

EFFECT OF DEFORMATION ON ELECTROCHEMICAL PROPERTIES OF THE DOUBLE LAYER AND SURFACE CHARGE OF METALS

E. M. Gutman, L. N. Petrov, and G. V. Karpenko

Fiziko-Khimicheskaya Mekhanika Materialov, Vol. 4, No. 2, pp. 149-156, 1968

Electrochemical measurements on plastically deformed metals revealed the previously predicted [1] deformation-induced shifts toward positive surface charge values and clarified the character of the intensification of the electrochemical heterogeneity of deformed metal surfaces (localization of activated anodes as a result of mechanochemical phenomena). The deformation-induced increase in the differential capacitance of the double layer is attributable to an increase in the intensity of physical (electrostatic) adsorption of SO_4^{2-} and HSO_4^- anions on a positively charged surface in sulfuric acid solutions. A necessary (but not always sufficient) condition of the effectiveness of cation-active inhibitors of corrosion of plastically deformed metals is their stable chemisorption at potentials in the range of deformation-induced changes in the surface charge (of the order of tenths of a volt on the ψ -scale).

Electrochemical corrosion of deformed metals is to a large extent determined by the physicomachanical state of the metal surface which should affect the structure and characteristics of the electric double layer formed at the metal/electrolyte interface. Since practically significant effects of deformation on electrochemical phenomena are observed only in the plastic deformation range [1], especially in the absence of brittle surface films, it is of some interest to investigate the effect of deformation of this kind on electrochemical properties of metal surfaces.

In the case of polycrystalline metals in uniaxial tension, the elastic deformation is uniformly distributed, while the plastic deformation is nonuniform, being accompanied by the formation of an orthogonal network of slip lines oriented in the direction of the maximum tangential stresses [2]. The transition from elastic to plastic deformation should therefore be accompanied by a disturbance in the uniformity of strain distribution. On metal surfaces there are always natural or artificial stress raisers at which the stress in an elastically strained specimen may reach the yield point. In such a case of nonuniform strain distribution on a metal surface, the most strongly activated are the anodic reactions in the plastically deformed regions (the mechanicochemical effect), while the remaining elastically strained surface is less intensely activated and may play the part of a cathode. The electrochemical characteristics of deformed metal surfaces are a result of simultaneously occurring anodic and cathodic reactions.

This investigation was concerned with the effect of plastic deformation on the differential capacitance and ohmic resistance of the electric double layer and on the electrode potential and surface charge of metals.

The experimental apparatus was based on that described in [3]* except that the impedance of electrodes studied was measured not only at the steady-state potential but also with the potential varying within wide limits which made it possible to construct curves of the differential capacitance of the double layer. The electrolyte employed (0.1 N aqueous H_2SO_4 solution) made it possible to study mechanicochemical effects in their pure form, since no oxide films are formed on iron electrodes in acid solutions of such a concentration; this was established by cleaning the electrode surface immersed in the electrolyte [4] and by differential capacitance measurements [5].** Moreover, the cathodic depolarization is activation- and not diffusion-controlled. The electrolyte used was sufficiently weak to eliminate the risk of producing significant changes in the metal surface during experiments lasting less than 5 min. In some experiments we used an electrolyte containing 1.5 g/l of one of the following inhibitors: KPI-1, AGMB, and BA-6. The electrolyte temperature during experiments was 20° C.

The teflon glands in the glass electrochemical cell were fabricated to cater to the increased specimen deformation range.

The experiments were carried out on steel 08SV(0.1% C; 0.35—0.6% Mn; 0.03% Si; 0.15% Cr; 0.3% Ni; 0.04% S and P) wire specimens 0.8 mm in diameter. After vacuum annealing at 930° C and degreasing, the specimens were coated with an acid-resistant varnish leaving exposed the surface of a cylindrical gage portion 2 or 10 mm

*An ohmic resistance/capacitance method was used in [3] to study the protective properties of oxide films on deformed aluminum.

