

INFLUENCE OF PLASTIC DEFORMATION ON THE SOLUTION OF IRON IN SULFURIC ACID

O. V. Kasparova and A. V. Plaskeev

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Gamma spectrometry is used to study the active and anomalous solution of high-purity iron in 1 N H_2SO_4 ($t = 22^\circ C$) in relation to its structural state; the role of mechanical cleaning of the surface in this process is elucidated. The results are explained on the basis of ideas concerning the energetic nonuniformity of the surface of the dissolving metal.

The experimental data so far obtained indicate that defects in the crystal structure of a metal have an important part to play in its corrosion resistance. It is known that a large number of such defects are created by plastic deformation, which has a specific but not unambiguous effect on the corrosion-electrochemical behavior of a metal; this effect depends, on the one hand, on the nature of the metal, and on the other, on the composition and conditions of action of the aggressive medium. The literature data indicates that deformation can influence the anodic behavior of iron in acid media [1]. Most authors have assessed this influence either on the basis of the results of corrosion tests or with the aid of potentiostatic methods. The latter, however, do not in themselves yield complete information on the solution kinetics of iron in the active state, let alone in the region of anomalous solution. In this connection, it seemed advisable to use analytical methods to make a more detailed study of the laws of active and anomalous solution of deformed and annealed iron in sulfuric acid.

EXPERIMENTAL METHOD

We investigated sheet specimens of high-purity iron* (0.005% C, 0.001% S, <0.003% P, <0.005% Cu, 0.04% Si) about 0.15 mm thick after cold rolling (degree of deformation about 90%) and also after subsequent annealing for 1 h at $800^\circ C$.

According to metallographic analysis data, the cold-rolled iron had the typical fibrous structure of a deformed metal elongated along the rolling direction, whereas the annealed iron was recrystallized.

Before making polarization measurements in 1 N H_2SO_4 ($t = 22^\circ C$), we cleaned the specimens with emery paper, using grade M20 paper in the last stage. The surface of the cleaned metal was parallel to the rolling plane.

The experiments were performed in an electrochemical cell of the clamp type; its design eliminated contact between the end surfaces of the specimens and the solution, and permitted the solution products of the specimens to be removed, by changing the solution without breaking the polarizing circuit, for quantitative analysis. The analysis was made by the radioisotope gamma-spectrometric method [2]; its high sensitivity enabled us to study the process of solution of iron over a wide range of potentials, including the region of cathodic polarization.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows the potential† dependences of the stationary rate of solution of annealed and deformed iron, obtained by the radioisotope method (curves 1, 2). Over a com-

*Chemical composition of iron given in mass %.

†Potentials are given relative to a normal hydrogen electrode.

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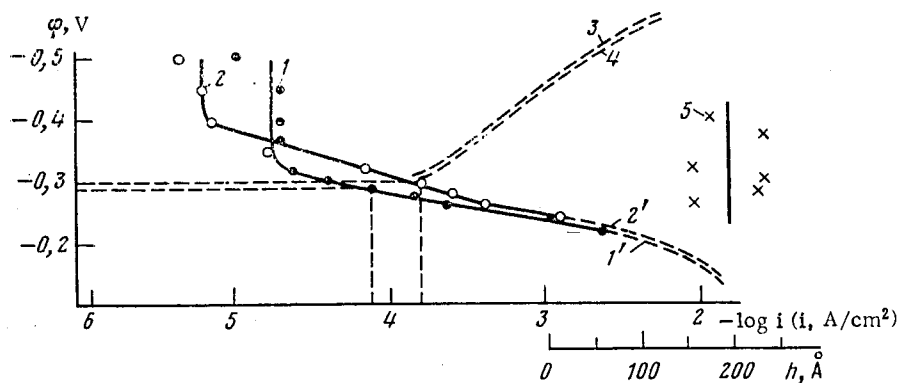


Fig. 1. 1, 2) Potential dependences of stationary rate of solution; 1', 2') anodic and 3, 4) cathodic potentiodynamic (0.9 V/h) polarization curves for annealed (1, 1', 3) and cold-rolled (2, 2', 4) iron, measured in 1 N H_2SO_4 at 22°C; 5) thickness of surface layer of cleaned annealed iron dissolving in nonstationary initial stage; horizontal and vertical dashed lines mark values of φ_{cor} and $-\log i_{\text{cor}}$, respectively.

paratively narrow range of potentials (from -0.32 to -0.22 V), the dependence for the annealed metal is a Tafel line with a slope of about 45 mV, while at potentials more negative than -0.32 V (the region of cathodic polarization) it corresponds to the process of so-called anomalous solution [3].

It is noteworthy that in the region of anomalous solution, the annealed iron is less stable than the deformed iron. At the same time, the transition to the Tafel dependence in the latter occurs at a more negative potential. As a result, on the positive side of -0.36 V the deformed specimen dissolves more rapidly than the annealed one. However, in the potential region in which this effect is observed, the Tafel line of deformed iron has a steeper slope (about 75 mV), so that the activating influence of deformation decreases with rise of potential, and becomes practically zero at -0.26 V. At potentials more positive than this value, solution of the deformed specimen is characterized by the same Tafel line as for the annealed one. The rate of solution of the iron determined by the analytical method coincides with the corresponding anodic current.

