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

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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 \( HSO_4^- \) \( HSO_3^- \) 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 \( \psi \)-scale).

Electrochemical corrosion of deformed metals is to a large extent determined by the physicomechanical 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 mechanochemical 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 mechanochemical 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, AGMIB, 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

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*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 micro-crevices 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 Δl = 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.

*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].