The Effect of Sorbed Hydrogen on the Dissolution of Iron in a Thiocyanate-Containing Sulfuric Acid

T.A. Nenasheva and A.I. Marshakov
Institute of Physical Chemistry, Russian Academy of Sciences
Leninsky pr. 31, Moscow, 119991 Russia

The investigation of electrochemical behavior of hydrogenated iron is very important for clarifying the mechanisms both of the anomalous dissolution of metals under cathodic polarization and the processes that result in the nucleation and growth of corrosion cracks in steels. The change in the rate of the cathodic evolution of hydrogen leads to a change both in the degree of the electrode surface coverage (θ) with hydrogen and in the concentration of hydrogen atoms in the metal phase (C). These values are interrelated, and one usually assumes that the adsorbed and absorbed atomic hydrogen forms are in equilibrium with each other. At the same time, there was a supposition that the centers of hydrogen absorption and desorption (by the bulk metal phase) may have different nature and be spatially separated. