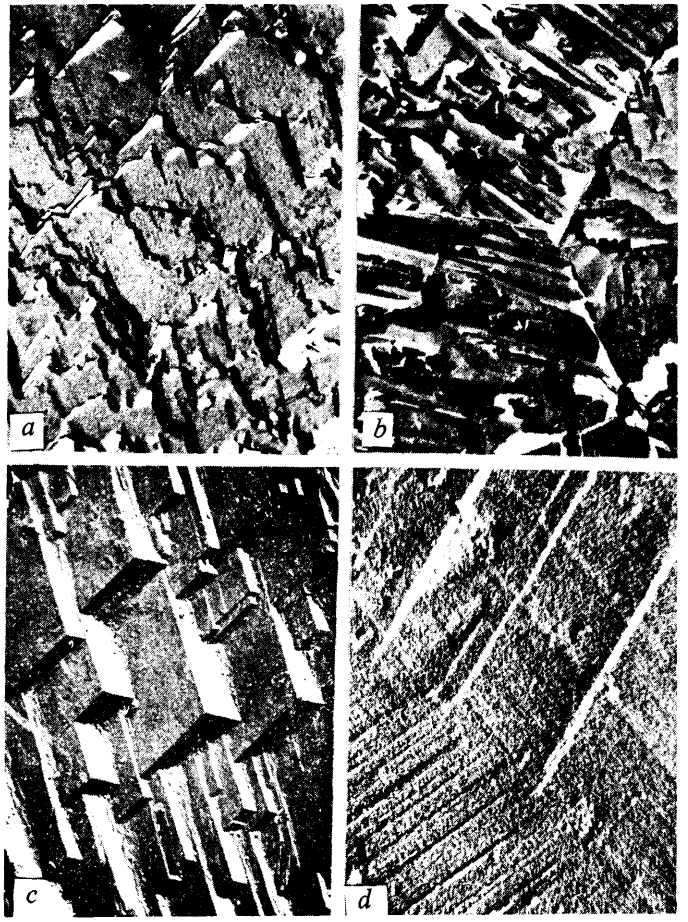


Figure 4. Dissolution steps on a [7(111)–(001)]Ni face (*a*), and on surfaces of high-purity (99.99%) polycrystalline samples of Ni (*b*) and Fe (*c*); magnification 12 000. Photomicrograph *d* shows a discontinuity of the density of dissolution steps on the surface of an Fe bicrystal.

If steps can travel not only along the x direction but also along the y axis on a face of a crystal (xy plane), an equilibrium shape of a crystal is described by[25]

$$z(x, y) = (\partial z / \partial x)x + (\partial z / \partial y)y - E_M(P), \quad (23)$$

where

$$x = (\partial E_M / \partial P)_x, \; y = (\partial E_M / \partial P)_y,$$
$$P = (\partial z / \partial x, \partial z / \partial y) = (P_x, P_y).$$

The term $E_M(P)$ is the free surface energy determined for a (hkl) face within the framework of the TSK model

$$E_M(P) = \gamma_S(\theta_L)|P| + \sigma_S(\theta)|P|^3 + \theta_L|P|^4,$$

where θ_L is the angle between the y axis in the direction of motion of the steps and σ_S is the specific surface energy.

In an analysis of the dissolution mechanism of metal crystals it is necessary not only to deal with the kinetic and morphological differences between the theory and experiment, but also to allow for the fact that the cooperative motion in the surface layer of a crystal (which differs considerably in the physical sense from the bulk) is practically dissipation-free. In a theory of solitons[26] a series of solutions of nonlinear diffusion equations has been proposed to describe a kink or a solitary wave (Figs. 3*b* and 3*c*). In practice it is possible to observe monatomic dissolution steps (Frenkel–Kontorova dislocations), by tunnelling electron microscopy, in an electrolyte and steps of significant height in the range 10^2 nm $\leqslant h \leqslant 10^4$ nm can be studied by optical spectroscopy and by the replica method (Figs. 2 and 4). It should be pointed out that a concentration wave which reaches the edge of a dissolution step may excite the passage of a kink in a plane perpendicular to the initial one. This process can account for the retention of an abrupt face on dissolution steps even after prolonged corrosion (Fig. 4).

We shall now go over from considering dissolution steps in the form of Frenkel–Kontorova dislocations [monatomic steps, see Eqn. (1)] to the dependences that describe the excitation of several surface layers of atoms. If the lattice step of a cubic Kossel–Stranski crystal (see Figs. 1*a* and 1*b*) is denoted by L_a, the potential describing the interaction of an immobile lower layer with the i-th atom in the upper layer is

$$U(x, t) = A[1 - \cos(2\pi x_i / L_a)], \quad (24)$$

where $x_i = ika$ is the displacement of the i-th atom and A is the amplitude.

The mean-square displacements of atoms in surface layers are anisotropic in respect of the dependence on the directions $<hkl>$ in a crystal and depending on its lattice (b.c.c., f.c.c., etc.). Subject to Eqn. (24), we obtain the following equation of motion:

$$m\ddot{x}_i = -2\pi A L_a^{-1} \sin(2\pi x_i / L_a) + \beta(x_{i+1} - 2x_i + x_{i-1}), \quad (25)$$

where making the substitutions $\Phi_K = 2\pi x_i / L_K$, $A = L_a^2 \overline{A}$, and $\beta = \overline{\beta} L_a^{-2}$ (β is the force constant) and going to the limit $L_a \to 0$ can yield one of the forms of the sine–Gordon equation

$$m\Phi_{tt} = \overline{L}_a \Phi_{xx} - (2\pi)^2 \overline{A} \sin \Phi, \quad (26)$$

where m is the mass of a soliton representing a dissolution step.

The solution of the soliton Eqn. (26) is a kink similar to a Frenkel–Kontorova dislocation

$$\varphi(x, t) = 4 \operatorname{arctg}\left[\exp 2\pi x \left(\overline{A}\overline{\beta}\right)^{1/2}\right], \quad (27)$$

which is formed at the expense of an energy

$$E_S = 4\pi^{-1}\left(\overline{A}\overline{L}_a\right)^{1/2}, \quad (28)$$

corresponds to 5–10 eV/atom and localised in a very small volume of a crystal (with a radius not exceeding 5*a*).

In general, the energy of a soliton is proportional to its mass (in accordance with the relationship similar to that used in the special

theory of relativity)

$$E_S = mV_0^2\left(1 - V_S^2/V_0^2\right)^{-1/2}, \quad (29)$$

where V_0 is the velocity of small-amplitude elastic waves (which is the velocity of sound in a metal). It follows from Eqn. (29) that if $E_S \leqslant 1$ eV, the velocity of a dissolution soliton, like that of a dislocation in a crystal, cannot exceed the velocity of sound in a given metal ($V_0 \leqslant 10^3 - 10^4$ m/s). In fact, numerous microscopic observations of the development of the morphology of the surfaces of metal crystals undergoing dissolution demonstrate that the velocities of dissolution steps are relatively low ($< 10^4$ m/s).

