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THERMODYNAMICS OF THE MECHANICO-CHEMICAL EFFECT
I. Derivation of Basic Equations. Nature of the Effect

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Methods of the thermodynamics of irreversible processes are used to derive linear phenomenological equations describing the mechanico-chemical and related effects. The nature of this effect and of the potential "debasement" during plastic deformation of metals is analyzed.

Corrosion of metals under stress is associated with the accelerating effect of mechanical stresses (strains) on the corrosion process; this effect, verified by experiment, is called mechanico-chemical effect [1]. In the absence of a quantitative description of this effect, however, it is difficult to understand its nature and to estimate how its magnitude is changed under the influence of various physico-chemical parameters.

In this article it is attempted to overcome these difficulties with the aid of methods of the thermodynamics of irreversible processes; the analysis of the problem is based on certain simplifying assumptions and corresponding models.

It is known that elastic strains have little effect on corrosion phenomena (with the exception of special cases such, for instance, as the destruction of passive films) and that the mechanico-chemical effect is usually associated with plastic strains produced in the tip of a growing corrosion crack.

We shall consider the deformation of a metal in the linear strain-hardening stage (the case of limited slip), when dislocations align themselves and move in a system of parallel slip planes and when no cross-slip takes place, since this case is most typical for the maximum manifestation of the mechanico-chemical effect, as shown by the results of statistical analysis of data on the susceptibility of metals and alloys to corrosion cracking [1].

Plastic deformation of a metal leads to entropy production which can be calculated on the basis of concepts of the dislocation theory of plastic deformation.

Let us introduce a concept of the chemical (local) potential of a dislocation which is determined in the following way. It was established by experiment [2, 3] that the density of mobile dislocations generated in a deformed metal is related to plastic strain ε (especially in the case of iron and LiF crystals) by

$$N = \alpha(\varepsilon - \varepsilon_0) = \alpha\Delta\varepsilon, \tag{1}$$

where α is a constant and ε_0 is the strain corresponding to the elastic limit.

Hence, the strain which at a constant stress τ and temperature T leads to the appearance of a single dislocation is equal to $1/\alpha$; the work done, which is equivalent to the increase in the isobaro-isothermal potential of the system during the "chemical reaction" of the formation of a single dislocation, i. e., to the chemical potential, is given by

$$\mu_D = \tau\frac{1}{\alpha}. \tag{2}$$

It should be noted that this method of determining the chemical potential of a dislocation may be used for any power functional dependence of N on $\Delta\varepsilon$.

The chemical affinity of the process involving the formation and motion of dislocations is determined from (2) as the difference between the values of the function of state $\Delta\mu_D$ corresponding to the stress difference between two stress states:

$$A = \Delta\mu_D = \frac{\Delta\tau}{\alpha}. \tag{3}$$

If the flux density of generated dislocations is defined as

$$\dot{n} = NV, \tag{4}$$

where V is the rate of the motion of dislocations, then—in accordance with concepts of the thermodynamics of irreversible processes—the entropy production due to deformation ("chemical reaction" of the formation of dislocations) is given by

$$T\sigma^{\mathrm{I}} = \dot{n}A. \tag{5}$$

Here A is the generalized force and $\dot{n}$ the generalized flux representing the "dislocation flux".

To express the flux and the coefficient of the corresponding linear phenomenological equation in terms of measurable values let us calculate $\dot{n}$ through the kinetic parameters.

It is known that the intensity of energy dissipation during plastic deformation is

$$\dot{w} = \dot{\varepsilon}_p \tau, \tag{6}$$

where the dot indicates differentiating with respect to time, and $\dot{\varepsilon}_p$ is the plastic deformation rate. On the other hand, if slip during plastic deformation is taken to be a result of the motion of linear edge dislocations on parallel slip planes under the influence of applied stresses, the dissipated energy is approximately equal to the work done by the external forces [4]:

$$w = \tau n b m, \tag{7}$$

where τ is a component of the applied stress acting in the slip plane, n is the number of discharging dislocations, b is the Burgers vector, and m is the area circumscribed by a moving dislocation.

Assuming, as is usual, a uniform volume distribution of dislocations at a density N and orienting the x coordinate axis normal to the metal surface so that its origin is on the surface of a unit cube, we determine the density of energy dissipated when dislocations present on a segment dx of a slip line in the vicinity of the coordinate x emerge and are discharged on the surface:

$$dw(x) = \tau b x N dx. \tag{8}$$

Integrating (8) between the limits 0 and x, we obtain

$$w = \frac{x^2}{2} b N \tau. \tag{9}$$

If a dislocation has a finite free path a, the metal surface is reached only by those dislocations which are generated in a surface layer of a thickness a. When $a = 1$, the number of dislocations reaching a unit surface area (1 cm^2) per unit time is NV. Consequently, the number of dislocations reaching the surface and discharged there when $\alpha < 1$ is NVa; this brings in the concept of the "effective" density of mobile dislocations $N^* = Na$.

The density of energy dissipated in a unit time by the discharge of dislocations reaching the surface from a depth equal to their free path a is

$$\dot{w} = \frac{dx}{dt} b N x \tau |_{x=a} = b N V a \tau, \tag{10}$$

where V is the dislocation velocity and t is time.

Comparing formulas (6) and (10), we obtain an expression for the deformation rate:

$$\dot{\varepsilon}_p = b N V a, \tag{11}$$

while equating (4) and (11) gives an expression for $\dot{n}$:

$$\dot{n} = \frac{\dot{\varepsilon}_p}{ba}. \tag{12}$$

The free dislocation path [5]

$$a = \frac{\Lambda}{\Delta\varepsilon}, \tag{13}$$

where Λ is a constant.

Under conditions of linear strain-hardening

$$\Delta\tau = \Theta \Delta\varepsilon \tag{14}$$

(where Θ is the strain-hardening coefficient) and at a constant deformation rate the rate of the movement of dislocations may be regarded as constant. *

Then

$$\dot{n} = \frac{\dot{\varepsilon}_p}{b\Lambda} \Delta\varepsilon = L_{11} A, \tag{15}$$

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*This follows from the known expressions for V, taking into account the strain hardening [3, 6] and the strain dependence of a [5], if the condition of a constant strain rate is satisfied.

where

$$L_{11} = \frac{\dot{\varepsilon}_p \alpha}{b\Lambda\Theta}, \tag{16}$$

$$A = \frac{\Delta\tau}{\alpha} = \frac{\Theta}{\alpha}\Delta\varepsilon. \tag{17}$$

It is easily seen that substituting expressions (15)-(17) in Eq. (5) gives a uniform quadratic form necessary for the linearity of phenomenological relations of the (15) type between fluxes and forces. In special cases, when no strain hardening takes place, searching for linear relations becomes pointless since their coefficients L_{11}, which determine the "conductivity," become variable, i.e., L_{11} increases with increasing $\dot{\varepsilon}_p$.

The intensity of electrochemical reactions (anodic dissolution) taking place on the surface of a metal in contact with an electrolyte depends on the overpotential η and corrosion current density I. The resulting entropy production is [7] given by

$$\sigma^{II} = \frac{1}{T} I\eta, \tag{18}$$

where current I is determined by the force η:

$$I = L_{22}\eta. \tag{19}$$

The coefficient L_{22} depends on the kinetics of the electrochemical reaction and is a measure of electrode polarizability. Since the polarizability during the propagation of a stress-corrosion crack is low [8], it is valid to assume that in this case polarization obeys a linear law and that L_{22} is equal to the reciprocal of the polarization resistance.

When a metal simultaneously undergoes deformation and electrochemical corrosion, the overall entropy production and the corresponding phenomenological equations are in the form

$$T\sigma \equiv T(\sigma^{I} + \sigma^{II}) = \dot{n}A + I\eta, \tag{20}$$

$$\dot{n} = L_{11}A + L_{12}\eta, \tag{21}$$

$$I = L_{21}A + L_{22}\eta, \tag{22}$$

i.e., the corrosion and deformation processes are not independent but affect each other. The degree of this mutual interdependence is regulated by the cross-coefficients which are related by the Onsager equation

$$L_{12} = L_{21}, \tag{23}$$

the coefficient L_{21} being a quantitative measure of the mechanico-chemical effect which is fully described by (22).

The physical meaning of L_{21}, i.e., the nature of the mechanico-chemical effect, can be elucidated and quantitatively studied on the basis of concepts of nonequilibrium electrochemistry [9], according to which the entropy production (in the absence of mechanical processes) is given by

$$T\sigma^{II} = \frac{I\tilde{A}}{zF}, \tag{24}$$

where z is the ionic valency of the metal, F the Faraday number, and the electrochemical affinity $\tilde{A}$ (for the case of ions of one kind passing from the metal to the electrolyte) is

$$\tilde{A} = \Delta\mu + zF\varphi, \tag{25}$$

where $\Delta\mu$ is the difference between the chemical potentials of an ion in the metal and in the electrolyte, and φ is the electric potential of the metal.

