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Metal surface charge change due to deformation

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Deformation potential for one dislocation and dislocation pile-up in a thin surface layer was examined. It is shown that the deformation potential changes the electron work of exit, the surface charge of metal and the structure of the double electrochemical layer. The differential capacity method was used as the principal method of measuring the metal surface charge. The plastic strain increases the positive charge of the metal surface. This effect reached a maximum according to successive stages of strain hardening. The zero-charge potential of the metal surface was shifted towards negative values by the amount of the deformation potential, with the formation of an internal double layer in the metal. For example, this shift achieved the value of -0.16 V in the case of iron in 0.1 N H_2SO_4.

1. Introduction

For metals, in the case of long-wave elastic fluctuations of density, proceeding from the condition of constant Fermi level over the entire crystal, the magnitude of the electron energy change has been found. It characterizes local electrical neutrality violation and the appearance of a deformation potential [1]

$$\Delta\varphi^{d}(r) = -\frac{\Delta\varepsilon_F}{e} = -\frac{2\varepsilon_F^{*}\delta(r)}{3e} \quad (1)$$

here r is the radius vector of the point where dilatation $\delta(r)$ (volume strain) takes place, ε_F is the Fermi energy, and ε_F^{*} for numerous metals is of the order 7–8 eV; e is the electron charge.

The electrons flow from compressed regions to extended ones, so that the Fermi level (chemical potential of the electrons) remains the same. As a result, extended regions acquire excess negative charge, while compressed ones acquire positive charge. The arising potential compensates exactly the Fermi level local distortion caused by deformation. In the case of elastic uniaxial tension of metals, maximum dilatation $\delta = (1 - \nu)e_{11} \approx 0.04\%$ (on average, Poisson coefficient $\nu = 0.3$), which corresponds to $\Delta\varphi^{d}_{\max} = -2$ mV. Naturally, such a small value of maximum potential change could not have been reliably detected in any kind of electrochemical experiments involving metal specimen deformation below the macroscopic elasticity limit. The arising of local deformation potentials does not define by itself any acceleration of electrochemical metal dissolution. In fact, in relation to the change in metal ion work of exit, it should be taken into account that the chemical potential of a metal consists of the chemical potentials of the ionic skeleton and the free electrons. Deformation potential is connected with the change in the second component. It is numerically equal to the energy change of free charge carriers – electrons – representing only a small part of the chemical potential of the metal. It is noteworthy that the lattice potential represents the main part of the chemical potential of the metal (especially for transition metals). The energy change of free electrons contributes to the chemical potential change of an atom only according to the statistical weight of free carriers. Therefore, to change the ion work of exit by the magnitude revealed by the shift of standard electrode potential (at the expense of the change in ionic exchange) equivalent to the maximum value of deformation potential, much more energy is consumed than is required for the change in the carrier energy by the value of the deformation potential. Even under maximum residual plastic deformations exceeding the yield point, the experimental value of the specimen dilatation is of the order of $\Delta V/V = \delta \approx 10^{-4}$ [2]. This corresponds to $\Delta\varphi^{d}_{\max} \approx -0.5$ mV.

Dilatation connected with anharmonicity may be described by the model of non-linear dislocation dilatation [3]. This makes it possible to calculate the average dilatation, $\Delta V/V$. The application of this model allows the influence of average non-linear expansion of homogeneously distributed dislocations on the electromagnetic phenomena connected with the carrier transfer processes inside the metal, to be followed. Here no detailed model of the deformation potential was applied. Instead, a tentative dependence of electromagnetic parameters on the non-linear dilatation magnitude was accepted, which involved, generally speaking, unknown coefficients. The observed influence of plastic deformation on carrier motion in metals can be well explained using the notion of deformation potential, if we refer the deformation potential value on the whole to the change in the conduction electrons energy. Deformation potential can appreciably influence electrochemical reactions in the case of a change in the electron work of exit. The latter is of essential importance for cathode

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reactions, because it changes both the overvoltage of ion discharge, and adsorption processes on the electrode surface.