As seen from Fig. 1, the influence of deformation on the process of solution of iron is observed chiefly in the region of cathodic hydrogen evolution. This is apparently why some authors [4, 5], who used only potentiostatic methods in their investigations, have often failed to detect this effect.

It must be emphasized that deformation has no appreciable influence on the rate of cathodic evolution of hydrogen (Fig. 1). This result agrees with the data in [6], according to which this influence occurs only if a sufficient quantity of impurity elements, in particular, carbon, is present in the iron.

Note that the corrosion of iron occurs in the region of potential in which deformation accelerates its solution (Fig. 1). For this reason, a deformed specimen is less stable than an annealed one.

These can be no doubt that the observed differences in corrosion-electrochemical behavior between deformed and annealed iron are due to structural features, primarily to the different degrees of imperfection of the lattice.

It is known [7] that cold deformation alters the shape and size of the crystallites, their crystallographic spatial orientation, and the fine structure of the metal. In particular, deformation causes large distortions of the lattice in the metal and sharply increases the dislocation density over that of the annealed material. The metal is thus brought into a state of disequilibrium with enhanced free energy.

The mechanism relating the reactivity of the metal to the imperfection of its crystal structure can be understood if, starting with the ideas in [8-11], we assume that active solution of the metal surface occurs mainly at a relatively small number of its so-called active centers. These centers may be persistent atomic steps formed, e.g., at the exit

points of screw dislocations at the surface of the metal [1]. Solution of these steps occurs by successive transfer of atoms into the solution from their positions on these steps. This chain mechanism of solution of the metal does not alter its surface energy, and is consequently the most favorable from the thermodynamic viewpoint [8].

It is logical to assume that the concentration of active centers on the surface of the dissolving metal depends on both the degree of imperfection of the lattice and the conditions of action of the aggressive medium. With relatively weak anodic polarization, the role of imperfect parts of the lattice as active centers of solution must be particularly important. A rise of potential is accompanied by an increase in the reactivity of the surface atoms and in the probability of their solution from the covered ("perfect") surface. In principle, the formation of vacancies on such a surface should help to form additional active centers. The influence of defects of crystal structure on the process of active solution of metal should then be less marked and, starting from some potential, may be altogether absent. This is confirmed by the results in Fig. 1.

As we have stated, in the region of anomalous solution there is a decrease in the reactivity of the deformed iron below that of annealed iron. Since imperfect parts of the surface can, according to the conditions of action of the aggressive medium, play the part not only of active centers of solution but also of passivation of the metal [1], these results might be explained by the hypothesis that in this range of potentials iron is in a peculiar passive state [9]. Evidence in favor of this hypothesis is provided by some recent data [12]. Nevertheless, it is not yet possible to give a definite explanation of the nature of the effect found by us.

It is characteristic that in the conditions of maintenance of a constant potential, the initial stage of solution of either annealed or cold-rolled specimens is characterized by a maximum rate, and is practically independent of the structural state of the iron (Fig. 2). Only after a time does the rate of solution decrease to some stationary limit. This dependence is typical of all potentials corresponding to the anomalous and Tafel parts of the polarization curve. The period in which this nonstationary process occurs decreases with rise of potential and, consequently, with increase in the reactivity of the metal (Fig. 2).

As remarked above, the specimen surfaces were mechanically cleaned before the experiment. It is known that the resulting surface layer has a very high degree of imperfection in comparison with the structure in the interior of the metal [7]. We may suppose that it is here that the iron has an enhanced reactivity during the initial stage of solution, and that the influence of structure begins to be felt only as the layer work-hardened by cleaning is removed.

The above hypothesis is supported by the fact that, regardless of the potential and, thus, of the reactivity of the metal as a whole, approximately the same quantity of iron goes into solution in the nonstationary stage of solution. The thickness of the dissolved layer, calculated from this quantity,* is $200 \pm 40 \text{ \AA}$ (Fig. 1, curve 5).

It is interesting to note that if, after attainment of a stable potentiostatic state on the surface of the metal (Fig. 2b, curve 3), its potential is made more positive, a new stationary state of the surface is reached practically instantaneously, in contrast with an electrode with a freshly cleaned surface (Figs. 2c-d, curves 5 and 5', 7 and 7', respectively). Apparently, when the specimen is previously polarized, the cold-worked layer is completely removed, and subsequently after a change of potential the reactivity of the surface is largely governed by the structural state of the metal as a whole.

It is characteristic that mechanical cleaning also accelerates the region of hydrogen evolution (Fig. 3). In the initial stage of contact of the specimen with the solution, the rate of this reaction is a maximum, and only after a time (as the cold-worked layer is removed) does it fall to the stationary value. If this layer is first dissolved at a more positive potential, then the stationary rate of hydrogen evolution is established practically instantaneously.

Thus, taken together, our results show that the parameters characterizing the process of solution of iron on the negative side of its passivation potential are dependent on its

*In the calculation we have assumed that the roughness factors of the initial surface and of the surface formed during solution are both equal to three [13].