From (24) follows a phenomenological equation:

$$I = \frac{L_{22}\tilde{A}}{zF}. \tag{26}$$

Overvoltage is expressed through the equilibrium potential φ_0:

$$\eta = \varphi - \varphi_0; \tag{27}$$

at the same time under equilibrium conditions (I = 0), according to the concepts of equilibrium electrochemistry, $\tilde{A} = 0$ and

$$\varphi_0 = -\frac{\Delta\mu}{zF}. \tag{28}$$

Substituting (27) and (28) in (22) and performing the necessary transformations, we obtain

$$I = \frac{L_{22}}{zF}\left(\frac{L_{21}}{L_{22}} zF \frac{\Delta\tau}{\alpha} + \Delta\mu + zF\varphi\right). \tag{29}$$

Comparison of (29) and (26) shows that the appearance of stresses $\Delta\tau$ produces an increase in the chemical affinity of the electrochemical (corrosion) reaction, or in other words (taking into account the fact that the chemical potential of metal ions in the electrolyte is independent of $\Delta\tau$) increases the chemical potential of ions in the metal (at φ = const) by a value

$$\Delta\mu_{M} = \frac{L_{21}}{L_{22}} zF \frac{\Delta\tau}{\alpha}. \tag{30}$$

Equation (30) reveals the physical meaning and clarifies the nature of the mechanico-chemical effect, showing it to represent an increase in the chemical potential of the metal as a result of plastic deformation, an increase which is associated with the weakening of atomic bonds in regions where dislocations emerge and are discharged on the metal surface and which facilitates electrochemical ionization of the metal.

The work required to form 1 g-ion of a metal, which is equal to $\tilde{A}$, consists of two parts: the "chemical" work $\Delta\mu$ and the "electrical " work φzF. An expression for the "chemical" work can be obtained on the basis of analysis of the cycle involving the ionization of the metal and its passing into solution:

$$\Delta\mu = L + \Sigma J + A_{p}, \tag{31}$$

where L and ΣI are energies of the change in the isobar potential of the metal during sublimation and ionization of sublimed atoms, respectively, and A_p is the ion solvation energy. Equation (31) gives the maximum work of spontaneous dissolution of metals.*

Bearing in mind that the last two terms in (31) describe properties of a free ion which are not directly associated with the deformation of the parent metal, we arrive at a conclusion that the corrosion-activating part of the deformation energy is expended mainly on reducing the necessary work of sublimation, since the latter is equal to the difference between chemical potentials of atoms in vacuum μ_0 and in the metal μ_M:

$$A_{c} = -L = \mu_0 - \mu_{M}, \tag{32}$$

the chemical potential μ_M being increased by $\Delta\mu_M$; it is understood that $\mu_0 > \mu_M$.

Under isobaro-isothermal deformation conditions the energy of sublimation may vary only as a result of geometrical distortions of the crystal lattice which are produced by relative movement of metal atoms and which lead to changes in the energy of chemical bonds. Since the metal is dissolved at its surface, an important part should be played by the surface energy which can be calculated as the work required to form a unit area of fresh metal surface γ.

The energy of sublimation of 1 g-atom of a metal is expressed in terms of γ (at 0^0 K):

$$L = \gamma S. \tag{33}$$

Here S is the total surface area of 1 g-atom of the sublimed metal particles which can be calculated from the atomic radius** r:

$$S = N\frac{4}{3}\pi r^2, \tag{34}$$

where N is the Avogadro number.

The sublimation energy related to one atom is

$$L^0 = \frac{4}{3}\gamma\pi r^2. \tag{35}$$

The sublimation energy of a surface atom is approximately 1/2 L^0, being only 1/4 L^0 in the case of an atom on the edge of a step formed by an array of dislocations discharged on a metal surface.

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*Strictly speaking, a term representing a negative product of the electron work function and the ion valency should appear in the balance equation (31). However, since it is impossible to measure the potential difference between points in two different phases, the value of actually measurable (against a reference electrode) equilibrium potential, as defined by $\Delta\mu$, will not contain this term which is cancelled in the expression for measurable emf [10]. Moreover, the value A_p in addition to the above given meaning should account for the specific influence of electrolyte anions on the escape of metal atoms from the lattice.

