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INTERDEPENDENCE OF CORROSION PHENOMENA AND MECHANICAL FACTORS ACTING ON METALS

E. M. Gutman

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The simultaneous progress of irreversible corrosion, plastic deformation, and adsorption processes is analyzed for the case of metals interacting with working media. The analysis is based on an expression obtained for the entropy production per unit time and on appropriate phenomenological equations quantitatively describing the interdependence of these processes and possible cross effects. The possibility of an autocatalytic mechanism of corrosion-mechanical fracture at the crack tip, resulting from a simultaneous influence of interlinked mechanicochemical and chemicomechanical effects and leading to spontaneous acceleration of crack growth, is postulated. A qualitative analysis is carried out of the dependence of the polarizability of metals on the magnitude of the deformation-induced shift in their electrode potentials. The role of surface and volume factors in the appearance of electromechanical heterogeniety of metals under strain is analyzed, and the nature of the reduction in the electron work function during plastic deformation of metals is discussed.

The rates of electrochemical dissolution and deposition of metals, ionization and discharge of working media components (in cases when their adsorption on an electrode is a controlling factor), and various reduction-oxidation reactions on active electrodes depend on the nature of the metal and on the physicomechanical state of the electrode surface.

From the standpoint of physicochemical mechanics of materials, the most interesting is the interdependence of the rate of metal dissolution (corrosion) and the physicomechanical state of the metal due to mechanical influences, because the destruction of a material subjected simultaneously to the action of active media and mechanical loads is associated with the localization and acceleration of adsorption-electrochemical processes at the tips of stress raisers [1].

The adsorption-electrochemical theory of stress corrosion formulated by G. V. Karpenko [1, 2] emphasizes the stimulating role of mechanical influences in adsorption and electrochemical phenomena taking place on active regions of metal surfaces, especially at the slip lines and in regions of the formation of ultramicroscopic cracks.

Although the acceleration of corrosion under the influence of mechanical factors (the mechanicochemical effect [3]) is, in macroscopic terms, a completely definite and independent phenomenon, its detailed mechanism should involve adsorption factors because one of the important concepts of the modern theory of anodic dissolution of metals [4] is the participation of surface-active components of the working media in the formation of metal complexes directly in the electrochemical stage, or in the formation of intermediate complexes (the so-called catalytic mechanism) which takes place, for instance, during the dissolution of iron.

Moreover, surface-active anions take part in the passivation and depassivation of metals to an extent which depends on metal properties [5, 6].

The bond strength and reactive power of complexes determine the type of the dissolution process and its rate. And so, the increase in the bond strength between adsorbed anions and surface atoms of a silver electrode is reflected in an increased aggressiveness of these anions when the electrode potential is shifted toward the more positive values [7].

Of some interest in this connection is the recently observed dynamic surface effect in chemical (catalytic) reactions which manifests itself as a reduction in the interfacial (catalyst surface) tension during chemical reactions, and which is a result of the formation of intermediate surface-active compounds [8, 9]; the necessary condition for the manifestation of this effect is that the sorption rate must be faster than the rate of desorption of a given intermediate compound [9].

Taking all this into consideration and summating the contributions of the mechanical and electrochemical processes [10] and of the surface (adsorption) effect of chemical reactions [8] to the entropy production of the system, we find the following expression for the entropy production per unit time S in the case of simultaneously progressing isothermal processes of corrosion, plastic deformation and adsorption:

$$T\dot{S} = \dot{n}A + I\eta + I_0(-\Delta\sigma), \qquad (1)$$

where n is the dislocation flux, A the generalized force proportional to the increase in strength $\Delta\tau$ [10], I the corrosion

flux, η the overvoltage of anodic dissolution of the metal ($\eta = \varphi - \varphi_0$, where φ is the metal potential and φ_0 the equilibrium potential), I_0 the rate at which the interface area between phases increases, and $\Delta\sigma$ the change in the surface tension.

From (1) we obtain a system of linear phenomenological equations:

$$\dot{n} = L_{11}\Delta\tau + L_{12}\eta + L_{13}(-\Delta\sigma), \tag{2}$$

$$I = L_{21}\Delta\tau + L_{22}\eta + L_{23}(-\Delta\sigma), \tag{3}$$

$$I_0 = L_{31}\Delta\tau + L_{32}\eta + L_{33}(-\Delta\sigma), \tag{4}$$

the Onsager reciprocal relations requiring the equality of cross coefficients

$$L_{ik} = L_{ki}. \tag{5}$$

Although, as was shown in [10], under conditions far removed from equilibrium the processes of metal corrosion and formation of dislocations (plastic deformation) are substantially nonlinear, the bilinear form for the entropy production (1) is retained in the range of operation of nonlinear laws, and a linear approximation gives a satisfactory description of states in the vicinity of the equilibrium state. At the same time, nonlinearity of the principal fluxes does not affect the linear character of cross fluxes.* Consequently, conclusions reached for cross phenomena on the basis of analysis of linear phenomenological equations will also be valid in a wider range of nonlinearity of the principal fluxes.

For simplicity, let us first consider cross phenomena for the case when there is no adsorption, so that there are only two conjugate processes, namely mechanical and corrosion.

In this case the system of linear phenomenological equations becomes [10]**

$$\dot{n} = L_{11}\Delta\tau + L_{12}\eta, \tag{6}$$

$$I = L_{21}\Delta\tau + L_{22}\eta, \tag{7}$$

Eq. (7) describing the mechanicochemical effect and Eq. (6) the effect which we called chemicomechanical [10]. However, in the absence of special conditions for noticeable manifestation of the latter effect, i.e., under normal conditions of the action of corrosive media (uniform corrosion) on polycrystalline metal parts, dislocations are discharged uniformly from a thin surface layer which does not affect the deformation of the part as a whole. The negligibly small contribution of the chemicomechanical effect to macroscopic strength characteristics becomes evident if one compares the actual rates of corrosion-mechanical processes with the rate of this effect which is determined by sonic speeds of the movement of dislocations.

Special conditions, in particular, exist in crack tips where continued crack propagation depends on the properties of one (in the case of transcrystalline fracture) or two (in the case of intercrystalline fracture) crystals. In these circumstances, the chemicomechanical effect, which leads to an increase in the chemical potential of surface atoms (i.e., the emergence of dislocations), stimulates the mechanicochemical effect which, in turn, facilitates the emergence of dislocations. This suggests strongly the possibility of autocatalytic*** process of corrosion-mechanical fracture at the tip of a crack leading to self-acceleration of its growth. In fact, a marked increase in the rate of growth of corrosion cracks with time was observed in [12].

The widely known hypothesis of the periodic electrochemical-mechanical mechanism of growth of corrosion-mechanical cracks [13] postulates that the corrosion process in a crack tip weakens the metal and so facilitates subsequent mechanical fracture. It is not stated, however, how this weakening takes place; moreover, while selective corrosion of a smooth surface does, in fact, lead to the formation of stress raisers, corrosion at a crack tip produces a reduction in the stress concentration [14].

*This proposition, in the case of corrosion-mechanical processes under consideration, is supported by experimental evidence [10].

**The system of equations (6) and (7) covers not only electrochemical but also chemical reactions if the overvoltage η is replaced by the chemical affinity of the reaction and the current I by the flux of matter (e.g., dissolution of metals in nonelectrolytic solutions or in low-melting metals). The necessary condition of the process is the existence of a difference between chemical potentials of atom in the solid and liquid phases (or, in Nernst's terms, adequate "solution elasticity"); it is because of a tendency to equalize these potentials that solid metal atoms pass in solution.

***This autocatalytic process must not be confused with the autocatalytic character of anodic reactions resulting from the acidification of the medium in anodic regions.

Accepting the possibility of autocatalytic process in the crack tip removes this contradiction between hypotheses of the periodic electrochemical-mechanical and continuous electrochemical mechanisms [3].

It seems desirable to analyze the possibility of the manifestation of various cross and conjugate effects (in various stationary states) and numerically to express them in terms of phenomenological coefficients; this will make it possible to find ways to determine these coefficients, i.e., quantitatively to describe the mechanicochemical effect.

In numerical terms the mechanicochemical effect is determined by the transference number at $\eta = 0$, which is calculated from (6) and (7):

$$\left(\frac{I}{\dot{n}}\right)_{\eta=0} = \frac{L_{21}}{L_{11}} \tag{8}$$

and which represents the corrosion current calculated per unit dislocation flux in a state of electrochemical equilibrium.