Thus, to describe mechanoelectrochemical phenomena under the applied stress, an elastic continuum model (with quasi-free electrons) with structural defects of the dislocation type may be accepted as a physical model of a metal. According to this model, the deformation potential due to the average dilatation of an elastically strained metal or to the average non-linear dilatation of dislocations does not practically influence the metal ion work of exit. Nevertheless, it exerts an effect on the electromagnetic transfer phenomena in metals and on the electron work of exit. As noted above, long-wavelength crystal lattice oscillations can induce a local electrical neutrality violation. It is characterized by a rather small deformation potential within the limits of linearly elastic macroscopic deformations. Average non-linear dilatation of dislocations (macroscopic average dilatation of a solid caused by plastic deformation) results in approximately the same low value.

2. Theory

Let us consider the role of dislocation pile-ups in the formation of a deformational potential. Edge dislocations cause local dilatation in the region obeying linear elasticity laws ($r \geqslant 2\bar{b}$) [2]

$$\delta = -\frac{\bar{b}(1-2\nu)\sin\theta}{2\pi(1-\nu)r} \tag{2}$$

Hence, the absolute value of local excess hydrostatic pressure is

$$P = \frac{(1+\nu)\mu\bar{b}\,|\sin\theta|}{3\pi(1-\nu)r} \tag{3}$$

where $\bar{b}$ is Burger's vector, μ is modulus elasticity in shear, θ and r are polar coordinates.

Comparing Equation 2 with the general expression for deformation potential (Equation 1), and taking into account the additive character of energy parameters during the formation of a planar pile-up involving n coplanar dislocations [4], we can find the final estimate of the local deformation potential caused by a planar pile-up involving n dislocations

$$\Delta\varphi_n^{\mathrm{d}}(r,d) = \frac{\varepsilon_{\mathrm{F}}^* n(1-2\nu)\bar{b}\sin\theta}{3\pi e(1-\nu)r} \tag{4}$$

It follows from Equation 4, in contrast to the mechanochemical effect (acceleration of electrochemical metal dissolution), that the deformation potential depends only on geometrical parameters, i.e. on the pile-up sizes, n. It does not depend on strain-hardening value, which may differ depending on the nature and the character of forces resisting dislocation motion. However, the dependence of the deformation potential on the elastic interaction between dislocations should cause its sensitivity to the dislocation substructure at various deformation stages. It should enhance the effect in the case of the formation of planar dislocation pile-ups at the stage of intense strain hardening, and reduce it in the case of the formation of sub-boundaries and cellular substructures at the stage of dynamic recovery.

The considered dilatation characterizes the crystal behaviour within the linear elasticity region. Its value averaged over the crystal is zero. However, strictly speaking, linear elasticity laws are inapplicable near dislocations. Therefore, a non-linear dislocation theory has been developed [3]. From the point of view of this theory, lattice dilatation is non-linear and may be described by the following equation

$$\delta = (1-2\nu)\frac{A_0\sin\theta}{\mu r} + \frac{A_0^2(A_1 + A_2\cos 2\theta)}{r^2} + \cdots \tag{5}$$

where $A_0 = -\mu\bar{b}/2\pi(1-\nu)$, A_1 and A_2 are magnitudes expressed in terms of linear and non-linear elastic constants.

Let us determine the average value of non-linear dilatation (Equation 5) over the entire crystal volume. It is essentially non-zero and may be obtained by integrating Equation 5 over the region of the dimension, r

$$\bar{\delta} = \frac{2A_0^2 A_1 \ln(r/r_{\mathrm{d}})}{r^2 - r_{\mathrm{d}}^2}, \tag{6}$$

where r_{d} is the dislocation core radius. We calculate the non-linear dilatation for each unit cell $\bar{b}^2$ located in a point with the coordinate r. From Equation 6 we obtain

$$\delta_{\mathrm{b}}(r) = \frac{1}{2\pi r}\frac{\mathrm{d}}{\mathrm{d}r}\left[\bar{\delta}\pi(r^2 - r_{\mathrm{d}}^2)\right] = \frac{A_0^2 A_1}{r^2} \tag{7}$$

In contrast to the average non-linear dilatation, $\bar{\delta}$, this magnitude is a local characteristic depending on the coordinate r (the averaging is carried out only over the azimuth angle, θ). Therefore, it reaches high values near dislocations. Substituting Equation 7 into Equation 1, we find the respective local deformation potential

$$\Delta\varphi^{\mathrm{d}}(r) = -\frac{2\varepsilon_{\mathrm{F}}^* A_0 A_1}{3er^2} \tag{8}$$

which, in contrast to $\Delta\varphi_n^{\mathrm{d}}(r,\theta)$ obtained from Equation 4, does not vanish when averaging over the crystal. It manifests itself independently of the azimuth angle of the reference point location regarding the dislocation axis at a specified distance from the latter. The local deformation potential due to the action of one planar pile-up of n dislocations may be finally expressed in the following form

$$\Delta\varphi_n^{\mathrm{d}}(r) = -\frac{\varepsilon_{\mathrm{F}}^* n(\mu\bar{b})^2 A_1}{6e\pi^2 r^2(1-\nu)^2} \tag{9}$$

The new surface forming during the process of edge dislocation exit creates a surface barrier, and edge dislocation pile-ups of considerable sizes may appear near the generated surface. In the present case, we consider a surface barrier connected with the resistance to the dislocations exit, which is caused by work consumption on forming a new surface on the slip step. Taking the width of the surface barrier with the pile-up of n dislocations before it, to be equal to the maximum dislocation width, we obtain $r \approx 10\bar{b}$ for

Equation 9. Substituting into Equation 9 typical numerical values (for our approximate estimations, we accept the orders of magnitude of non-linear elastic constants obtained for copper) $\varepsilon_F^* = 7$ eV, $\nu = 0.3$, $r = 10\bar{b}$, $r_d = 2\bar{b}$, $\mu = 83$ GPa, $A_1 \approx 10^{-21}$ m^4/N^2, we can estimate the deformation potential for the points of a thin layer near the surface: $\Delta\varphi_n^d(r, \theta) \approx -0.0165n$ V. For example, for the magnitude $n = 10$, it leads to $\Delta\varphi_n^d \approx -0.16$ V.

The absolute value of the deformation potential is numerically equal to the deformational distortion of the Fermi level (before its flattening). Finally, it characterizes the change in the conduction electrons energy, which may affect the work of exit of an electron. Frumkin [5] has formulated the following statement: the zero-charge potential of a metal, φ_N, is proportional to the Volta-potential value. Numerous investigations confirmed the dependence

$$\varphi_N = \frac{\omega_m^e}{F} - 4.7 \qquad (10)$$

where ω_m^e is the work of exit of an electron.

Therefore, one should assume the influence of deformation on the zero-charge potential, φ_N, (or the zero-point potential). The mechanism of this phenomenon can be presented as follows. Frenkel [6] proved the existence of a double surface electric layer in metals formed by a cloud of free (non-localized) electrons above the metal surface and positive ion-atoms of the crystalline lattice skeleton (surface cations). We term this layer the Frenkel double layer. The Frenkel double layer is always characterized by the existence of a potential jump, including the case of the absence of a charge excess on the metal surface, i.e. in the zero-point of the metal (just as the potential jump which is connected with the orientation of the solvent dipoles).

Deformational local lattice dilatation near the metal surface leads to electrons being drawn-off from the adjacent regions, including the double Frenkel layer, due to the Fermi level flattening. The arisal of a local deformation potential of the extended region is accompanied by the opposite change of the potential of the regions that have accomplished the function of electron donors. Non-localized electrons of the double Frenkel layer are the least tightly bound with ion-atoms of the crystalline lattice skeleton (concerning electrons of the internal regions). They are the first to be drawn into the extended regions of the crystal, baring the surface monolayer of positively charged ion-atoms of the lattice skeleton. Such a redistribution of electrons results in the formation of a double electrical layer, consisting of a negatively charged plate (extended under-surface crystal regions) and a positively charged plate (mono-layer of drawn-out positive surface ion-atoms). For brevity we call such a deformation-induced double layer *an internal double layer* of the metal. At the same time, the structure of the Frenkel double layer is changed due to a partial passage of external electrons into the metal. Therefore, the potential jump hindering the exit of electrons from the metal is reduced, and, hence, the work of exit of electrons also decreases (the chemical potential level of the electrons inside the metal remains unchanged). The positive plate of the internal double layer increases the positive charge of the metal surface and affects the structure of the double electrochemical layer, orienting solvent dipoles and changing the electrostatic adsorption of electrolyte cations and anions. According to Equation 10, the reduction of the electron work of exit results in an equivalent shift of the zero point towards negative potentials. This corresponds to an increase in the positive charge of the metal surface.

Let us calculate the magnitude of the deformational shift of the zero point. If we imagine that a large piece of metal was subjected to a uniform dilatation, then the deformational distortion of the Fermi level, $\Delta\varepsilon_F/e$, inside it leads to a nearly equal (numerically) change in the potential jump in the Frenkel double layer, because the Fermi level is flattened over the entire crystal only due to the passage of the electrons of the external plate of the Frenkel double layer into the crystal, and their amount is insufficient for ε_F to acquire the initial value. In the present case, we obtain

$$\left|\frac{\Delta\varepsilon_F}{e}\right| \approx |\Delta\chi_0| \qquad (11a)$$

$$\frac{\Delta\omega_m^e}{e} = 0 \qquad (11b)$$

because the potential jump, χ_0, in the Frenkel double layer (surface potential of the metal in a vacuum) and the level of the chemical potential of electrons, undergo opposite changes, so that the work of exit remains unchanged. Thus, according to Equation 10, the zero charge potential of the metal surface will remain unchanged although, due to the increase in the surface potential jump, the Galvani-potential of the metal, $g_m = \chi_0 + \psi$, grows (ψ being the external potential forming the basis of Volta-potential formation).

If a piece of metal undergoes a heterogeneous dilatation only in the sites of dislocation pile-up, then we may assume, to a sufficient precision, that inside the region of the under-surface pile-up influence, a thin layer of the expanded lattice adjacent to the surface, accepts electrons from the Frenkel double layer, creating an excess positive charge on the surface. It seems quite logical to estimate the order of magnitude of the thickness of this thin surface layer interacting with external electrons, as half the distance between the surface atoms plane and the next underlying atomic plane, because for such scales, lattice dilatation at the distances of $r \approx 10\bar{b}$ from the dislocation core may be assumed to be homogeneous. The lower boundary of the layer chosen in such a way may be taken as a neutral cross-section, dilatation occurring on both sides of it. Below this cross-section, electron deficiency is filled at the expense of the entire volume of the metal, and above it, at the expense of external electrons.

The Fermi level is, in essence, the electrochemical potential of electrons in metals. Enjoying a certain freedom in the choice of a standard state and in the separation of chemical potential into a chemical and an electrical part, which cannot be accomplished using thermodynamic methods, but is quite reasonable from the point of view of atomistic ideas, we can write the expression for the electrochemical potential of electrons in a metal as follows

$$\varepsilon_F = \tilde{\mu}_e = \mu_e + e\chi_0 + e\psi \qquad (12)$$

where μ_e is the chemical potential of electrons in metals depending, in particular, on their concentration, and ψ is the external potential.