**The absence of oxide films was proved also by a clearly manifested frequency dispersion of capacitance and resistance (which disappears when passivation takes place) and by the time dependence of steady-state potential observed during our experiments.

long. To ensure electrical insulation, the jaws of the machine for straining the specimens in uniaxial tension were made of textolite. A screw was used to apply the load, and the strain was measured with a dial indicator accurate to 0.01 mm. The distance between the jaws and the overall specimen length (180 mm) made it easy to mount the electrochemical cell and auxiliary vessels on the specimen in such a way that the specimen gage portion (coaxial with the cell) was positioned opposite the capillary of a 2 N mercury sulfate reference electrode and within a supplementary coaxial electrode made of platinum gauze.

The impedance of the double layer was measured with an R-568 electronic bridge. The working frequency of 10 kc was chosen because special tests had shown that at this frequency the frequency dispersion of differential capacitance practically disappears so that the results of measurements are not affected by the presence of microcrevices which can be formed on specimen surface [6] when its roughness is increased due to plastic deformation.

The ac voltage on the cell did not exceed 10 mV, which ensured a satisfactory accuracy of the differential capacitance measurements.

For dc polarization we used a platinum electrode separated from the cell by a wet ground-glass joint. A galvanostat with preselected settings was used for polarization in the construction of differential capacitance curves; a large ballast resistance (50 kohm-50 megohm) of the galvanostat precluded its influencing the working of the ac circuit. In other measurements the dc polarization to a given potential level was effected with the aid of a galvanostat with a manually controlled stabilized electronic current source.

Prepared specimens were held for a day in a desiccator, after which the cell (with a specimen mounted in it) was assembled and filled with the electrolyte.

Under the experimental conditions employed the steady-state potential* was reached quite rapidly (in a few seconds) at which stage the measurements were started.

It was established that the fracture always takes place in the specimen gage portion, which, to a certain extent, is due to the fact that this part of the specimen is acted upon during the test by the electrolyte.

Special measurements were taken to account for the variation in the surface area of the specimen gage portion due to elongation; their results were used to introduce corrections in the capacitance and resistance measurements.

The specimens were deformed in steps of $\Delta l = 5$ mm. The electrochemical measurements were made immediately after each change in the specimen length.

The potential was maintained constant by manual adjustment. At the moment of deformation there was a sudden change in the potential recorded by a high-resistance electronic voltmeter. When the new steady-state potential was reached (which took a few seconds) the capacitance and resistance were measured after which the potential was manually adjusted to a given constant level at which the impedance was again measured.

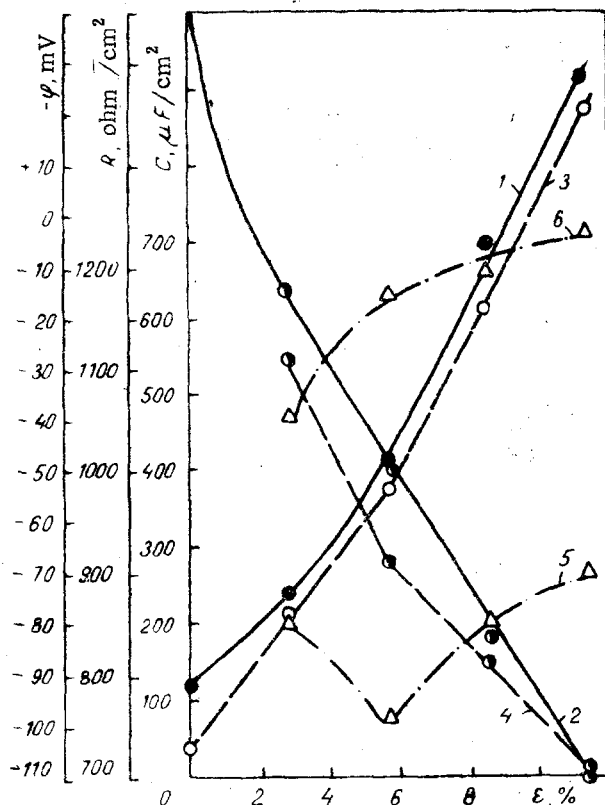


Fig. 1. Strain (ϵ) dependence of the change in potential $\Delta\phi$ and of the differential capacitance and resistance of the double layer under anodic polarization conditions: 1) C at the potential of 700 mV; 2) R at the same potential; 3) C at the steady-state potential reached after the deformation; 4) R at the same potential; 5) $\Delta\phi$ for 2 mm long specimen gage portions; 6) $\Delta\phi$ for 10 mm long specimen gage portions.