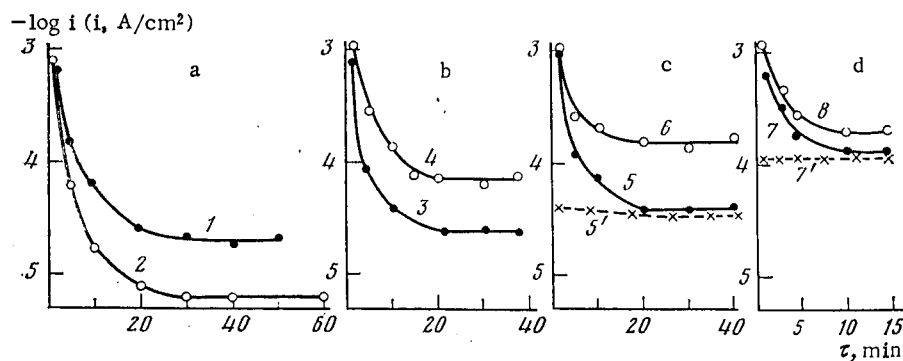


Fig. 2. Time dependence of rate of solution of annealed (1, 3, 5, 5', 7, 7') and cold-rolled (2, 4, 6, 3) iron in 1 N H_2SO_4 (22°C) at the following potentials, V: a) -0.45; b) -0.32; c) -0.3; d) -0.28; 5', 7') after preliminary polarization at $\varphi = -0.32$ V for 40 min.

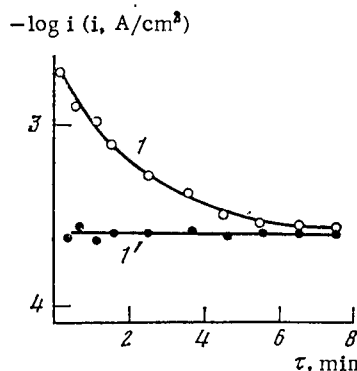


Fig. 3. Time dependence of rate of evolution of hydrogen on surface of annealed iron (1, 1') in 1 N H_2SO_4 at 22°C, $\varphi = -0.35$ V; 1') after preliminary polarization at $\varphi = -0.32$ V for 40 min.

structure. This must be taken into account in predicting corrosion losses in acid nonoxidizing media and in analyzing the mechanism of solution.

CONCLUSIONS

1. The radioisotope method is used to study the process of active solution of cold-rolled and annealed high-purity iron in 1 N H_2SO_4 at 22°C. It is found that deformation accelerates the solution of iron in the active region at potentials between -0.36 and -0.26 V. For annealed iron the slope of the Tafel line is about 45 mV, and for deformed iron it is about 75 mV. When the potential is shifted toward the positive, the accelerating influence of deformation on the process of solution of iron is reduced, and starting at a potential of -0.26 V, it practically disappears.

2. In the region of anomalous solution, deformation appreciably reduces the reactivity of the iron and shifts the potential corresponding to the start of this region toward the negative.

3. Preliminary mechanical cleaning of the surface sharply increases both the reactivity of the metal itself and the rate of evolution of hydrogen from its surface. According to a rough calculation, the cold-worked surface layer with enhanced reactivity is 200 ± 40 Å thick.

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ENHANCING THE STRESS CORROSION CRACKING RESISTANCE OF HIGH-STRENGTH STEEL Kh13

N. I. Zhigacheva and A. A. Nazarov

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The causes of failure of high-strength steel Kh13 in pure water are discussed; a heat-treatment procedure is suggested to prevent brittle corrosion fracture of the steel, initiated by hydrogen.

In various components of power machinery in contact with aqueous media, both good mechanical characteristics and resistance to brittle corrosion fracture are demanded of hardened carbon steel Kh13. However, if maximum hardness and strength are obtained by the usual heat-treatment procedures, the steel cannot be used in contact with aqueous media.

It is known [1] that when steel with $\sigma_t > 850$ MPa is used in very pure water, there are cases of its brittle fracture due to hydrogen embrittlement [2-4].

Solution of the problem of combining high strength and hardness with resistance to brittle corrosion fracture involves investigations of the influence of phase processes during heat treatment of martempered steel on the liability to such fracture.

We have investigated steels 20Kh13, 30Kh13, and 14Kh17N2 of commercial origin, with compositions corresponding to All-Union State Standard (GOST) 5632-72, and steels 05Kh13N6M2, 05Kh15N5M2, and 05Kh12N2M made in the laboratory (Table 1). The specimens, in the form of rectangular plates measuring $30 \times 30 \times 3$ mm, were tested either in their original state (hardened to martensite from 1050°C in water) or after thermal age hardening at 200-600°C at 25°C intervals lasting between 2 and 10,000 h. It has been shown [2, 3, 5] that on the basis of a solution containing CuSO_4 and H_2SO_4 , it is possible to create a hydrogenating corrosion medium with a redox potential imparting the active-passive state to steel of type Kh13 at the boiling point of the solution.

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