V. Soliton dissolution models

It follows from Eqn. (28) that a dissolution step forms a kink if the directional motion of atoms takes place in a surface layer of a crystal. Such motion is local and, as demonstrated by the above analysis, is in the nature of beats. The question is what are the mean-square displacements $(\overline{AL}_a)^{1/2}$ necessary for the appearance of a kink and what are the reasons for the displacements? The reasons can be adsorption of chalcophilic surfactant particles on the surface of a crystal or a charge (electron) density wave. The amplitude of waves moving tangentially relative to the surface (surface Rayleigh waves) decays exponentially with distance from the surface. These elastic waves in the bulk of a crystal represent superposition of waves with longitudinal and transverse components; in the case of surface waves it is not possible to separate the components.[27]

In the approximation of an ideal lattice the thermal vibrations of atoms in deeper layers can be estimated as follows. The distribution of the amplitudes of the vibrations is described by the Gaussian[28]

$$P_L(U) = \left(2\pi\langle U^2\rangle\right)^{-3/2} \exp\left[-U^2/2\langle U^2\rangle\right], \quad (30)$$

where $< U^2 >$ are small amplitudes of the distributions. In the $1-D$ case, we have

$$P_L(U) = \exp\left[-U_x^2/2\langle U_x^2\rangle\right]\left(2\pi\langle U_x^2\rangle\right)^{-1/2}. \quad (31)$$

For cubic crystals, we obtain

$$\langle U_x^2\rangle = \langle U_y^2\rangle = \langle U_z^2\rangle = 1/3\langle U^2\rangle.$$

In the $2D$ case the square of the thermal amplitude of the vibrations is $< U_S^2 > = < U_x^2 > + < U_y^2 >$. The Debye temperature is $\theta_D = h_P \nu_D / k_B$ and, therefore,

$$\langle U^2\rangle = \frac{3h_P^2 T}{m_a k_B \theta_D^2}\left[\Phi\left(\frac{\theta_D}{T}\right) + \frac{\theta_D}{4T}\right], \quad (32)$$

where

$$\Phi(\xi) = \frac{1}{x}\int_0^x \frac{y\,dy}{e^y - 1}$$

is the Debye function, m_a is the mass of an atom, and h_P is the Planck constant. The Debye function can be represented graphically by a straight line when the coordinates are $\Phi(\theta_D/T)$ and θ_D/T; then, in the case of low amplitudes in the distributions, we have

$$\langle U^2\rangle = 439.2\left[\left(\frac{\Phi(\xi)}{x} + \frac{1}{4}\right)\Big/ m_a\theta_D\right], \quad (33)$$

where $\xi = \theta_D/T$. The Debye temperatures and the mean-square deviations are listed in Table 1 for a number of d metals and it follows from this table that the maximum values of θ_D and the minimum values of $< U_x^2 >$ are exhibited by the d metals with a half-filled d shell (Cr, Mo, W). These are the metals that form the most stable oxide structures and have a higher resistance to chemical action. The thermodynamic stability of the transition metals is related to the ease of the $s \rightarrow d$ electron transition; it rises steeply along the $3d < 4d < 5d$ series of metals (and this is accompanied by a rapid fall of θ_D at high values of $< U_x^2 >^{1/2}$).

Table 1. Parameters of d metals at 293 K.

Metal	Type of lattice	a, nm	θ_D, K	$\langle U_x^2\rangle^{1/2}$, nm
V	b.c.c.	0.3024	360	0.0082
Cr	b.c.c.	0.2884	485	0.0061
Fe	b.c.c.	0.2867	420	0.0068
Ni	f.c.c.	0.3524	425	0.0065
Cu	f.c.c.	0.3615	315	0.0084
Nb	b.c.c.	0.3300	275	0.0079
Mo	b.c.c.	0.3147	380	0.0057
Rh	f.c.c.	0.3803	340	0.0061
Pd	f.c.c.	0.3890	275	0.0074
Ag	f.c.c.	0.4086	215	0.0093
Ta	b.c.c.	0.3306	245	0.0064
W	b.c.c.	0.3165	310	0.0050
Pt	f.c.c.	0.3923	225	0.0066
Au	f.c.c.	0.4078	170	0.0087

The displacements of atoms in the surface layers of the metals have their own cooperative characteristics. Anisotropic mean-square displacements are inversely proportional to the frequency ($\nu_D = k_B T/h_P \approx 10^{13}$ s^{-1}) of vibrations of single atoms near their equilibrium positions:[29]

$$\langle \overline{AL}\rangle^{1/2} \equiv \langle U_{\vec{r}}^2\rangle = (h_p/2m_a)\int_0^{\lambda_m} \lambda^{-1/2}\rho_{\vec{r}}(\lambda)\coth(h_p\lambda^{1/2}/2k_BT)\,d\lambda, \quad (34)$$

where λ_m is the maximum value of the square of the frequency; $\rho_{\vec{r}}(\lambda)$ is the spectral density due to the vector $\vec{r}$. Displacements (quasi-stable pulsations) each reach several nanometers. Cooperative displacements of atoms due to the passage of a soliton in the form of a kink facilitate mass transfer of metal ions to a solvated state in the solution $M_L^{n+} \rightleftarrows M_S^{n+}$. The resultant local supersaturation in the electrode layer induces a delay before the appearance of the next soliton. Improvement in convection conditions [lower values of δ and ν_c, see Eqn. (11)] increases the frequency of appearance of a dissolution soliton.

A different soliton solution can be in the form of a solitary wave. We shall base it on the Boussinescq equation[30] for the $1-D$ case. We shall assume that there are N particles with a unit mass m_a and fixed final points; $x_{r,i}^{\rightarrow}$ is the displacement from an equilibrium

position of the i-th particle in the direction $\vec{r}$; then, the equation of motion can be written in the form

$$\ddot{x}_{\vec{r},i} = f\left(x_{\vec{r},i+1} - x_{\vec{r},i}\right) - f\left(x_{\vec{r},1} - x_{\vec{r},i-1}\right), \quad (35)$$

where

$$f(x_{\vec{r}}) = \gamma x_{\vec{r}} + \alpha < x^2_{\vec{r}} >,$$

i.e. the nonlinearity is quadratic and α and γ are the constants which can be determined experimentally. We shall introduce $L_a = \sqrt{2a}$ (lattice step) and define the variable representing the displacement $x = ika$ (here, $k = \sqrt{2}$) as the distance along the lattice; we shall also define the slope $P = dz/dx$ as $x_{\vec{r}} = L_a P$. Then, $\varphi = \partial P/\partial x$ is described by the Boussinescq equation

$$\varphi_{xx} - \varphi_{tt} + 6\left(\varphi^2\right)_{xx} + \varphi_{xxxx} = 0. \quad (36)$$

We shall identify the cases in which a soliton solution is obtained. The existence of such a solution was pointed out by Hiroma.[31] We shall seek the solution in the form $\varphi(\zeta) = \varphi(x - V_i t)$. Substituting in Eqn. (36) and integrating twice from respect to ζ, we obtain

$$\varphi_{\zeta\zeta} = A_\zeta + B - \left(1 - V_i^2\right)\varphi - 6\varphi^2, \quad (37)$$

where A and B are integration constants. We shall assume that $A \equiv 0$. We shall show that in this case there is a soliton described by

$$d^2\varphi / d\zeta^2 = B - \left(1 - V_i^2\right)\varphi - 6\varphi^2. \quad (38)$$

We shall substitute $d\varphi/d\zeta = z$ in Eqn. (38), which gives

$$d^2\varphi / d\zeta^2 = (dz / d\zeta)(d\zeta / d\varphi) = (dz / d\varphi)z,$$

$$zdz = [B - (1 - V_i^2)\varphi - 6\varphi^2]d\varphi$$

or

$$z^2/2 = B\varphi - \frac{1}{2}\left[\left(1 - V_i^2\right)\varphi^2\right] - 2\varphi^3 + D,$$

where D is an integration constant. We shall introduce

$$B\varphi - \frac{1}{2}\left[\left(1 - V_i^2\right)2\varphi^2\right] - 2\varphi^3 + D = f(\varphi), \quad (39)$$

and then we shall integrate Eqn. (39) as the equation of conservation of motion of particles in a field with the potential $f(\varphi)$ bearing in mind that φ and $\zeta = x - V_i t$ are the spatial and temporal coordinates. A solitary wave on the surface of a crystal appears if the roots of the cubic polynomial obey the condition $\gamma = \beta \neq \alpha$, where $\gamma \leqslant \beta \leqslant \alpha$.

Since $\lim_{\zeta=\pm\infty} \varphi(\zeta) = \varphi_{\pm\infty} = \gamma$, it follows that by introducing $\alpha - \gamma = \Phi_z$ and integrating (Φ_z is the amplitude of a displacement normal to the surface of a dissolving crystal), we obtain the following solution in the form of a solitary wave:

$$\varphi(\zeta) = \varphi_\infty + \Phi_z \operatorname{sech}^2 \sqrt{\frac{\Phi_z}{2}}\left[x - \left(\Phi_\infty + \frac{\Phi_z}{3} t\right)\right]. \quad (40)$$

An analysis of Eqn. (40) demonstrates that, in contrast to a kink [see Eqns. (1), (10), and (27)], a solitary wave describes less satisfactorily the process of dissolution (Fig. 3). It is found that the solitary-wave mechanism of dissolution begins to predominate when the density of a metal ρ is low, the directional interparticle interaction forces $\vec{\varepsilon}$ are weak, and the values of Δa are large. Shorter characteristic times of adsorption of the particles in the solution are required in the case of a solitary wave. Suppression of the motion of a kink is usually due to adsorption of the solution particles and the formation of stable films on steps.[29–32]

Therefore, we have to distinguish the motion of small (monatomic steps, representing Frenkel–Kontorova surface dislocations) and large (high dissolution steps) solitons on the surface of a crystal. Depending on the anodic value of a voltage η_a [and, consequently, on the supersaturation near the surface $\Delta\gamma^* = f(\eta_a)$], there can be quite considerable differences in the morphology of the dissolving surface. The experimental observations of Heusler et al.[36] of the distribution of steps with different kink concentrations ($\beta_{0,k}$) on a close-packed (110)Fe and 'loose' (112)Fe faces, dissolved in 1 M $NaClO_4$ and 1 M $HClO_4$ solutions, had demonstrated that $\beta_{0,k}$ depended linearly on $\eta_a = \partial \ln \beta_{0,k}/\partial \eta_a = F/RT$ (F is the Faraday constant) and increased on enhancement of the potential E of the iron electrode. The average distances between the steps $\overline{L}_0$ (when η_a = const) decreased (but the density β_0 increased) on increase in pH; $d\tan\overline{L}/d\mathrm{pH} = -0.6$.

The velocity of large parallel dissolution (growth) steps is described by a relationship similar to Eqn. (11) if use is made of the theory of Burton, Cabrera, and Frank.[8,24] If the velocity of these steps V_S is proportional to the flux

$$V_S = L_0 J_S / S_{hkl}, \quad (41)$$

the flux becomes

$$J_S = \frac{2}{L_0}\Gamma_\infty D_V \left(\frac{\Delta\gamma^*}{\gamma_\infty}\right)\frac{\sqrt{2}}{\bar{x}_S}\tanh\left(\frac{L_0}{\sqrt{2}\bar{x}_S}\right), \quad (42)$$

where Γ_∞ is the maximum coverage of the surface by particles M_L^{n+} and

$$\tanh\left(\frac{L_0}{\sqrt{2}\bar{x}_S}\right) = [1 - \exp(-2L_0/\sqrt{2}\bar{x}_S)]/[1 + \exp(-2L_0/\sqrt{2}\bar{x}_S)].$$

If $\bar{x}_S = a$ (where a is the lattice parameter), the quantity $\sqrt{2}\bar{x}_S$ corresponds to a lattice step

$$(L_a = \sqrt{2}a = \sqrt{2}\bar{x}_S)$$

and the whole surface area of a crystal becomes active.

If (case i) the distance between the steps is considerably less than the mean free path of ions M^{n+} on a step, $L \ll \bar{x}_S$, then

$$\tanh(L_0/\sqrt{2}\bar{x}_S) \to L_0/\sqrt{2}\bar{x}_S$$

and the flux depends linearly on the supersaturation

$$J_S = \tau_{\mathrm{surf}} \nu_D \Delta\gamma^*,$$

where τ_{surf} is the lifetime of surfactant particles M_L^{n+} in a surface layer given by $\tau^{-1}(M_L^{n+}) \approx \nu_D \exp(-\Delta H_{\mathrm{des}}/k_B T)$ and ΔH_{des} is the heat of desorption of the M_L^{n+} particles in the course of the process $M_L^{n+} \to M_S^{n+}$.

If (case ii) $x_S \ll L_0$, then

$$\tanh(L_0/\sqrt{2}x_S) \to 1$$

and the flux is governed by the surface morphology:

$$J_S = [L_0/\sqrt{2}\bar{x}_S]^{-1} \tau_{\mathrm{surf}} \nu_D \Delta\gamma^*.$$

The M^{n+} ions in the metal lattice (M_L^{n+}) are not equivalent to the ions M_S^{n+} in the low-entropy electrode layer of the electrolyte. In the electrolyte they are solvated, whereas in the metal lattice they are

screened by the electron gas. The high supersaturation $\Delta\gamma^*$ in terms of the M^{n+} ions in the electrolyte layer in the quasi-liquid excited state of the surface layer of the metal allows us to construct a model of dissolution in the form of matched shock waves (bora wind) in the electrolyte of height h_1 and a kink h_0 in the metal (Fig. 3*a*). The velocity of such a fast large dissolution soliton, which appears under anodic potentials, is governed by its height h (the larger the value of h, the higher the soliton velocity):

$$V_{S,B} = [Gh(h_0 + h) / 2h_0]^{1/2}. \quad (43)$$

Here, G is the shear modulus and the heights are related by $h = h_1 + h_0$. If $h_0 \neq 0$ and $h_1 \gg h_0 \approx a$, $h \approx h_1$, then Eqn. (43) becomes

$$V_{S,B} = (Gh^2 / 2a)^{1/2}. \quad (44)$$

The rate of dissolution of a metal predicted by this model depends differently on the heights of the layers in the electrolyte and in the metal.

The models of cooperative dissolution events allow us to explain many new experimental observations that cannot be accounted for by the Burton–Cabrera–Frank (BCF) theory. The soliton mechanism of dissolution allows us to understand the primary event in corrosion of perfect ideally smooth (on the atomic scale) surfaces of single crystals. According to the BCF theory, dissolution of a defect-free ideal face of a metal is impossible, because there is no defect to stimulate the first elementary dissolution event. However, in spite of our better understanding of real crystals, which always have defects, the BCF theory is still valuable,[24] especially as the physical interpretation of the dissolution and growth processes assumed in this theory is very simple and attractive.

What are the reasons (stimuli) responsible for the appearance of a dissolution soliton? They include, above all, local fluctuations of the surface concentration (or density) when the solution particles are adsorbed and the surface coverage by a surfactant is less than one monolayer ($\theta_{surf} < 0.2$ monolayer) and also a metastable state of the surface layer characterised by an increase in the entropy factor and the appearance of fluctuations of strains in this layer. In the case of singular low-index faces a dissolution soliton may appear also because of the alternating, along the z axis, difference between the lattice parameter in the first atomic layers of a surface layer of a metal, which is damped nature $\Delta a_2 = \pm a \exp(-kz)$, where k is the damping (attention) coefficient. The lattice parameter a, occurring also in Eqn. (44) for the velocity of a large dissolution soliton, implies also the physical meaning of the dimensions (or mass) of an atom $\Omega \propto f(a\ m_a)$. At low binding energies E_{M-M}, when the dissolution of M involves solitary waves (Fig. 3*c*), the change in the parameter Δa_z is of fluctuating nature on transition from the state $V_{S,2}$ to the state $V_{S,3}$.

Discontinuous fluctuations of the density in the case of solitary waves (when a phase transition takes place) correspond to dissolution[37]

$$\varphi(x,t) = (10\Gamma\varphi'' / \varphi^{v})^{1/2}\tau^{-1}, \quad (45)$$

where $\tau = x/h_0$ is the time, $\Gamma = h\varphi'''(\vec{\varepsilon})/\varphi''(\vec{\varepsilon})$ is the Grüneisen constant, $h_0 = a(1 + \Delta a)$, and $\varphi(\vec{\varepsilon}) \equiv \varphi[a(1 + \Delta a)]$.

Therefore, the greater the value of Δa, the higher the strains $\vec{\varepsilon}$ in the surface layer and the most probable is the spallation of a $2-D$ plate of thickness $h_0 \approx a$ from the bulk of the metal crystal when this plate has the parameters of the interior of the crystal.

The points of emergence of dislocations on a highly heterogeneous surface of an imperfect crystal give rise to a 'loose' adsorption-active position, the preferential filling of which by the solution particles may induce the appearance of a dissolution soliton (spherical kink). As the process of the dissolution of a metal develops, a linear subsurface effect creates concentric waves and soliton kinks. The motion of the resultant kink during the dissolution of a crystal is then no longer related to the subsurface defect, but it is governed by the indices $<hkl>$ of the surface (by direction of motion of the dissolution steps).

A dissolution step (which in the simplest case is a Frenkel–Kontorova dislocation) can start to move under the influence of a very small ($\Delta a \approx 0.001$ nm) tangential displacement of each atom along the x, y, and/or normal (along z to the surface). When the degree of hydrogenation of a metal is low (the process of hydrogenation is practically always accompanied by the dissolution of a metal), the displacements as a result of modification of the surface by hydrogen may be particularly large ($\Delta a \approx 0.010$ nm). For example, when the surface coverage with hydrogen is $\theta_H = 0.3$ monolayers, the displacement of W atoms in the first surface layer on the (100)W face reaches $\Delta a_{12} \approx 0.003$ nm, whereas for the (011)Ni face it is $\Delta a_{12} = 0.011$ nm (Ref. 38). Surface atoms go over to a metastable state after the passage of a dissolution soliton and this facilitates rapid solvation of the resultant intermediate products, since it gives rise to a slowly moving fluctuation characterised by a lower density of the investigated metal and a higher concentration of the solution particles involved in the solvation process. However, the capillary forces by themselves are insufficient to initiate the first dissolution event and we have to allow for the electronic structure of the metal being dissolved and of the particles being adsorbed (this represents a state of non-Coulomb 'glue' in a double electrical layer located on the metal side).

The soliton mechanisms are fully acceptable (they agree with experiments) for the description of motion of linear defects in surface layers of crystals containing hydrogen[1,3] as well as condensed adsorbed layers of H_3O^+ where a proton can move.[39] In the case of epitaxial matching the double electrical layer between the condensed metal (M) and electrolyte phases when the continuity is preserved across the phase boundary, the cooperative model (Fig. 3*a*) describes practically all the corrosion processes. The soliton dissolution mechanism is capable of accounting for the differences between the rates of corrosion of semiconductor alloys of the III-V type, and of crystalline and amorphous structures with the same chemical composition. A close-packed amorphous structure (representing a disordered alloy of the d elements with one another or with nonmetals), where only the short-range order is preserved, is characterised by a low corrosion rate because of an irregular motion of a soliton along the surface. The dependences of the velocity of propagation of steps (dissolution solitons), with positive or negative deviations from the closest packing, on the index (hkl) of a face and on the direction of growth $<hkl>$ of a crystal was estimated theoretically in Ref. 40 and observed experimentally for hydrogenated low-index faces of nickel single crystals in sulphate solutions.[41]

In the stepped surface model the probability that a particle being adsorbed reaches a step moving 'upwards' is not equal to the probability for a step moving 'downwards' (Ref. 40). This unusual situation can be understood if we turn back to Fig. 1*c*. An adatom diffusing along the x axis along a close-packed terrace to its edges becomes more strongly bound in a 'niche' which is at a position S, than at the 'edge of a dip' L ($E_S > E_L$, $\Delta E = E_S - E_L$). In the

former case an atom is reflected by a potential barrier of a monatomic step (external projection), whereas in the latter it 'drops' into the potential well (E_L). Diffusion of an adatom along the y axis (parallel to a step) depends weakly on the step density β_0^{-1}.

The dependence of dissolution of 'loose' faces of an Ni crystal in 0.5 M H_2SO_4 solution on the direction of removal of layers of crystallographically identical faces[32] can be explained by differences in the adsorption activity of dissolution steps moving along different directions. There is some analogy between this model and positive and negative kinks on dislocations. In the BCF theory these kinetic differences are explained as follows. In the $2-D$ case the slope of the surface after the passage of dissolution steps is

$$P \equiv (dz / dx) = h\beta_0,$$

and the sinking of the surface of a dissolving crystal (velocity of displacement along the z axis of a plane normal to the surface of a crystal) is given by

$$-(dz/dt) = \frac{P}{\rho}\left(\frac{m_a}{2\pi k_B T}\right)^{1/2} = hJ_s.$$

Allowing for the functional relationship between the flux J_S and the density of steps β_0 plotted using the coordinates β_0 and J_S, we can describe two types of step motion: inhibited and uninhibited. In the latter case at low densities β_0 there is a proportionality between β_0 and J_S. For all β_0 the $\beta_0 = f(J_S)$ curve has a negativity curvature ($\partial^2 J_S/\partial\beta_2^0 < 0$) and the velocity of a single dissolution step is higher than the velocity of a kinetic wave: $V_S > V$. If $V_S = V$, there is a proportional relationship, but this time it is between β_0^2 and J_S and the curvature of the kinetic wave exhibits reversal of the sign ($\partial^2 J_S/\partial\beta_2^0 < 0$). It should be pointed out that the efficiency of the action of a surfactant depends on the direction of motion of waves: it is possible to suppress the wave process by a small amount of a surfactant that blocks the wave nucleation centres.

Initiation of the formation of dissolution steps and their propagation on the surface of a crystal occurs when a metal is subjected to tensile elastic loads that alter the values of γ_S. In this case the range of protectic (inhibiting) concentrations of a surfactant moves toward higher values.[42,43] There is special interest in the propagation of a soliton in surface layers of metals covered by oxides, which can be insulating or semiconducting. High-intensity fields in the oxides ($>1 \times 10^5$ V/cm) give rise to electrostriction phenomena and generation of solitons at the metal–oxide surface, where the electrostrictive strains are concentrated.

VI. Inhibition of motion of dissolution steps

The problem of drag or acceleration of steps during dissolution or growth of a crystal by inhibiting (stimulating) impurities is very important in the practical sense and its solution has attracted the interest of many electrochemists and physicists working on crystals. The mathematical solutions proposed for the growth of a crystal with a stepped surface are based on the following mechanism. Impurities are captured by a step moving during the growth of a crystal ($2-D$ process) and their motion disturbs the Boltzmann distribution. The concentrations of impurities in a surface layer formed by the passage of such a step are not the equilibrium values. The process of relaxation results in a redistribution of the impurities in the surface layer during the passage of the second step. Therefore, in the kinetic estimates an important characteristic is the density of steps β_0, the frequency W at which they occur, the height h, the frequency f of jumps of impurity atoms into the surface layer from the bulk of the metal, and the frequency f_L of jumps of impurities between bulk layers.

In the case of monatomic spallation (Frenkel–Kontorova dislocations) the solutions of these problems can be obtained using the theory of dislocations: blocking of the motion is due to the formation of chain-like segregations (clouds) along the line of a defect.[21] In the case of a linear $1-D$ system, a chain of atoms in which a defect inhibiting the chain vibrations is incorporated at distances characterised by a period L_D (the defect may be an adparticle of an inhibiting surfactant with a mass exceeding the mass of a crystal atom, $m_d > m_a$) and the solution of the equation of motion of the type given by Eqn. (35) reduces to the differential Korteweg–de Vries equation, which has the following soliton solutions[44]

$$\frac{\partial W_D}{\partial\tau} + \Phi_D W_D \frac{\partial W_D}{\partial\zeta} + V_{S,D}\frac{\partial^3 v_D}{\partial\zeta^3} = 0, \qquad (46)$$

where

$$\Phi_D = (\alpha_D/2\eta_D)\theta^3,\ V_{S,D} = \left(\delta_D\theta^4/2\eta_D\right)\frac{\partial v_D}{\partial\zeta} = W_D.$$

The constants Φ_D and $V_{S,D}$ determine the amplitude and velocity of a soliton with a defect. The parameter

$$\theta = (\eta / \eta_D)^{1/2} = (m_a K_D \beta_D^2 / m_D K\beta^2)^{1/2}$$

contains the constants β and K (velocity constant), as well as m_a (mass of an atom of M): the index D denotes that a particular property describes a defect;

$$\alpha = -3\beta\eta^{1/2},\ \delta = \eta / 12,\ \tau = \varepsilon^3\eta t,\ \xi = \varepsilon(x - t),$$

$$x = \eta^{1/2} n = m_a(2k\beta^2)^{1/2},\ \varepsilon = (m_a - m_D) / m_a$$

is the order parameter. Near a surfactant particle adsorbed and incorporated in the metal lattice we can expect the appearance of additional spherical solitons similar to kinks of subsurface dislocations. The length of an arc for spherical solitons is πr_0 (r_0 is the radius of a critical nucleus). The process of motion of a dissolution step across the resultant obstacles (spherical solitons) is retarded in the $2-D$ case when the condition $L_D \geqslant 2r_0$ is obeyed.

The velocity of a wave described by a Korteweg–de Vries equation of the type (46) is determined by the amplitude Φ_D and the higher the amplitude of the wave, the faster its motion. This is in good agreement with the experimental observations of the process of dissolution of nonsingular faces of crystals with a relatively low ($<99.6\%$) degree of purity. Irregular incorporation (departure from the period L_D) of many inhibiting particles with a large mass m_D destroys a dissolution soliton. Multidimensional ($2-D$ and $3-D$) variants of the Korteweg–de Vries equations demonstrate[26] the possibility of appearance of specially active localised states due to their interaction with solitons.

The lowering of the amplitude and reduction in the velocity of a dissolution step is due to its coarsening and broadening (Figs. 3*b* and 3*c*). Multilayer steps also become coarser as a result of adsorption of the solution particles. The criterion of this dynamic process is[45]

$$E_S^2 / (h\rho\Delta\mu\, k_B T) \simeq r_0 / L_0 \leqslant 1,$$

where $\Delta\mu = \mu_S - \mu_L$; $L_0 = \beta_0 D_{surf}$ is the correlation length; E_S

is the free energy of a step; as pointed out above, in the case of $2-D$ nucleation, we have $V_S \propto K\Delta\mu$ and the critical radius is $r_0 = E_S/h\rho\Delta\mu$.

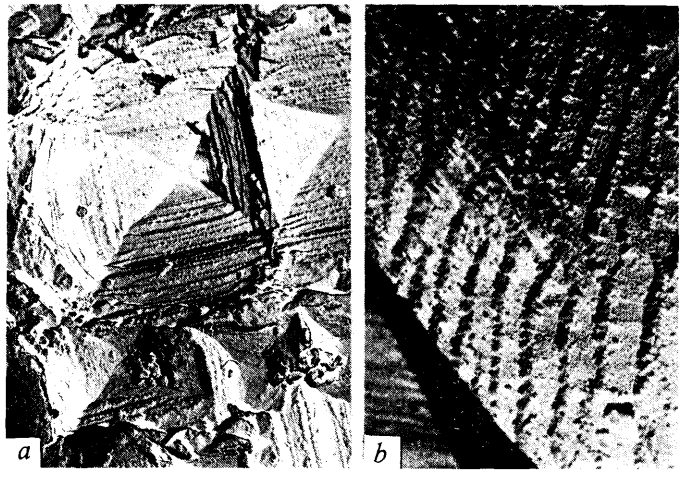


Figure 5. Blocking of the motion of dissolution steps by clusters of adparticles from a solution on [5(111)−(001)]Ni (*a*) and [9(110)−(001)]Cu (*b*) faces; magnification 9000.

The surface energy of a vicinal stepped F face (Fig. 1*a*) consists of two terms:[18]

$$E_V = E_0\cos\theta + (E_S/h)\sin\theta,$$

where E_0 is the surface energy of a terrace (close-packed singular face). When the angle is $\theta = 0, \pm\pi/2, \pi$, the values of E_V have sharp minima. Spreading of a multilayer step occurs when the surface energy E_S is much less than the surface energy of a terrace ($E_S/\gamma_S h \ll 1$), as shown in Fig. 5, but the opposite behaviour is observed and a clear step is conserved if $E_S/\gamma_S h \approx 1$ (see Fig. 4).

Numerous experimental data confirm that the velocity of large solitons depends on the distance between them L_0 (in general, it depends also on β_0: the higher the value of β_0, the lower the velocity V_S). A dependence of the wave velocity on amplitude h follows even from a $1-D$ analysis, which leads to the simple dependence

$$V_S = \left(\frac{hg}{2\pi} + \frac{2\pi\gamma_S}{h\rho}\right)^{1/2},$$

(g is the gravitational contant), from which it follows that lowering of h reduces rapidly the role of the first term and increases the importance of the capillary forces (second term). In the case when $h \approx b$ (the latter representing the distance between the atoms) the Thomson equation reduces to Eqn. (4).

A dissolution step of dislocation dimensions ($h \approx b \approx a$) may be decelerated by the adsorpton of point defects or the emission of vacancies in the course of its motion. The drift (directional) velocity of a step travelling a distance l along x under equilibrium conditions in the system formed by a dissolution step and a point defect can be estimated from [46]

$$V_S = \frac{4\pi D_V}{h}\left[\exp\left(\frac{\Delta a\langle U_S^2\rangle l\beta_0^{-1}}{k_B T}\right) - 1\right] \quad (47)$$

(where D_V is the diffusion coefficient of a point defect). For low values of Δa the velocity of the steps is

$$V_S \propto \frac{4\pi D_V \Delta a\langle U_S^2\rangle l\beta_0^{-1}}{hk_B T}, \quad (48)$$

and for large values, it is

$$V_S \propto \frac{4\pi D_V}{h}\exp\left(\frac{\Delta a\langle U_S^2\rangle l\beta_0^{-1}}{k_B T}\right). \quad (49)$$

The term $<U_S^2>1\beta_1^{-1}$ represents the area 'swept through' during the motion of a dissolution step. When Δa influences not only the adsorption of surfactant on a step, but also the actual mechanism of the distribution of a surfactant in a double electrical layer located in the electrolyte near the crystal surface, hyperbolic functions appear in the relationships for the velocity

$$V_S \propto \sinh\frac{\Delta a\langle U_S^2\rangle l h}{k_B T}. \quad (50)$$

In electrochemical terms the strength of the dissolution current i_a is given by an expression similar in form to Eqns. (11), (41), and (42), which is natural because the initial assumptions are based on the kinetic representations of the BCF theory. The steps may travel in the form of concentric circles, Archimedes spirals, or linearly extended formations. Without allowance for the kinks on the steps the above description is still quite accurate and has been confirmed by experiments. In the $2-D$ case the slope of concentric steps is described by[47]

$$(dy/dx) = (x + ky)/(kx - y). \quad (51)$$

Integration of Eqn. (51) yields a dependence of the type

$$r = r_0\exp(K\varphi), \quad (52)$$

where $\varphi = \arctan(y/x)$ and $r_0 = (x^2 + y^2)^{1/2}$. If $K = 0$, concentric points propagate from the origin of the coordinates. If $K > 0$, an Archimedes spiral is observed. Eqns. (51) and (52) describe a stable pattern. When dealing with the multidimensional case of the dynamics of changes in a concentric (spherical) kink, considered by I A Bogolyubski and B G Makhan'kov in 1976 (see Ref. 26), it is necessary to base the analysis on the Klein−Gordon equation

$$(\partial^2\varphi/\partial x^2) + (\partial^2\varphi/\partial y^2) - \varphi_{tt} = F(\varphi), \quad (53)$$

which in the one-dimensional case reduces to the sine−Gordon Eqn. (2) if $F(\varphi) = \sin\varphi$. In a situation when $F(\varphi) = \varphi^{IV}$. The initial conditions for a spherical kink expanding from the origin can be written in the form of a steady-state solution of Eqn. (53), which is $\varphi(r, 0) = \tanh(r - r_t)/\sqrt{2}$ and the running radius is $r_t \gg 1$. Numerical calculations on a computer[26] showed that such a kink first collapses (at $t > 0$) and then expands giving rise to what is known as a pulson. In experiments such a situation is encountered when an edge dislocation emerges on the surface of a crystal. The propagation conditions become easier when a screw dislocation emerges on the surface and then a pulson gives rise to a nonvanishing dissolution step.