*In this context the steady-state potential means the potential at which no movement of the potentiometer needle could be visually observed.

**In nonequilibrium processes the reaction rates defined by phenomenological equations depend on the momentary values of generalized thermodynamic forces [7]. For this reason, a "step-like" increase in strain (load) produces in the first moments a series of electrochemical reactions which are not complicated by electrochemical and diffusion relaxation phenomena in the double layer and which, therefore, should be the object of investigation [8].

The dependence of the differential capacitance C and resistance R of the double layer on the degree of deformation of specimens with a gage portion 2 mm long at a potential of 700 mV* are as shown in Fig. 1. The same values but at steady-state potentials established as a result of deformation are represented by broken curves. It will be seen that increasing the degree of deformation leads to an increase in the differential capacitance and to a reduction in the ohmic resistance, the relationship in both cases being close to linear.

In the entire deformation range studied the potential was shifted toward the negative values in the range 70–100 mV (curve 5 in Fig. 1); the initial values of $\Delta\phi$ differed from the steady-state values shown in Fig. 1 by not more than 20 mV.

In tests on specimens with a gage portion 10 mm long (i. e., with a 5 times larger gage portion surface area) the strain dependence of C and R retains its general character although the changes in these properties are smaller. On the other hand, the magnitude and character of the variation in $\Delta\phi$ are substantially changed and the scatter of results obtained for various specimens is wider. As shown by curve 6 in Fig. 1, $\Delta\phi$ in this case is much smaller than that recorded for specimens with a gage portion 2 mm long, showing a marked tendency to decrease with increasing strain ϵ . In other similar experiments the values of $\Delta\phi$ were even smaller (zero, and on occasion, positive), without adherence to any quantitative relationship. Beyond all doubt is the fact that the value of $\Delta\phi$ diminishes as the surface area is increased 5-fold.

Figure 2 shows the potential dependence of the differential capacitance for undeformed and deformed specimens with a gage portion 10 mm long. The steady-state potential values of C are indicated by solid arrows, while broken arrows indicate the minimum values of C corresponding to the potential ϕ_n of an uncharged specimen surface. In the cases of an undeformed specimen (curve 1) these two potentials coincide; this is in agreement with some published data [6] although, according to other data [9], the zero point of iron is shifted slightly toward the positive potential values.

Deformation (curve 2) has little effect on the steady-state potential but produces a considerable shift of the potential of an uncharged surface toward more negative values. Similar effects are observed at higher degrees of deformation (curve 3). If the change in the surface charge is measured on the Antropov ψ -scale, i. e., in terms of the shift of ϕ_n , one reaches a conclusion that the deformation of a practically uncharged surface leads to the appearance of a positive charge $\Delta\phi_n = 0.1-0.16$ V (on the Antropov scale). As ϵ is increased, $\Delta\phi_n$ initially increases and then remains practically constant or even decreases (similar changes were observed on specimens in an HCl solution).

It was of some interest to measure C of the double layer of specimens deformed in the presence of surface-active substances (corrosion inhibitors) with a view to determining the possible effect of deformation on the adsorbability of corrosion inhibitors and exploring the possibilities of using such inhibitors to protect plastically deformed metals.

These measurements were carried out at steady corrosion potentials in inhibitor-containing media at various degrees of deformation (Fig. 3); at the same time the steady-state potentials were determined. As shown by data in Fig. 3, the addition of inhibitors reduces the magnitude of C and makes it almost independent of strain, this effect being most pronounced with the inhibitor KPI-1, less so with AGMB and least of all with BA-6. At the same time, the deformation-induced debasement of the steady-state potential is more pronounced in the presence of the inhibitor KPI-1 (curve 4 in Fig. 3) than in an uninhibited acid (curve 5).