The second effect is the appearance of a dislocation flux (related to a unit corrosion current) in the absence of macroscopic stresses (the chemicomechanical effect):

$$\left(\frac{\dot{n}}{I}\right)_{\Delta\tau=0} = \frac{L_{12}}{L_{22}}. \tag{9}$$

Since in this case the corrosion flux is associated with the existence of overvoltage and a corresponding electric current, this effect, manifesting itself in the absence of a "pressure gradients," may be interpreted as a specific "electro-osmosis of dislocations" produced by an electric potential gradient. The detailed picture is sufficiently clear; the dissolution of a metal surface (the corrosion flux) promotes the discharging of dislocations piled up against surface barriers and so facilitates their migration from the metal interior to the surface.

The third effect is expected to be manifested in the absence of corrosion ($I = 0$) under steady-state conditions and is determined by the potential difference corresponding to a unit stress:

$$\left(\frac{\eta}{\Delta\tau}\right)_{I=0} = -\frac{L_{21}}{L_{22}}. \tag{10}$$

This effect may be called mechanicoelectrical, since mechanical processes produce an electric potential difference whose sign is opposite to the sign of the overvoltage of the corrosion process and which therefore retards transport of dislocations. In other words, formula (10) represents the dislocation "transport potential" closely associated with the "debasement" of the equilibrium potential [10]. The Onsager reciprocal relations define the relationship between the chemicomechanical and mechanicoelectrical effects:

$$\left(\frac{\eta}{\Delta\tau}\right)_{I=0} = -\left(\frac{\dot{n}}{I}\right)_{\Delta\tau=0}. \tag{11}$$

The fourth effect is produced when under steady-state conditions there is no dislocation flux ($\eta = 0$) and represents the stress per unit potential difference (overpotential), i.e., the "electroosmotic pressure" of dislocations:

$$\left(\frac{\Delta\tau}{\eta}\right)_{\dot{n}=0} = -\frac{L_{12}}{L_{22}}. \tag{12}$$

Here the sign of $\Delta\tau$ is opposite to that which stimulates corrosion in accordance with the mechanicochemical effect; as a result, the "electroosmotic pressure" of dislocations produces a reduction in the corrosion flux due to overvoltage η. The relationship between this and the mechanicochemical effect is described by

$$\left(\frac{\Delta\tau}{\eta}\right)_{\dot{n}=0} = -\left(\frac{I}{\dot{n}}\right)_{\eta=0}. \tag{13}$$

In this way we obtained four symmetrical effects expressed by the ratio of fluxes or forces. It is easy to obtain four additional expressions for these effects in which ratios of fluxes and forces are used:

the mechanicochemical effect

$$\left(\frac{I}{\Delta\tau}\right)_{\eta=0} = L_{21}, \tag{14}$$

the "electroosmosis" of dislocations (chemicomechanical effect)

$$\left(\frac{\dot{n}}{\eta}\right)_{\Delta\tau=0} = L_{12}, \tag{15}$$

the "transport potential" of dislocations

$$\left(\frac{\eta}{\dot{n}}\right)_{I=0} = -\frac{L_{21}}{L_{11}L_{22} - L_{12}L_{21}}, \tag{16}$$

and the "electroosmotic pressure" of dislocations

$$\left(\frac{\Delta\tau}{I}\right)_{\dot{n}=0} = -\frac{L_{12}}{L_{11}L_{22} - L_{12}L_{21}}. \tag{17}$$

Effects (14) and (15) are related by

$$\left(\frac{I}{\Delta\tau}\right)_{\eta=0} = \left(\frac{\dot{n}}{\eta}\right)_{\Delta\tau=0}, \tag{18}$$

and effects (16) and (17) by

$$\left(\frac{\eta}{\dot{n}}\right)_{I=0} = \left(\frac{\Delta\tau}{I}\right)_{\dot{n}=0}, \tag{19}$$

which reveals the symmetrical character of these phenomena.

At this stage the ways of experimental determination of phenomenological coefficients L_{11}, L_{22}, and $L_{12} = L_{21}$ may be indicated. L_{22} is determined from polarization curves. L_{21} is found from (14) by measuring I for a given $\Delta\tau$ under static potential conditions $\eta = 0$. Finally, L_{11} can be calculated from (17) after measuring $\Delta\tau$ (compressive stress) for a given value of I under galvanostatic conditions, with a rigidly fixed specimen to prevent its deformation ($n = 0$).

