INFLUENCE OF MECHANICAL AND THERMAL TREATMENT OF IRON ON THE EFFECTIVENESS OF CORROSION INHIBITORS

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We showed earlier [1-3] that a preliminary mechanical or thermal treatment of iron exerted a substantial influence on the adsorption of surface-active substances from aqueous solutions. This was explained by changes in the free surface energy of the metal resulting from changes in its microstructure (changes of defect concentration and of texture). It was shown that specimens of Armco iron and specimens obtained by zone melting, which were subjected to deformation, adsorbed more surface-active substances than specimens subjected to firing. The dependence of the adsorption properties of iron on the preliminary treatment (deformation or firing), disclosed by these experiments, was of interest because of its possible influence on the effectiveness of corrosion inhibitors.

We investigated the corrosion behavior of polycrystalline specimens of Armco iron and specimens obtained by zone melting, and of single crystals of silicon-containing iron (transformer steel)* in deaerated 1 N H_2SO_4 solutions at $t = 20°C$. The corrosion rate was determined by measuring the quantity of liberated hydrogen and also by weighing. Both methods gave similar results.

It was shown in [1] that a sharp decrease of the adsorption of surface-active substances on iron preliminarily subjected to cold rolling and then to heating at different temperatures occurred when the temperature was raised from 600 to 750°C. Thus, we investigated the corrosion of iron plates obtained by zone melting and subsequently subjected to cold rolling followed by heating at the above temperatures. The specimens were heated under vacuum ($2 \cdot 10^{-5}$ mm Hg) for 4 h and for 2 h in hydrogen (200-300 mm Hg), and then cooled and transferred to a cell provided with a buret for corrosion measurements.

As can be seen, the corrosion rate of iron in a pure acid solution is lower for specimens heated at 750°C than for those heated at 600°C. However, in the presence of corrosion inhibitors, the dissolution of specimens heated at 600°C is less than that of specimens heated at 750°C. The change in this relationship is connected with higher adsorbability of the inhibitors on iron heated at 600°C, compared with specimens heated at 750°C. The coefficient of inhibition (γ), equal to the ratio of the corrosion rate in pure acid to

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*The composition of Armco iron, specimens obtained by zone melting, and silicon-containing iron has been given in [2].

TABLE 1. Influence of Heating Temperature on Corrosion Rate of Iron Specimens Obtained by Zone Melting ($t = 20°C$)

Solution composition	Heating temp., °C	Corrosion rate, $\times 10^5$ g/cm·h	γ
1 N H_2SO_4	600	20	1,0
1 N $H_2SO_4 + 10^{-5}$ N KI	600	1,8	11,1
1 N $H_2SO_4 + 10^{-6}$ N KI $+ 10^{-4}$ M tribenzylamine	600	1	20
1 N H_2SO_4	750	8	1,0
1 N $H_2SO_4 + 10^{-5}$ N KI	750	6	1,3
1 N $H_2SO_4 + 10^{-5}$ N KI $+ 10^{-4}$ M tribenzylamine	750	2,5	3,2

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the corrosion rate in acid with addition of an inhibitor, is much higher for iron heated at 600°C. Investigations of the corrosion of Armco iron gave similar results. The change in the adsorptive activity of iron and in the effectiveness of corrosion inhibitors is caused by changes in the microstructure of the metal surface [1, 2].

TABLE 2. Average Corrosion Rate of Faces of Silicon-Containing Iron Single Crystal (× 10^5, g/cm^2·h)

Solution composition	Face index	
	(100)	(110)
1 *N* H_2SO_4	7,4	5,9
1 *N* H_2SO_4 + 10^{-6} *N* KI + 10^{-4} *M* TBA*	2,2	4,2
1 *N* H_2SO_4 + 10^{-4} *N* H_2S	19,7	7,9
1 *N* HCl	3,2	4,7

* tribenzylamine

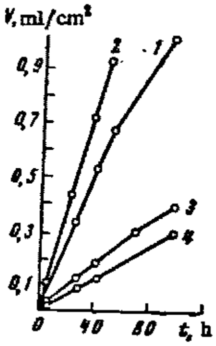

Fig. 1. Curves of hydrogen liberation during corrosion of iron specimens obtained by zone melting in 1 N H_2SO_4 (1 and 2) and 1 N H_2SO_4 + 10^{-5} M iodoethylquinoline (3 and 4); curves 1 and 3 relate to specimens subjected to heating only; curves 2 and 4 relate to specimens additionally deformed (by 5%).

We also investigated the corrosion behavior of plates of Armco iron and plates obtained by zone melting heated at 800°C and then deformed by 5% stretching. Figure 1 gives the results of corrosion measurements. In 1 N H_2SO_4, the dissolution rate of the heated specimens was considerably less than that of the deformed specimens. When iodoethylquinoline was introduced, this relationship was reversed (and the corrosion was decreased) because of the higher adsorptive activity of the deformed specimens compared with the heated specimens. It should be pointed out that the increase of the dissolution rate caused by deformation (in the absence of corrosion inhibitors) is not connected with the increase of the real surface of iron, as suggested by Foroulis and Uhlig [4] to explain experimental results obtained by Green and Saltzman [5], because our measurements of the double layer capacity of iron showed that the increase of the real surface of iron after 5% deformation was insignificant. Apparently, the increase of the dissolution rate in this case was caused by the increase of the surface energy due mainly to the increase of the number of defects in the crystal lattice.

As during the deformation by rolling and a recrystallizing heating the texture of iron substantially changes [6],* we investigated the corrosion behavior of individual faces of single crystals of silicon-containing iron (about 3% Si). The single crystals were first electropolished, and then heated at 800°C under vacuum (4 h) and in hydrogen (2 h). The single crystals were used in the form of platelets having a surface area of 1-2 cm^2 and a thickness of 0.05 cm. The investigated faces formed the main surfaces of the platelets. The edges of the platelets were coated with polystyrene to separate them from the solution. In 1 N H_2SO_4, the (100) face dissolved more rapidly than the (110) face (Table 2). This relationship was reversed when a surface-active substance was introduced into the solution, because of the higher adsorptive activity of the (100) face compared with the (110) face [2].† Therefore, in an acid solution containing a corrosion inhibitor (1 N H_2SO_4 + 10^{-6} N KI + 10^{-4} M tribenzylamine), the dissolution of the (100) face proceeds more slowly than in the case of the (110) face.

When a corrosion stimulator (10^{-4} N H_2S) was introduced, the difference between the dissolution rates of the (100) and (110) faces increased. As the adsorption of S^{2-} ions on the (100) face is higher, the rate of dissolution of this face increases to a greater extent than that of the (110) face. Chlorine ions exert some inhibiting effect on dissolution of iron so that the (110) face dissolves in 1 N HCl more rapidly than the (100) face. It should be mentioned that data relating to corrosion in 1 N HCl have a qualitative character only, because the real surface of specimens increases during the corrosion process.

The foregoing results are of importance for estimation of the effect of surface-active substances on dissolution of faces of single crystals. Thus, for instance, the addition of a dissolution stimulant results in a more rapid dissolution of faces of one type, whereas an inhibitor may influence more strongly the dissolution of another face.

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* After deformation by rolling, the structure of iron is (100). Heating at high temperatures results in an increase of the concentration of the (110) and (111) faces on the iron surface.

† The higher adsorptive activity of the (100) face can be explained by its higher free surface energy resulting from its lower reticular density, compared with the (110) face.

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