To understand the meaning of the results obtained, let us compare $C = f(\epsilon)$ curves for specimens with a gage portion 2 and 10 mm long, plotting as the ordinate values of C referred to the entire surface area of the specimen gage portion (Fig. 4). Curves 1 and 3 in Fig. 4 correspond to curves 1 and 3 in Fig. 1 while curves 2 and 4 were constructed from results of experiments corresponding to curve 6 in Fig. 1 (specimen gage portion length = 10 mm). It follows from Figs. 1 and 4 that in the case of undeformed specimens ($\epsilon = 0$) external anodic polarization produces an increase in C . Since the anodic shift in the potential was 280 mV for curves 1 and 3 in Fig. 1 and 255 mV for curves 2 and 4 in Fig. 4 (the initial steady-state potentials differed slightly), the increase produced by a 100 mV potential shift in the capacitance per unit surface area was 25 and more than 20 $\mu\text{F}/\text{cm}^2$ in the former and latter case, respectively. This means that changes in the surface area of the gage portion of deformed specimens has no effect on the specific capacitance of

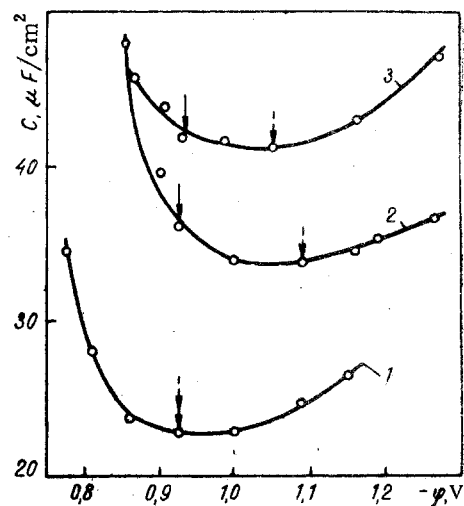


Fig. 2. Potential (ϕ) dependence of C plotted for undeformed and deformed specimens: 1) $\Delta l = 0$; 2) $\Delta l = 5$ mm; 3) $\Delta l = 15$ mm. (Solid arrows indicate steady-state potentials, broken arrows indicating the potentials of uncharged surfaces.)

*Anodic polarization (in the range of active dissolution of iron) suppressed cathodic reactions and precluded hydrogen charging of the steel.

the double layer. Differences in the absolute values of C correspond to differences in the gage portion surface area (Fig. 4). However, these differences in C disappear with increasing degree of deformation, this effect being associated with the electrochemical heterogeneity of the surface.

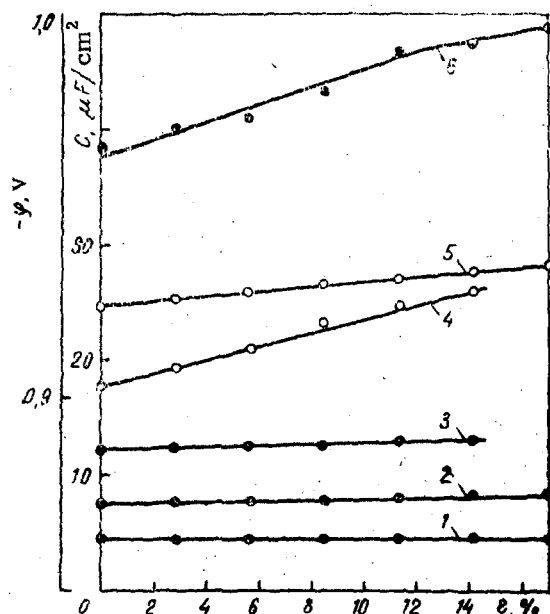


Fig. 3. Dependence of C (under steady-state corrosion potential conditions) on ϕ and ε : 1, 2, 3) C in the presence of inhibitors KPI-1, AGMB, and BA-6, respectively; 4, 5) Steady-state potential ϕ in the presence of the inhibitor KPI-1 and in an uninhibited acid, respectively; 6) C in an uninhibited acid.

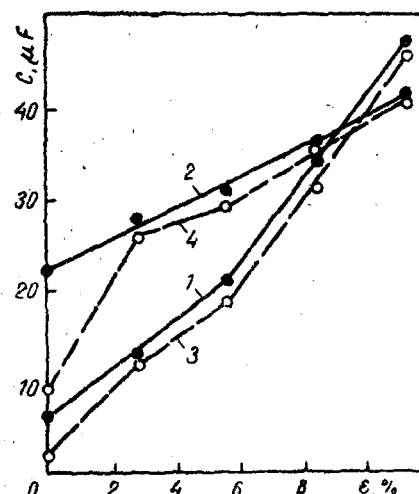


Fig. 4. Dependence of C (referred to the entire surface area of the specimen gage portion) on the degree of deformation (under anodic polarization conditions): 1, 2) C at a potential of 700 mV for specimens with a gage portion 2 and 10 mm long, respectively; 3, 4) C at the steady-state potential for specimens with a gage portion 2 and 10 mm long, respectively.