The reciprocal relation of coefficients $L_{13} = L_{31}$ shows that the effect of surface tension on the dislocation flux is determined by the extent to which the rate of change in the surface area is affected by stress. If this rate (i.e., the rate of deformation) is slow, the contribution of surface effects in Eq. (2) is small, i.e., the mechanical properties of metals are not markedly affected by the variation in the surface tension and vice versa. This is in agreement with the existence of an optimum deformation rate for the manifestation of the adsorption-induced reduction in strength postulated by P. A. Rebinder [15, 16]. Equation (2) is therefore a quantitative formulation of the basic proposition* of Karpenko's [1] adsorption-electrochemical theory.

The relation $L_{23} = L_{32}$ shows that the influence of changes in the surface tension on the corrosion fulx (of unstressed metals) is conjugate with the effect of potential difference (overpotential) on the rate of variation in the surface area. There is no experimental evidence of the manifestation of this effect during metal corrosion. It is very likely that sufficiently accurate measurements would reveal the existence of this effect; compared with the influence of $\Delta\tau$ and η, however, a slight reduction in the surface tension $\Delta\sigma$ due to adsorption has no substantial effect on the rate of corrosion, not to mention the fact that surface-active compounds often act as corrosion inhibitors (e.g., acid corrosion of iron and cobalt is retarded by surface-active halide ions [18]). A substantial reduction in the surface tension, however, should stimulate corrosion, as indicated by the fact that the rate of anodic dissolution of metals is accelerated by several surface-active substances [4]. Evidently, in this case one must consider the actual operating mechanism of adsorption of various medium components.

This variable character of the influence of adsorption phenomena ($\Delta\sigma$) on corrosion is associated with the multistage character of anodic dissolution of metals [19]. The catalytic mechanism of anodic dissolution of iron [20] presupposes the formation of an intermediate surface-active compound $(FeOH)_{ads}$ during the reaction. Hydroxyl ions as such are not surface-active (in the sense of intrinsic adsorption), so that adding to a solution some effective surface-active substances (e.g., chlorine ions or corrosion inhibitors) capable of displacing OH^- ions from a metal surface suppresses the catalytic mechanism and retards corrosion. One should therefore conclude that the corrosion-accelerating effect of adsorption phenomena (reduction in the surface tension) described by Eq. (12) is entirely due to the surface effect of the chemical process [8] and is associated with the formation of intermediate surface-active compounds (complexes) during the reaction.

*Hydrogen embrittlement [17] is not considered in this context since hydrogen absorption is a volume phenomenon (although surface adsorption of hydrogen atoms makes a contribution to $\Delta\sigma$).

The adsorption of working media components is determined both by their nature and by the adsorption power of a given metal which to a large extent depends on the electrochemical and physicochemical state of its surface. It may be postulated that plastic deformation, which affects this state, should have a noticeable influence on the adsorption power of metals for the following reasons: the physical anion adsorption is increased due to an increased anodicity and positive charge of the surface; increasing the degree of surface roughness produces an increase in the real adsorption area, i.e., the apparent coverage of the surface [21]; in the case of transition metals there is a reduction in the proportion of chemisorption for which the donor-acceptor interaction of the adsorbate with vacant d-levels is responsible, since it is known [22] that increasing the degree of deformation intensifies the scattering of s-electrons into the d-band.

The electrode polarizability $\partial\eta/\partial I$ (or $\partial\varphi/\partial I$) near the equilibrium (linearity range) coincides with the polarization resistance $R = \eta/I$ and is independent of η. Away from equilibrium the polarizability is strongly dependent on η [10]:

$$r(\eta) = \frac{\partial\eta}{\partial I} = \frac{b}{i^0} e^{-\frac{\eta}{b}} \tag{20}$$

(where b is a constant and i^0 the exchange current) and does not coincide with R. Consequently, the polarizability in this case assumes a differential meaning and is manifested as a resistance to alternating currents, while corrosion is controlled by the resistance to direct currents R.