The structure of equations of the (42) type describing dissolution dynamics becomes more complex in the electrochemical case. Then if a step propagates in the form of an Archimedes spiral,[16] the velocity (current density i) of dissolution is controlled by an electrochemical term multiplied by a hyperbolic function that describes the transport of charges in a double electrical layer at the phase boundary

$$i = i_0\{\exp(\alpha nF\eta_a/RT) - \exp[-(1-\alpha)^n F\eta_c/RT]\}\frac{L_0}{2\pi r_0}\tanh\left(\frac{2\pi r_0}{L_0}\right), \quad (54)$$

where $a \approx 0.5$ is the coefficient of transport by the anodic and cathodic reactions, η_c is the cathodic overvoltage, R is the gas constant, and n is the valence of the electrode reaction,

$$L_0 = (nFD_{M^{n+}}\bar{c}/i_0)^{1/2}\exp(-\alpha nF\eta_a/2RT),$$

$$\tanh\left(\frac{2\pi r_0}{L_0}\right) = [1-\exp(-4\pi r_0/L_0)]/[1+\exp(-4\pi r_0/L_0)].$$

Bockris and Dem'yanovich[48] used, as in the preceding case [Eqn. (54)], the ideas of Whitham[13] to derive a similar relationship for linearly extended steps

$$i = i_0\{\exp(\alpha nF\eta_a/RT) - \exp[-(1-\alpha)nF\eta_c/RT]\}\times$$
$$\times\left(\frac{4\beta_0 D_{M_K^{n+}}}{P}\right)\tanh\left(\frac{P}{4\beta_0 D_{M_K^{n+}}}\right)^{1/2}, \quad (55)$$

where

$$P \equiv L_0^{-1} = i_0\Big/\left(nFC_{S,M_{S,K}^{n+}}\exp\left[-(1-\alpha)nF\eta_K/RT\right]\right), C_{S,M_{S,K}^{n+}}$$

$C_{S,M_{S,K}^{n+}}$ is the equilibrium concentration of M^{n+} on a step, and $D_{M_K^{n+}}$ is the surface diffusion of M^{n+}. The steps disappear when the correlation length is large, so that

$$P \le \beta_0 D_{M_K^{n+}}, \left(4\beta_0 D_{M_K^{n+}}/P\right)^{1/2}\tanh\left(P/D_{M_K^{n+}}4\beta_0\right)^{1/2} = 1$$

and Eqn. (55) reduces to the usual equation of electrochemical kinetics.[16] In the other case when $P \gg \beta_0 D_{M_K^{n+}}$, Eqn. (55) becomes

$$i = i_0\{\exp(\alpha nF\eta_a/RT) - \exp[-(1-\alpha)nF\eta_c/RT]\}\frac{4\beta D_{M_K^{n+}}}{P}. \quad (56)$$

At low anodic overvoltages ($\eta_a < 0.1$ V) and when the radius of curvature of an Archimedes spiral satisfies the condition $r > L_0$, a segment of the spiral travels at a velocity

$$V_S = V_\infty(1 - r_t/r_0).$$

Linearly extended steps are not related to a point source of expansion. The substitution $P^{-1} = \beta_0 \equiv 2L_0$ allows us to obtain from Eqn. (55) a very simple expression for the velocity of such steps:

$$V_S = i_0(L_0C_0nF)^{-1} = i_0(0.5\beta_0C_0nF)^{-1}, \quad (57)$$

from which it follows that if i_0, an increase in the equilibrium concentration C_0 of M_S^{n+} in the solution and of the density of steps β_0 lowers V_S. This conclusion applies also in the case of propagation of steps during growth of a crystal. If the flux deduced from Eqn. (41) is

$$J_S = S_{hkl}V_S/L_0 \quad (58)$$

and the law describing growth obeys the Arrhenius dependence

$$J_S = KC_{surf}\nu_D\exp(-E_S/RT) \quad (59)$$

(C_{surf} is the concentration of a surfactant in the solution, E_S is the metal–surfactant binding energy on a step—see Fig. 1*e*), then the combination of Eqns. (58) and (59) yields

$$V_S = KS_{hkl}^{-1}L_0C_{surf}\nu_D\exp(-E_S/RT). \quad (60)$$

It is clear from Eqn. (6) that the velocity of steps (solitons) of dissolution may be influenced decisively by impurities in the form of inhibiting surfactants in the solution. The concentration of impurities on terraces $C_{A,surf}$ in front of a step and on a step $C_{S,surf}$ are different. The values of $C_{A,surf}$ and $C_{S,surf}$ are related functionally to the parameters of motion of steps by the expression $C_{A,surf} = C_{S,surf}[1 - \exp(-K\beta_0)]$. During the motion of a step the surfactant impurities are pushed away when the surface drops and go into solution (which is opposite to the burying of impurities in a growing crystal).

Inhibiting impurities may 'poison' the motion of steps when crystals with a low degree of purity are dissolved (see Fig. 5) and the blocking particles (the elements C, S, P) are supplied to the surface from the bulk of a crystal which is dissolving: the particles of carbon, sulphur, or phosphorus which cluster on the steps of the surface of a metal lower the dissolution rate. At low concentrations of such particles on the surface ($\theta_{C,S,P} < 0.2$ monolayers) we have the opposite effect of acceleration of the anodic process. For example, in the case of Ni–2.9% P alloys the density of the anodic current i_a increases in acid media, whereas in the case of Ni–12.3% P there is a reduction in i_a (Ref. 49). Examples of this kind are particularly numerous in the case of carbon steels when inert carbon from dissolving cementite Fe_3C decelerates the motion of the dissolution steps. However, the rate of dissolution of low-carbon steels may be higher than that of high-purity zone-melted iron (99.99%) because of the high level of elastic stresses in the matrix. The stresses are induced in α-iron by cementite precipitates.[50]

The velocity of a dissolution step (soliton) depends on the surface tension (stress) in a crystal γ_S. The velocity constant K in Eqn. (60) can be expressed in the form $K = (2\pi\gamma_S)^{1/2}$. A strong reduction in γ_S as a result of adsorption of a surfactant (for example, adsorption of nucleophilic particles such as Hal^-, OH^-, and H^-) on a hydrophilic surface of a *d* metal reduces strongly V_S. If the adsorption of a surfactant is described by the Langmuir isotherm

$$\theta_{surf} = \frac{\Gamma_i}{\Gamma_\infty} = \frac{C_{surf}}{\Lambda + C_{surf}}, \quad \Lambda = \frac{\Gamma_\infty\nu_D\exp(-\Delta H_{ads}/k_BT)}{(kT/2\pi m_D)^{1/2}},$$

the lowering of γ_S on adsorption of a surfactant (heat of adsorption ΔH_{ads}) from solutions with a concentration C_0 can be expressed using

$$d\gamma_S/dC_0 = (\Gamma_i k_BT)/C_{surf}$$

and the Shishkovskii equation, so that the final result is

$$\Delta\gamma = k_BT\Gamma_\infty\ln(1 - \Gamma_i/\Gamma_\infty) < 0.$$

The most effective surfactant (reducing γ_S) impurity is adsorbed hydrogen.

When a Langmuir adsorption equilibrium is established and also when γ_S begins to depend linearly on C_{surf}, the reduction in the surface tension $\Delta\gamma$ begins to influence decisively the propagation of a dissolution step, so that its velocity becomes

$$V_S = \theta_{surf}\Pi[E_{surf} - \Delta E_{surf}\exp(-Kt)], \quad (61)$$

where $\Pi = 1 - \exp(-\Delta\mu/k_BT)$ is the undersaturation of a solution in respect of the M_L^{n+} particles, $\Delta E_{surf} = E_{surf} - E_M$, E_M and E_{surf}

are the surface energies of clean and inhibited surfaces, respectively. The physical meaning of the dimensional velocity constant K follows from the above relationship. An adsorbed surfactant quenches oscillations and destroys a soliton and reduces (possibly to zero) the velocity of its propagation on a surface.