**The "specific volume defect" [11] is not considered here.

These concepts, although simplified and schematic, illustrate the character of the variation in the chemical bond forces which accompanies changes produced in the total surface energy by escaping atoms, and explains the increased corrosion activity of "fresh" dislocations [1, 6]. If it is borne in mind that the influence of atomic bond forces extends over a distance larger than the lattice parameter, the maximum thermodynamic instability of an atom which is present on the edge of a step at the moment of its formation and which is being rapidly dissolved becomes self-evident.

Externally this is manifested in the existence of "instantaneous" active dissolution centers [1].

The above concepts should be supplemented by the contribution of the "instantaneous" excited electron state of an atom passing through metastable positions at the moment of formation of a dislocation step, which may increase its chemical activity and solvation power and reduce the ionization potential. The existence of this contribution is indirectly proved by experimental data on electron emission from deformed metal regions and on the reduction in electron work function of regions in which dislocations emerge on a metal surface [12]. Moreover, it was shown in [13] that plastic deformation of metals produces changes not only in the fine crystal structure around dislocations but also in the structure of the electron energy spectrum (changes in the s-d exchange interaction).

Increasing (by deformation) the chemical potential of a metal to a value ($\mu_M + \Delta\mu_M$) leads to a displacement of the equilibrium potential toward the negative values (equivalent to an increase in the thermodynamic instability of the metal);* this potential shift is given by

$$\Delta\varphi = -\frac{\Delta\mu_M}{zF}. \tag{36}$$

The physical meaning of the "debasement" of equilibrium potential can be explained in the following way. The formation of a metal crystal (containing defects) by electrodeposition entails performing electrical work, the $\varkappa$th part of which is transformed into dislocation energy:

$$\Delta w = \Delta nez\varkappa\eta, \tag{37}$$

where η is cathodic polarization, ez is the ion charge, and Δn the number of deposited atoms.

If dislocations are removed (by deformation) from a metal in a state of equilibrium, the energy loss due to discharging dislocations will be

$$\Delta w^* = \mu_D \, \Delta N, \tag{38}$$

where μ_D and ΔN denote, respectively, the chemical potential and number of discharging dislocations.

A new equilibrium state will be reached if during the same time an equivalent number of dislocations is produced by a counteracting electrodeposition process, i. e., when $\Delta\omega = \Delta\omega^*$. Consequently, in the new equilibrium state there appears additional cathodic polarization $\varkappa\eta$, which can be determined by equating (37) and (38), and which produces "debasement" of the equilibrium potential.

Here, in a full measure, is manifested the Le Chatelier-Brown thermodynamic principle, whose direct consequence is the phenomenon under consideration, i. e., the "debasement" of equilibrium potential.

Equation (22) shows that stresses (strains) activate the corrosion process so as to ensure that the polarizability $\partial\eta/\partial I$, proportional to $1/L_{22}$, remain unchanged and the effect of stress manifest itself in an increase in the corrosion current at a constant potential φ. This conclusion is in agreement with experimental data [15] on the effect of plastic deformation on polarization curves. Increasing the degree of plastic deformation produces a shift of the anodic curves "potential/logarithm of the corrosion current" toward the higher (by several orders of magnitude) current values without changing their shape, which is equivalent to a parallel displacement of the anodic polarization curve toward the negative values of φ over a distance equal to the shift in the equilibrium potential (36).

For this reason, changes in the linear polarizability under the influence of deformation may take place only when conditions are created for the manifestation of the negative difference effect (e. g., destruction of oxide films on aluminum alloys [16]).

Equation (21) shows that overpotential η affects the deformation process (the dislocation flux) in a way which is independent of $\Delta\tau$: $\partial\dot{h}/\partial\eta$ does not depend on $\Delta\tau$. In other words, the appearance of overvoltage η at $\Delta\tau = 0$ may produce a dislocation flux and, consequently, strains. It would be appropriate to call this phenomenon (by analogy to that previously discussed) chemico-mechanical effect. The above conclusion is qualitatively supported by the results of tests [17] in which a cadmium single crystal specimen undergoing steady-state creep (under a constant load) showed a sharp increase in its elongation after immersion in a corrosion-active electrolyte (a sulfuric acid solution); similar effects were

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*This does not contradict calculations in [14] showing negligible variation in the equilibrium potential, since these calculations were carried out for static loads in the elastic strain range.

produced by anodic polarization of this specimen in an electrolyte. The physical meaning of this effect is that the dissolution of surface atoms by corrosion currents facilitates the discharge of dislocations piling up against the surface "barrier."

The system of phenomenological equations (21) and (22) covers not only electrochemical corrosion but also various kinds of chemical corrosion (gaseous corrosion, corrosion in nonelectrolytes and in liquid metals and nonionic substances), if the electrochemical affinity ($\tilde{A} = zF\eta$) is replaced by the chemical affinity of the appropriate reaction and the corrosion current I by the flux of a given substance across a phase boundary.