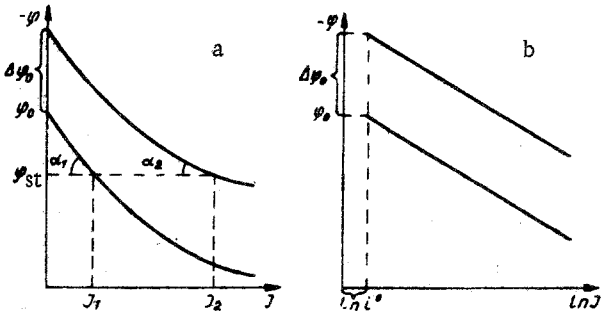

Fig. 1. Effect of plastic deformation on anodic polarization curves (φ denotes the potential and I the anodic current): a) a shift of the equilibrium potential $\Delta\varphi_0$ produced a reduction in the polarizability ($\alpha_2 < \alpha_1$) at a constant potential level φ_{st}; the corrosion current $I_2 - I_1$; b) the anodic polarization curve is shifted toward the more negative potential levels by parallel displacement (as shown experimentally in [24]; the exchange current i^0 is independent of $\Delta\varphi_0$.

Consequently, using the concept of "polarizability" as a characteristic of corrosion is justified only when it coincides with the polarization resistance R, i.e., near the equilibrium. As shown in [10], R in the linear range is not changed under the influence of the mechanicochemical effect.*

In the nonlinear range ($\eta \gg b$) the polarizability varies as a result of mechanical action; however, this variation is a result rather than a cause of the mechanicochemical effect (Fig. 1). If a metal is anodically (potentiostatically) polarized from the equilibrium potential φ_0 to a potential φ (so that $\eta \gg b$), and if then there is a small shift in the equilibrium potential $\Delta\varphi_0$ (so that $\Delta\varphi_0 \ll b$), then

$$r(\eta) = \frac{b}{i^0} e^{-\frac{\eta}{b}} e^{-\frac{\Delta\varphi_0}{b}} \approx r_0\left(1 - \frac{\Delta\varphi_0}{b}\right), \tag{21}$$

where r_0 is determined from (20).

It follows from (21) that the polarizability of a polarized anode should decrease with increasing shift of the equilibrium potential. In practice this shift is almost impossible to measure (at least in the case of technical metals), since the micro-anodes of a metal electrode are almost always polarized (due to electrochemical heterogeneity of its surface) so that only the steady-state corrosion potential φ_{st}, to which the corrosion current i_c corresponds, can be measured.

*As in a previous work [10], the role of mechanical destruction of the continuity of oxide and other surface films on metals is not considered in this article either.

The actually measurable overvoltage $\eta = \varphi - \varphi_{st}$ is determined by its dependence on the polarizing current i_A:

$$\eta = b \ln \frac{i_A}{i_c}. \tag{22}$$

Accordingly, the polarizability is given in this case by

$$r(\eta) = \frac{b}{i_c} e^{-\frac{\eta}{b}}; \tag{23}$$

when the steady-state potential is changed ($\Delta\varphi_{st} \ll b$) as a result of mechanical action during potentiostatic polarization, we have

$$r(\eta) = \frac{b}{i_c} e^{-\frac{\eta}{b}} e^{-\frac{\Delta\varphi_{st}}{b}} \approx r_0 \left(1 - \frac{\Delta\varphi_{st}}{b}\right), \tag{24}$$

where r_0 is found from (23).

If it is accepted that mechanical processes have no significant effect on the operation of microcathodic regions of deformed metals and activate mainly anodic reactions [23], $\Delta\varphi_{st}$ and $\Delta\varphi_0$ will be directly proportional to each other, in which case the actually measured value $r(\eta)$ should decrease with increasing degree of deformation.*

The variable character of the effect of deformation (in the absence of surface films) on the "debasement" of the steady-state potential is due to the dependence of this phenomenon on both the variation in the rate of anodic processes and the character of cathodic processes (Fig. 2). In particular, the more effective are cathodes on the metal surface (i.e., the weaker is their polarization), the smaller is the variation in $\Delta\varphi_{st}$ and the larger is the increase in the corrosion flux as a result of deformation. Moreover, the cathode efficiency may be increased during plastic deformation due to an increase in the degree of metal surface roughness (microslip) equivalent to an increase in the surface area (and therefore in the "macroscopic" density of the exchange current of the cathodic reaction) relative to the area of an ideally smooth surface [24]. The cathodic reaction is also facilitated by the deformation-induced reduction in the electron work function discussed below; as a result, $\Delta\varphi_{st}$ is reduced so that the change in $r(\eta)$ becomes insignificant.