How can one block the motion of a dissolution step and thus increase the resistance of a crystal to the chemical action of an electrolyte? The first sufficiently rigorous thermodynamic solution of the problem of disappearance of a step on a singular F face was obtained by Onsager (1946). He used the Ising representations ($2-D$ model) of complete blocking by surfactant particles of one of two adjacent terraces separated by a step on which no surfactant adsorption takes place. In the interpretation of Dunning,[51] the thermodynamic solution is as follows. Let us assume that the potential energy per unit surface area is $E_{surf}/2a_0^2$ (a_0 is the Madelung parameter). A surfactant adsorbed on one of the terraces (θ_{surf} = 1 monolayer) is transferred to an unoccupied terrace and this is accompanied by simultaneous formation of surface vacancies on a deblocked terrace. The transition occurs as a result of diffusion on the surface of an ideal terrace and undoubtedly this is a correlated process which does not necessarily follow the shortest path. The total path or the displacement $<U^2(t)> = f\lambda^2 t$ is governed by the mean length of an elementary (from one adsorption centre to another) jump λ and by the frequency of such jumps f.

The formation of a vacancy increases the surface energy by $4E_{surf}/2a_0^2$, which is the energy of four dangling bonds. The surface energy density is then

$$E_M = E_{surf}/2a_0^2 + \theta_{surf} 4E_{surf}/2a_0^2 \quad (62)$$

and it is the same for adjacent terraces when the degrees of coverage of the steps by vacancies and surfactants become equal ($\theta_{surf} = \theta_V$). Such a situation occurs at T = 0 K. At higher temperatures it follows from the BCF theory that

$$E_S(T) = (E_{surf}/2a_0^2)\left\{2 - \frac{1}{2}\left[1 + (2/\pi)(1-k_1^2)^{1/2} K(k_1)\coth\eta\right]\right\}. \quad (63)$$

where

$$\eta = E_{surf}/2k_BT, k_1 = 2\sinh\eta/\cosh^2\eta$$

and

$$K(k_1) = \int_0^{\pi/2} \left(1 - k_1^2 \sin^2 \nu_i\right)^{-1/2} d\nu_i$$

is an elliptic integral.

The nonlinear relationship (63) includes the main energy parameters of blocking of a step, such as the binding energy of the nearest neighbours, the distance between the interacting particles, and the vibration frequencies of adparticles. The relationship (63) is used widely in computer modelling of modification of crystal surfaces due to external perturbations.

However, this model ignores the change in the energy of vibrations of adparticles. The dependence of $E_S(T)$ on the value of the Jackson–Temkin factor $\eta_1 \exp(-E_{surf}/2k_BT)$ is described by the Avrami–Kolmogorov equation $E(T) = (1 - \eta_1)^n$; a tangent to the curve representing the dependence at a point corresponding to a transition temperature T_c obeys the condition $\sinh H_c = 1$ and, consequently, $T_c \approx 0.57E_{surf}/k_V$. At the transition temperature the surface coverages become equal, $\theta_{surf} = \theta_V = 0.5$ monolayers, and the step separating the terraces disappears.

It was established quite early that the adsorption activity of steps and kinks is considerably higher than the activity of terraces (Fig. 3). An atom on a step (S) or in a kink (K) has at its disposal a large number of d holes the filling of which requires a lower energy: $E_K > E_S > E_L > E_s$ (E_A). The energies of chemisorption of chalcophilic particles (oxygen and hydrogen) on stepped surfaces of transition b.c.c. metals are calculated out by Jardin et al.[52] Differences between the energy characteristics of steps and terraces on surfaces of d.c.c. crystals were quite large: −3.78 and −5.90 eV for oxygen atoms, and −2.30 and −3.78 eV for adsorbed H atoms. In contrast to a metal/gas contact, when there is no need to allow for the short-range order in condensed thin layers adsorbed in different ways on terraces and steps, in the case of metal/electrolyte systems this order is of decisive importance. Purely topological treatments of dimensional effects on adsorption of solvated inhibiting surfactant particles have proved insufficient.

In models of this kind[53] the influence of impurities in a solution on the motion of dissolution steps is considered in two separate variants: blocking of 'loosely' packed steps, which occurs mainly due to adsorption at kinks, and also as a result of formation of discontinuous irregular adparticle islands on close-packed steps (Cabrera fence—see Fig. 5). According to Bliznakov,[54] blocking by a substance being dissolved on a nonideal surface of a crystal by surfactant fluxes may be achieved independently. Consequently, the overall rate of dissolution is a sum of the partial rates of dissolution of a metal $V = \sum_{ij} V_{ij}$. We then have

$$V_i = \Gamma_i(1-\theta_{surf})\exp(-E_a/k_BT), \quad (64a)$$

$$V_j = \Gamma_i\theta_{surf}\exp[-(E_a + \Delta H_{ads})/k_BT. \quad (64b)$$

The surface concentration Γ_i of adparticles is a function of the lifetime of surfactant particles on the surface of a metal $\tau_{surf}^{-1} = \nu_D \exp(-\Delta H_{des}/k_BT)$ and of the heat of desorption of surfactants from the surface ΔH_{des}. Combining Eqns. (64a) and (64b), and introducing the notation

$$E_a = 0.5E_{surf},\ V_{0,l} = \Gamma_i \exp(-E_{surf}/2k_BT),$$

$$E_S(T) = 1 - \exp(-E_{surf}/2k_BT),$$

where $V_{o,l}$ is the rate of dissolution of a crystal in a pure solution, we obtain the simple dependences:

$$V_S = V_{0,l}[1 - \theta_{surf} E_M(T)]. \quad (65)$$

If θ_{surf} = 1 monolayer and E_a = const, it follows from Eqn. (65) that

$$E_M(T) = (V_{0,l} - V_\infty) / V_{0,l}, \quad (66)$$

or if the rate of adsorption of a surfactant exceeds significantly the limiting rate $V_{surf} \gg V_\infty$, we find that

$$V_S = V_{surf}(1 - \theta_{surf}). \quad (67)$$

The blocking of the surface by screening can be allowed for by means of Eqn. (67), but we have to know the density of states β_0 and at least qualitatively the evolution of this density:

$$\beta_0 = f(t).$$

Even the early models have allowed for the energy aspects of adsorption-active linearly extended surface defects in dealing with the adsorption isotherms, so that the pre-exponential terms in Eqns. (64a) and (64b) are modified. In the case of sympathetic changes in the concentrations of a surfactant in the solution C_{surf} and on the surface of a metal Γ_i under conditions of a weak supersaturation

$\Delta\gamma^*$, the velocity of dissolution steps V_S decreases linearly on increase in $\Delta\gamma^*$ [see Eqn. (61)]. Experimental estimates of V_S for transition metals are in agreement with the Langmuir isotherm and are described by dependences of the type[55]

$$V_S = 2\theta_{surf}\Delta\gamma * \left(\frac{2(1-\theta_{surf})}{1+\Delta\gamma*\theta_{surf}}\right)^{1/2}\left[1-\left(\Delta\gamma*\theta_{surf}\frac{1-\theta_{surf}}{1+\Delta\gamma*\theta_{surf}}\right)^2\right]^{-1/2}. \quad (68)$$

At low supersaturations $\Delta\gamma^* = \Delta\mu/k_BT$ the evolution of a step in accordance with the screw dislocation mechanism is faster than at other defects [for example, at (111) stacking faults on f.c.c. crystals[56]]. According to Ref. 56, this is due to the relationships between the nucleation times t_n and the time t_S taken by a step to rotate around a point of emergence of a dislocation dipole on the surface. In the case of low values $\Delta\gamma^*$ we have $t_n > t_S$, whereas at high supersaturations we find that $t_n < t_S$.

An approach based on formal kinetics has been developed subsequently to allow for the formation of discrete $2-D$ and $3-D$ surfactant lattices on substrates with local dangling bonds. In the $1-D$ Ising case the process of blocking of step motion by adsorption of the solution particles is considered on the basis of square $\{IL_a\}$ lattice of a $2-D$ crystal (Fig. 1*a*). This is a very simplified model of the surface of a crystal with growth steps. Atoms in deeper layers $I \geqslant L_a$ lie on the steps and the density of dangling bonds for them is higher.