More precise data on the nature of the mechanico-chemical effect can be obtained by studying the effect of deformation on the electron structure and electron energy spectra of metals [13] with particular reference to concepts of stable electron configurations [18], since the scattering of electron waves on lattice defects (dislocations etc.) should produce changes in the statistical weight of stable d-configurations due to $s \rightarrow d$ transitions, thereby changing the thermodynamic stability of metals and their capacity to act as donors or acceptors in reactions with the elements of working media.

Summary

1. It was established by methods of the thermodynamics of irreversible processes that the mechanico-chemical effect is quantitatively described by a set of linear phenomenological equations which relate the mechanical phenomena of the formation and motion of dislocations to electrochemical processes involved in metal corrosion, and that this effect is a manifestation of a plastic deformation-induced increase in the chemical potential of metals.

2. The deformation energy activates metal corrosion mainly by reducing the energy of sublimation of metal atoms.

3. The existence of "instantaneous" active centers of dissolution of a deformed metal is associated with specific characteristics of the configuration of chemical bonds of metal atoms and with the metastability of their excited electron state at the moment of the formation of a dislocation step on the metal surface.

4. The "debasement" of the equilibrium potential of a metal during plastic deformation is a direct result of the operation of the Le Chatelier-Brown thermodynamic principle.

5. When the negative difference effect cannot be manifested, the corrosion-activating influence of deformation leads to an increase in the corrosion current (at a fixed anode potential) by "debasing" the equilibrium potential and, hence, providing a general parallel displacement of the anodic polarization curve.

6. Deformation and corrosion phenomena are interdependent since, linked to the mechanico-chemical effect, there is another effect which may be called chemico-mechanical and which consists in facilitating the emergence of dislocations on a metal surface as a result of the dissolution of metal atoms and the resulting reduction in the free surface energy (surface energy "barrier").

7. The introduction of a concept of the "chemical potential of dislocations" makes it possible to express the entropy production due to plastic deformation of metals (under isothermal conditions) as a bilinear form of generalized flux and force which are represented, respectively, by the "dislocation flux" and by the chemical affinity of the "reaction" of the formation of dislocations (which is proportional to the degree of strain hardening during plastic deformation) related by a linear phenomenological equation.

REFERENCES

1. T. P. Hoar, Corrosion, **19**, 331, 1963.
2. A. S. Keh and S. Weismann, Proceeding of the Conf. on Electron Microscopy and Strength of Materials, Interscience Publishers Inc., N. Y. 231, 1963.
3. W. G. Johnston, J. Appl. Phys., **33**, no. 9, 1962.
4. A. M. Freudenthal and J. H. Weiner, J. Appl. Phys., **27**, no. 1, 1956.
5. Collection: The Role of Dislocations in Strengthening and Weakening of Metals [in Russian], Izd. "Nauka," Moscow, 1965.
6. G. T. Hahn, Acta Met., **10**, 727, 1962.
7. P. van Rysselberghe, J. Phys. Chem., **57**, 275, 1953.
8. N. D. Tomashov and N. I. Isaev, DAN SSSR, **132**, no. 2, 1960.
9. S. R. De Groot, Thermodynamics of Irreversible Processes [Russian translation], GITTL, Moscow, 1956.
10. N. A. Izmailov, Electrochemistry of Solutions [in Russian], Izd. Khar'kovskogo gosumiversiteta, 1959.
11. P. N. Dzhaparidze, FKhMM [Soviet Materials Science], no. 4, 1966.
12. V. S. Kortov and R. I. Mints, FKhMM [Soviet Materials Science], no. 3, 1966.
13. I. Ya. Dekhtyar, D. A. Levina, and V. S. Mikhalenkov, DAN SSSR, **156**, no. 4, 1964.

14. E. M. Zaretskii, ZhPKh, **20**, no. 9, 1947.
15. N. D. Green and G. A. Saltzman, Corrosion, **20**, no. 9, 1964.
16. N. D. Tomashov and N. I. Isaev, Transactions of the Physical Chemistry Institute AS USSR [in Russian], 7, 1959.
17. I. Kramer and L. Demer, Uspekhi fiziki metallov, Moscow, 9, 1964.
18. G. V. Samsonov, Ukr. Khim. zhurnal, **31**, 233, 1965.
19. Collection: Catalysis [Russian translation], IL, Moscow, 1963.

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