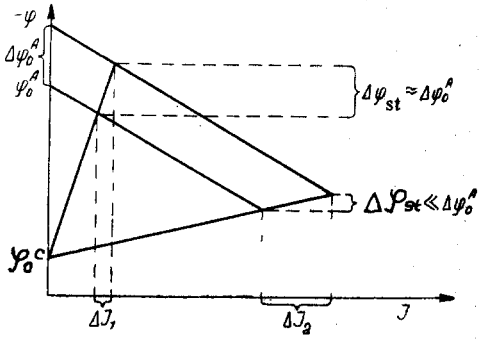

Fig. 2. Dependence of mechanically-induced acceleration of metal corrosion on the character of cathodic reactions (φ is the potential, I cathodic or anodic current φ_0^A the equilibrium anodic potential, and φ_0^C the equilibrium cathodic potential). Intensifying the cathodic control weakens the influence of deformation on the corrosion rate and increases the degree of debasement of the steady-state potential.

In this connection the results of [25] are of considerable interest. Using a microelectrode and a low-frequency pulse method, the authors of this work measured the polarizability at the tip of a growing crack during stress-corrosion tests on alloy MA-2 and established that reducing the effective surface area around a crack from 0.5 to 0.005 cm^2 (by painting the surface with an insulating varnish) decreases the polarizability of a well developing crack by approximately two orders of magnitude. Measurements of the steady-state potential during crack propagation [26] revealed its debasement, sharp in the initial and gradual in the later stages. The polarizability varies in the same way: the very formation of a crack is accompanied by a steplike reduction in the anodic polarizability which subsequently continues to decrease in a more gradual way. There is no doubt that the initial stage (reflected in large $\Delta\varphi$ and Δr) is associated with the damage of surface oxide films at the moment of crack formation. In the latter stages, however, the mechanicochemical effect comes more into play, although the results of the influence of this effect and of the damage of oxide films are additive.

In practice, metals become activated at lines of intersection of slip planes with the metal surface, i.e., locally (the distance between slip planes being hundreds and thousands Å). As a result, the nonactivated surface of a much larger area is a quite effective cathode. Since increasing the cathode efficiency intensifies corrosion during

*In the absence of overvoltage or at $\eta \ll b$ (linearity range)

$$i_A = i_c \frac{\eta}{b}, \quad R = \frac{b}{i_c},$$

i.e., small $\Delta\varphi_{st} \ll b$ produce no changes in the polarization resistance R (or, which amounts to the same, polarizability r).

plastic deformation (Fig. 2), pitting (i.e., local) corrosion is especially favorable for the nucleation of corrosion-mechanical cracks (this being a specific case of the "basin principle" [27]).

On a macroscopic scale, the plastically deformed and undeformed metal regions (crack tips and the remaining surface, respectively) form corrosion elements of the galvanic cell type [28] with a complex current and potential distribution [29] which is further complicated by the fact that we are dealing here with crevice corrosion phenomena [30].

The resulting electrochemical heterogeneity of metal surface regions is determined by two factors: a) differences in the equilibrium potentials (thermodynamic stability) due to the mechanicochemical effect; different electron states (reflected in different conductivities, thermo emf and other properties) leading to the appearance of a contact potential difference which thermodynamically may be described as a deformation-induced change in the chemical potential of electrons in the metal or in the electron work function. Whilst the first of these factors relates to surface phenomena [10], the second relates to volume processes. Comparison of the rates of electrochemical reactions determined on a previously deformed metal and on a metal undergoing deformation at fast strain rates points to the predominance of the first factor associated with continued emergence of "new" dislocations on the metal surface. This view is supported also by the fact that the contact potential usually represents only a small portion of the reversible emf of an electrochemical system [31]. For instance, the contact Volta potential (determined from the difference in the electron work functions) of the couple copper-zinc is 0.3 V, while the emf of the system $Zn \left| \begin{matrix} Zn\,SO_4 \\ a=1 \end{matrix} \right| \left| \begin{matrix} Cu\,SO_4 \\ a=1 \end{matrix} \right| Cu$ is 1.11V.