The electron work of exit equals $\omega_m^e = -(\mu_e + e\chi_0)$, and according to the free electron model, at the Fermi level we obtain

$$\mu_e = \mu_e(0) + H_e \qquad (13)$$

where $\mu_e(0)$ is the chemical potential of an electron at the lowest occupied level, and H_e is the total width of the energy spectrum of a filled band.

The deformation of the highest occupied level, ΔH_e, immediately brings about such a deformation of the lowest level, $-\Delta\mu_e(0)$, equal in absolute value, so that the level μ_e is constant. The compensation occurs at the expense of the electron density redistribution, and the addition to the carrier energy, $\Delta\mu_e(0)/e$, represents the arising deformation potential (Equation 1).

Under the considered conditions, the distribution of local deformation potential is asymmetric, although its average integral over the volume equals zero according to charge conservation law. Within a limited region of the extended lattice near the dislocation pile-ups, its magnitude is of the order of Equation 9, while in the remaining region of non-deformed crystal, due to its much larger sizes, the exit of compensating electrons exerts only a slight influence on the electron density and causes a negligibly small potential change.

One can always choose a thin surface metal layer in order to assume that electron deficiency in this layer is completely covered at the expense of the external electron cloud of the Frenkel double layer with a respective change in the external potential, ψ. (The thickness of this layer has been estimated above.) Because in this case, too, lattice dilatation or compression changes the chemical potential $\Delta\mu_e$ (at the outset of the deformation, electrical neutrality is not violated, and only the chemical part of the energy changes), the equilibrium condition, $\Delta\mu_e = 0$, may be provided by electron redistribution at the expense of the electrons of the Frenkel double layer. This will cause a change in the surface potential jump, χ_0. The magnitude of the latter is defined by compensation conditions: $\Delta\chi_0 = -\Delta\mu_e(0)/e = \Delta\varphi^d(r)$, where $\Delta\varphi^d(r)$ is the deformation potential in a thin surface layer.

Now the general condition of constant electrochemical potential ($\Delta\varepsilon_F = 0$) requires an equivalent change in the external potential $\Delta\psi = -\Delta\chi_0 = -\Delta\varphi^d(r)$. Subsequently, the work of exit is changed: $\Delta\omega_m^e/e = \Delta\chi_0$. Consequently, the zero-charge potential shift takes place, $\Delta\varphi_N = \Delta\omega_m^e/e = \Delta\varphi^d(r)$, as was to be established. Because the changes in surface and external potentials compensate each other, the local Galvani-potential remains unchanged, and the metal remains equipotential ($\Delta\chi_0 = -\Delta\psi$). According to Equation 9, $\Delta\varphi^d(r) < 0$. Then $\Delta\varphi_N < 0$, too which points to the arisal of additional local positive charge on the deformed metal surface interacting with the electrolyte.

Thus, it can be supposed that the dependence of the change in the electron work of exit on the plastic deformation degree should be analogous to the change in the metal mechanochemical activity at various deformation stages [7]. At the strain-hardening stage, the effect should be enhanced due to the interaction of dislocations in planar pile-ups, while at the dynamic recovery stage, it should weaken. Local increase in the surface charge leading to rearrangement of the adjacent double electrochemical layer may be experimentally detected, if it leads to an increase in the capacitance of this layer, which may be presented as a system of local capacitors connected in parallel. In particular, for low-carbon steel ($n \approx 10$), the shift of the minimum of differential capacity curves (towards negative potential values) should equal $\Delta\varphi_N = \Delta\varphi_n^d \approx -0.16$ V. This is comparable with the measured value, as will be shown below.