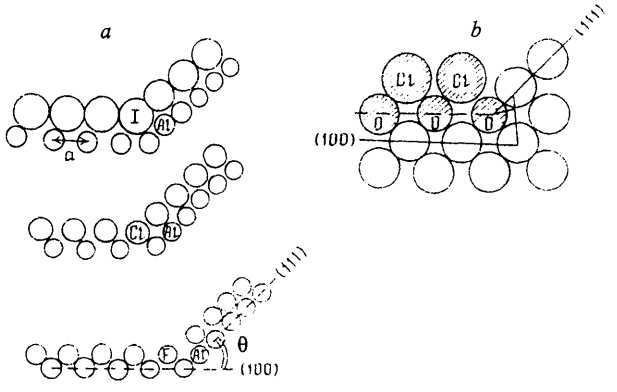


Figure 6. Schematic representations of the adsorption of Hal^- ions on clean (*a*) and oxygen-coated (*b*) stepped [*n*(001)−(111)]Al surfaces.[57]

In a practical analysis of inhibition of dissolution of a metal it is possible to use quite productively the principle of dimensional correspondence, particularly in studies of dissolution of individual faces of metal single crystals in aqueous solutions of the acids HF, HCl, HBr, and HI. For example Politizky and Fischer carried out a pioneering work[57] on the dissolution of stepped Al faces ({001} terraces + {111} close-packed steps) and found that the F^- ions were readily adsorbed in highly coordinated *s* states both on steps and terraces, whereas Cl^- and Br^- ions reached the *s* positions only on cubic {001} faces. Large I^- ions were unable to maintain the *s* states on {001} faces or on {111} octahedral faces (Fig. 6).

In modern interpretations,[58] subject to allowance for the relationship between the electrochemical characteristics of dissolution of Al in halide solutions and the changes in $\{hkl\}$ on a surface, it is usual to consider partial or total transfer of charge in the course of adsorption (Table 2) and formation of an intermediate particle in a two-stage electrochemical process:

$$Al + 2Hal^- \rightleftarrows AlHal_{2,ads} + 2c, \quad (69a)$$

$$AlHal_{2,ads} \rightleftarrows AlHal_2^+ + c, \quad (69b)$$

followed by a fast chemical stage

$$AlHal_2^+ + Hal^- \rightarrow AlHal_3.$$

The transported charge (represented by the Esin−Markov coefficient K_{EM}) depends on the topology of the particles adsorbed on the surface of a metal, starting from the reticular density S_{hkl} of the surface. A reduction in S_{hkl} and an increase in the dimensional mismatch $\Delta r_{hkl} = r_{hkl,Al} - r_{Hal}$ on transition from the (111)Al to the (011)Al surface makes possible a strong adsorption of the F^- ions at a multicentre *s* position. The values of the Gibs potential ΔG and of the normal potentials E_0 depend strongly on the nature of the Hal^- ion, and it is found that the F^- ions are characterised by anomalously high values of these quantities.

Table 2. Correlation between electrochemical parameters of dissolution in halide acids and crystallographic characteristics of aluminium.

Parameter		F^-	Cl^-	Br^-	I^-
Ionic radius, nm		0.136	0.181	0.195	0.216
Atomic radius, nm		0.072	0.099	0.114	0.133
$\Delta r_{hkl} = r_{hkl,Al} - r_{Hal}$, nm	(111)Al	−0.012	−0.039	−0.054	−0.073
	(001)Al	+0.071	+0.044	+0.029	+0.010
	(011)Al	+0.016	+0.089	+0.074	+0.055
ΔG_{AlHal_3}, eV		−12.76	−6.61	−5.24	−3.26
$E_{0,Al/Hal}$, V		4.25	2.20	1.74	1.08
$E_{0,Hal^-/Hal}$, V		2.85	1.36	1.07	0.54
$E_{0,Al/Hal^-}$, V		−1.40	−0.84	−0.67	−0.54

Halogen ions adsorbed in multicentre states on {001} and {011} of f.c.c. crystals 'feel' quite comfortable. The 'loosely' packed steps on the Al surface are blocked effectively by the I^- ions[59] and the change in the capacitance of a single-crystal Au electrode is then well correlated with the terrace length L_M and with β_0. There is experimental evidence that the electrochemical activity of steps is higher also in the case of other crystals of noble metals (Pt, Pd) with a stepped surface. 'Poisoning' of steps (and this applies even more strongly to kinks) results in an effective deceleration of the motion of steps in a corrosion process by the high concentrations of the

halogen ions, in accordance with the series $F^- > Cl^- > Br^- > I^-$ ($C_{Hal} > 10^{-1}$ monolayers). In the case of solutions containing Hal^- on an oxygen-coated stepped surface of Al the oxygen adatoms are gradually displaced by halogen atoms, as postulated by Fischer.[60]

Naturally, the blocking of steps on the surfaces of transition *d* metals and their passivation are performed effectively by oxygen atoms. This process occurs in several stages depending on the coverage θ_0. Direct experiments on well-investigated stepped faces are needed to obtain reliable electrochemical data: they should be carried out by the methods of low-energy electron diffraction (LEED) and an analysis of the electron energy loss spectra (EELS) when hydrogen and oxygen are adsorbed simultaneously.[11,61] Oxygen adsorbed on (001)Ni forms structures with a periodicity $p(2 \times 2)$ when the coverage is $\theta_0 = 0.25$ monolayers; at higher coverages of $\theta_0 = 0.5$ monolayers they transform into $c(2 \times 2)$ structures; in the case of the close-packed (111)Ni face we can expect $p(2 \times 2)$ structures for $\theta_0 = 0.25$ monolayers and $(\sqrt{3} \times \sqrt{3})R30°$ for $\theta_0 = 0.33$ monolayers. Low coverages of (110)Ni with oxygen ($\theta_0 < 0.1$ monolayers) do not modify this phase, which has the loosest structure; high values of θ_0 cause filling of long bridge positions and give rise to $a(2 \times 1)$ structures. The results of investigation by the EELS method of a system of this kind indicate that hydrogen is adsorbed in the molecular form only by kinks (Table 3). If oxygen fills kinks and steps, then hydrogen atoms can be adsorbed only on (001)Ni terraces. When $c(2 \times 2)$ structures appear on terraces at high values of θ_0, the nonsingular stepped (510)Ni surface is transformed into (410)Ni or (610)Ni.

Table 3. Density of adsorbed hydrogen layers on (510)Ni surfaces, determined by the EELS method.

State of adsorbent	Position	Energy loss, meV	
		hydrogen	deuterium
Atom	vacancies on terraces	58	43 60
Atom	short bridge, step	103 142	78 102
Atom	long bridge, step	95 154	71 115
Molecule	kink	28 83 147 398	21 69 116 286

It has been found subsequently[62] that deceleration of the motion of steps is largely due to easier formation of stacking faults on steps which penetrate terraces. Formation of such specially active adsorption positions enhances adsorption and gives rise to kinks on dissolution steps (Fig. 6). Chains of precipitates of inhibiting surfactants form along a step saturated with stacking faults, the motion of such a step slows down, and the result is a reduction in the rate of dissolution of a metal.

VII. Conclusions

We shall conclude our analysis of the cooperative models of dissolution of crystals by stressing the following features. The development of the cooperative models will depend in future on determination of the characteristic features of dissipation-free motion of a dissolution step along a basal plane of a crystal in contact with an electrolyte. These features are related to the conversion of a step from the normal to the superfluid state.[63] The problem has been solved for quantum crystals and the approach is fully applicable to a hydrogen sublattice in surface layers of *d* metals.

The models based on soliton solutions of the equations of motion of ensembles of particles, including elements of the catastrophe theory, provide a picture which is clearest from the physical point of view. Important aspects of the approaches described above are an allowance for change in the fine structure of double electrical layers of a metal and an adjoining electrolyte, for modification of the first layers in a crystal, for changes in the electron and photon subsystems of such a crystal, and for local processes of the solution particles. The cooperative models of dissolution are the most general and are capable of describing dissolution even of defect-free singular faces. This would have been impossible in the case of molecular-kinetic models

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