Under static conditions, however, (e.g., during the intervals of step-like crack propagation) the second factor may play a substantial part. Generally speaking, the volume effect of plastic deformation makes a substantial contribution to transfer phenomena in conductors of the first kind [32] when a small potential difference produces a large current, but has practically no influence on the process of transfer through a phase boundary (a metal-electrolyte interface) where much higher emf are required. In the latter case the predominant part is played by surface effects which consist in an increase in the chemical potential of surface atoms, this increase being associated with an increase in the chemical potential of dislocations being discharged during the process of strain hardening [10].

Moreover, the experimentally observed reduction in the electron work function due to plastic deformation of metals is a local surface effect. As shown in [33, 34], the exoelectron emission centers are situated in points of the emergence of dislocations (etch pits) and slip lines on the metal surface which is associated with the reduction in the electron work function at these points [35].

The roughening of a metal surface as a result of plastic deformation was considered in [36] as a specific dispersing process lowering the electron work function in the same way as the chemical potential of a solution is increased by decreasing the radius of curvature of the phase boundary; a quantitative estimate of this effect is in good agreement with experimental data.

On the other hand, the reduction in the electron work function may be attributed [36, 37] to a reduction in the dipole moment of the Frenkel double layer on a metal surface (whose field retards electron emission) resulting from the distortion of the ordered surface structure [38, 39], i.e., to a reduction in the surface potential barrier.*

The magnitude of this effect depends also to a definite extent on the surface finish [33, 40, 41]. This, it has been stated [36], makes it difficult to decide which explanation of the nature of this effect is to be preferred. In our opinion, this is only an apparent difficulty and the above outlined explanations do not contradict each other, being only different mutually supplementary expressions of the same thermodynamic laws. In fact, since increasing the surface area of a substance is accompanied by an increase in the isobar-isothermal potential, increasing the degree of dispersion of a substance increases its ability to become separated from a given phase during any given process (e.g., an increase is produced in its chemical activity, solubility, saturated vapor pressure, etc.); similar effects are produced by the weakening of the internal structure and by various deviations from the perfect crystal structure (e.g., a transformation from a crystalline to amorphous state produces a sharp increase in the chemical activity of a substance [42]).

Since there is no basis for assuming a change in the thermodynamic potential of metal atoms in vacuum, the deformation-induced increase in the chemical potential of a metal is equivalent to a reduction in the surface potential barrier (acting also with respect to electrons whose chemical potential forms a part of the chemical potential of metals).

Consequently, both processes, i.e., the increase in the chemical potential of electrons due to dispersion and the reduction in the dipole moment of the double layer due to lattice distortions, require an adequate amount of work of

*It is pointed out [37] that if the volume effect of deformation (associated with an increase in the volume) were operating, the sign of the change in the work function would be opposite to that actually observed.

deformation expended on increasing the isobar metal potential and represent in the final analysis different aspects of a single process of increasing the chemical potential of metals.

The influence of the surface finish is associated with adsorption phenomena and may also be described in the framework of laws of the thermodynamics of surface phenomena.

It may be postulated that the deformation-induced reduction in the surface potential jump inhibiting the electron emission is not only due to a reduction in the dipole moment of the Frenkel double layer, but also due to the formation of a positive surface charge associated with the formation of an "internal" double layer consisting of positively charged ionized atoms (the outer plate) and an uncompensated negative charge (the inner plate) concentrated near the surface. The appearance of an "internal" double layer in a metal is associated with an outward slip of ionized surface atoms* as a result of the weakening of atomic bonds during the deformation. Excited ionized atoms of this kind approach the intermediate state which is characteristic of an adsorbed ion and which is considered in the applications of the theory of absolute rates of reactions to electrode processes [43]. It is evident that the retaining force is reduced and metal dissolution facilitated if there is any possibility of electrons escaping from the inner plate of the double layer (cathodic depolarization).

Consequently, the reduction in the electron work function due to plastic deformation is associated with an increase in the chemical potential of a metal at points of emergence of discharging dislocations on the metal surface and may therefore serve as a sensitive index of changes in its thermodynamic stability.

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*This is accompanied by an inward flow of the "electron fluid" from the advancing ionized atoms (since this gives the known energy gain) which forms the negative plate of the "internal" double layer.

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Institute of Physics and Mechanics,
AS UkrSSSR, L'vov