3. Experimental procedure

We have investigated electrode impedance (differential capacity and resistance) of the surface of a low-carbon steel specimen under uniaxial tensile loading in 0.1 N H_2SO_4 electrolyte. The chosen electrolyte made it possible to investigate mechanochemical effects in the absence of an oxide film. It was established by scrapping the electrode surface under the electrolyte and measuring differential capacity. A glass electrochemical cell (Fig. 1) was fabricated taking into account improved requirements to sealing glands made of polytetrafluoroethylene because of a broad interval of the specimen deformation values. A wire specimen of

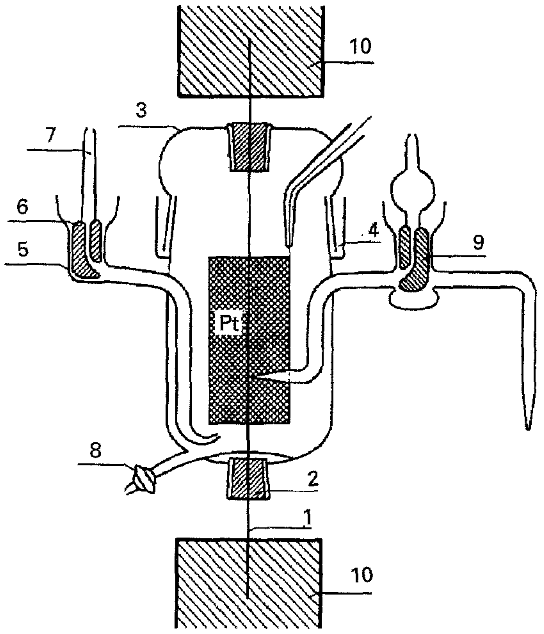

Figure 1 Schematic view of the electrochemical cell for metals under stress. 1, specimen (working electrode); 2, hermetizing plug; 3, movable vessel lid; 4, gap for hermetizing fluid; 5, solution filling funnel; 6, hermetizing ground-in plug; 7, gas forwarding tube; 8, tap for solution disposal; 9, intermediate ground-in plug of reference electrode; 10, clamps of tensile test machine; Pt, platinum counter electrode. The cell has double walls for thermostatic temperature stabilization (not shown).

low-carbon steel (0.1% C, 0.5% Mn, 0.03% Si, 0.15% Cr, 0.3% Ni, 0.04% S and P) 0.8 mm in diameter, was vacuum annealed at 1203 K, degreased and coated with acid-proof varnish. A cylindrical operating portion of a specified length (2 or 10 mm) was left uncoated. To ensure electrical insulation, the clamps of the tensile test machine operating in uniaxial tension were made of fabric-based laminate composite. Stepwise strain was accomplished using a screw and measured by a special indicator to an accuracy of 0.01 mm. The distance between the clamps and the total specimen length (approximately 100 mm) made it possible to locate the electrochemical cell with specimen, electrodes and auxiliary vessels in a specific manner. The operating portion of the specimen (on the cell axis) was located opposite the capillary of 2N mercury–mercurous sulphate reference electrode within the limits of coaxial auxiliary electrode made of platinum net. The double layer impedance was measured with an electronic bridge at the operating frequency of 10 kHz. Special investigations have shown that the frequency-response dependence of differential capacity practically disappears at this frequency. Hence, the results are not distorted by the presence of microcracks on the surface formed due to microroughness increase under plastic deformation. A.c. voltage at the cell did not exceed 10 mV, ensuring a satisfactory precision of differential capacity measurement. To realize polarization by direct current, an auxiliary platinum electrode was used, separated by a tap from the cell (not shown in Fig. 1). When measuring differential capacity curves, polarization was carried out using a galvanostat with specially chosen control stages. A high value of the galvanostat ballast resistance (up to 50 MΩ) ruled out its influence on a.c. circuit operation. Special measurements were carried out to account for the change in the operating portion area of the specimen. The results of capacitance and resistance measurements were recalculated on their basis, using correction factors.