From this standpoint, the double layer of real metal surfaces in electrolytes should be regarded as a system of parallel "condensers," each corresponding to a local surface microregion with a given surface charge. Since the surface as a whole may be regarded as equipotential, differences in local surface charges are associated with differences in the capacitance of the respective local "condensers." The measured value of the macroscopic differential capacity is therefore the sum of local capacitances of the double layer connected in parallel. In accordance with the theory of electrical circuits, the overall capacitance of the circuit will be determined mainly by the "condensers" with the highest capacitance.

Consequently, the closeness of the values of C recorded (at certain deformation stages) for specimens of widely differing surface areas is due to the fact that increasing the degree of plastic deformation increases the intensity of electrochemical heterogeneity and leads to a localization of the strain-induced activation of separate surface regions (maximum capacitance "condensers"), the area of which is very much smaller than the total area of the specimen gage portion and whose number decreases during the localization process independently of the surface area of the specimen gage portion. In the final deformation stages (i.e., just before fracture), the measured value of C is determined entirely by the local capacitance of the region in the fracture zone; this is illustrated by the intersection of curves in Fig. 4.

The electrical heterogeneity of a specimen surface affects also both the deformation-induced change in the potential $\Delta\phi$ and the measured magnitude of this potential. In this case the effect of the surface area of the specimen gage portion is opposite to that previously discussed, i.e., while the overall differential capacitance becomes independent of the working surface area, the potential — or rather the change in potential $\Delta\phi$ — is strongly dependent on this parameter (curves 5 and 6 in Fig. 1). This is due to the mechanism of the formation of the overall electrode potential during deformation: The deformation-induced localization of activated anodic reactions increases the effective cathode surface area* and the intensity of cathodic reactions which leads to a reduction in the shift of steady-state potential [1].

*The division of a metal surface into anodic and cathodic regions is to a certain extent conditional; however, it facilitates the analysis of the predominant factors of electrochemical heterogeneity.

Analogous effects are observed under anodic polarization conditions except that the role of cathodes is played by those regions of the, on the whole, anodically charged surface which are not activated by deformation and which, under conditions of intensified localization of activated regions, make a definite contribution to the stabilization of the potential.

Naturally, this contribution is larger in the case of specimens with relatively large (say, 10 mm long) gage portions. This is why $\Delta\varphi$ recorded for specimens of this kind is considerably smaller (at all the degrees of deformation studied) than that observed on specimens with a short gage portion and why it tends to decrease with increasing strain. This is also why a noticeable deformation-induced debasement of the potential (by up to 100 mV) was first observed with the aid of an electrochemical microprobe at the tip of an artificial stress raiser [10].*

A small shift of the steady-state corrosion potential (curve 5 in Fig. 3) linearly increasing with increasing ϵ should, according to theoretical considerations [1], lead to an approximately linear reduction in the polarizability with increasing strain; this view was supported by experiment.

To elucidate the nature of the deformation-induced increase in the differential capacitance, let us consider curves in Fig. 2. Anodic polarization of an undeformed specimen (curve 1) to an extent equal to the deformation-induced shift of the potential of an uncharged surface (curve 2) produces an increase in the capacitance which is approximately equal to the deformation-induced increase under steady-state potential conditions. Comparison of curves 1 and 3 in Fig. 2 shows that shifting φ_n by 100 mV as a result of deformation increases the capacitance under steady-state potential conditions by $20 \mu\text{F}/\text{cm}^2$ which is close to the previously cited increase in the capacitance due to anodic polarization (100 mV) of undeformed specimens. It is significant that in all the experiments the deformation-induced increase in the capacitance was of the same order of magnitude** as that due to an equivalent increase in the positive surface charge produced by anodic polarization of undeformed specimens. This shows that the predominant part in the phenomenon under consideration is played by physical (electrostatic) adsorption of SO_4^{2-} and HSO_4^- anions which depends on the surface charge and which increases as the metal surface charge increases as a result of deformation.