4. Results and discussion

Fig. 2 shows the results of the measurement. Deformation slightly changes the steady potentials, while the zero-charge potential is shifted towards negative values, the surface becoming positively charged. According to theoretical analysis, the shift of surface charge towards positive values passes through a maximum with growing deformation. It increases at the stage of strain hardening and then decreases somewhat, as in the case of the mechanochemical effect [7]. Similar results were also obtained in HCl solution. Measuring the surface charge change by the shift of zero-charge potential, φ_N, it may be concluded that the deformation of a practically uncharged surface (in non-strained state φ_N is close to φ_s) leads to the appearance of a positive charge. This is characterized by $\Delta\varphi_N$ shift of the order of 0.1–0.16 V (a change towards negative potential), which agrees with the calculated value obtained above.

To clarify the nature of differential capacity increase in the process of deformation, we compare the curves presented in Fig. 2. The anodic polarization of a non-deformed specimen, equal to the zero-charge potential shift caused by deformation ($\Delta l = 5$ mm), leads to a capacitance increase approximately equal to that observed at the deformation under steady potential conditions. The comparison of the curves for $\Delta l = 0$ and $\Delta l = 15$ mm shows that a φ_N shift of 100 mV, caused by deformation, led to an increase in capacitance by 20 μF cm^{-2} at a steady potential. This coincides with a capacitance increase in undeformed specimens at the anodic polarization by 100 mV for a steady potential. In general, all the experiments revealed a trend of increasing capacitance by a magnitude of the same order as in the case of anodic polarization, equivalent to an increase in the positive charge of the deformed metal surface. This points directly to the predominant role of physical (electrostatic) adsorption of SO_4^{2-} and HSO_4^- anions, which depends on the surface charge and increases with the metal positive charge growth due to its deformation.

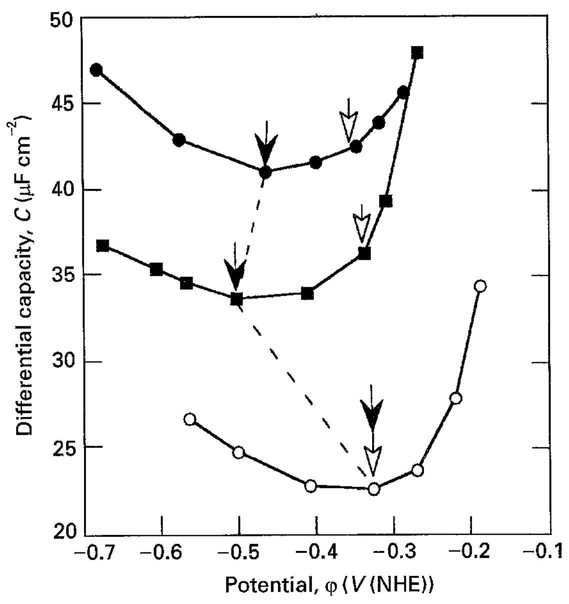

Figure 2 Dependence of differential capacity on potential for undeformed and deformed specimens. (—▷) Steady potential, (—▶) zero-charge potential. NHE, normal hydrogen electrode. Δl(○) 0, (■) 5 mm, (●) 15 mm.

Chemisorption of these ions (at the expense of π-bond interaction with partially filled acceptor *d*-levels of iron), apparently does not play a decisive role owing to its low significance here. Nevertheless, we could have expected a certain decrease in the positive charge resulting from anion chemisorption. The differential capacity increase at the zero-charge potential and the sharp drop of the curves given in Fig. 2 with increasing strain (as also occurring with increasing acid concentration) may be caused by intensification of the anodic processes. The latter leads to the enrichment of the electrode layer with sulphate and hydrosulphate anions, the potential of the minimum differential capacity remaining unchanged.

5. Conclusion

The deformational shift of zero-charge potential shown above is of essential importance in the adsorption ability and electrochemical behaviour of a deformed metal. The internal double layer formation and the change of the electron work of exit can also significantly influence the contact potential difference for deformed metals. Monitoring the arisal of additional positive charge on the deformed metal surface interacting with an electrolyte is convenient if the differential capacity method is used.

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