The chemisorption of these anions (due to interaction of π -electrons with unfilled d-levels of iron) plays no decisive part in this case, though one could expect a certain reduction in the positive surface charge due to chemisorption of anions. It is possible that the deformation-induced increase in the capacitance corresponding to the potential of uncharged surfaces and flattening of the minima of curves in Fig. 2 (similar to that produced by increasing the acid concentration [6]*** is due to the intensification of the anodic state as a result of which the layer adjacent to the electrode becomes enriched with sulfate and hydrosulfate anions.

In view of the predominantly electrostatic character of the influence of deformation on the adsorbability of working media components, the capacitance should become less strongly dependent on deformation in media containing surface-active additives with pronounced chemisorptive properties (corrosion inhibitors). This postulate is, in fact, proved by curves 1, 2, and 3 in Fig. 3, since the deformation-induced changes in the metal surface charge in the range 0.1–0.2V (on Antropov's φ -scale) are still in the range in which the differential capacitance is independent of the potential of undeformed iron in electrolytes containing inhibitors KPI-1, AGMB, and BA-6, this effect being due to the chemisorption of these substances [11].

This leads to a conclusion that plastic deformation of iron has practically no effect on the chemisorption of corrosion inhibitors studied. At the same time, it does not mean that the protective properties of inhibitors (which are usually related to their adsorbability) are also unaffected by plastic deformation of metals. For instance, the adsorption of KPI-1 is practically independent of ϵ (curve 1 in Fig. 3), while the intensity of debasement of the steady-state potential in the presence of an inhibitor (curve 4) is even higher than in an uninhibited acid (curve 5); this is due to the continuity of the passivating action of the inhibitor in isolated surface regions being broken by deformation which leads to the onset of localized anodic processes (similar to pitting) in these regions. The convergence of curves 4 and 5 points to a weakening of the protection at high degrees of deformation.

If the action of an inhibitor does not lead to the formation of brittle passivating films, neither its adsorptive nor protective properties are affected by plastic deformation; for instance, the protective power of the inhibitor AGMB

*It should be pointed out that from the point of view of obtaining a measurable effect it is unimportant whether the activation of the metal or the destruction of surface films take place at the tip of a stress raiser or whether (depending on the actual experimental conditions) both these phenomena take place simultaneously.

**It should be borne in mind that each curve in Fig. 2 was obtained for a different specimen so that a certain degree of scatter of the experimental points was unavoidable; this does not affect the argument which is concerned with the qualitative features of the phenomena in question.

***The minimum capacitance potential remains the same.

(unlike that of the inhibitor KPI-1) remains high even in the case of plastically deformed specimens [12].

REFERENCES

1. E. M. Gutman, FKhMM [Soviet Materials Science], no. 5, 1967.
2. B. A. Kuznetsov, Izv. AN SSSR, seriya Metally, no. 3, 1967.
3. N. D. Tomashov and N. I. Isaev, Transactions of the Institute of Physical Chemistry AS USSR [in Russian], no. 7, Moscow, 1959.
4. G. V. Akimov and G. B. Klark, Izv. AN SSSR, OKhN, 3, no. 1, 1941.
5. P. Popat and N. Hackerman, J. Phys. Chem, 65, no. 5, 1961.
6. E. O. Ayazyan, DAN SSSR, 100, no. 3, 1955.
7. R. Haase, Thermodynamics of Nonreversible Processes [Russian translation], Izd. Mir, 1967.
8. E. M. Gutman, FKhMM [Soviet Materials Science], no. 3, 1967.
9. L. I. Antropov, ZhFKh, 12, 1494, 1952.
10. A. V. Ryabchenkov, ZhFKhm, 26, no. 4, 1952.
11. E. M. Gutman and L. N. Petrov, FKhMM [Soviet Materials Science], no. 2, 1967.
12. A. K. Mindyuk, E. M. Gutman, and G. V. Karpenko, FKhMM [Soviet Materials Science], no. 4, 1966.

21 August 1967

Institute of Physics and Mechanics
AS UkrSSR, L'vov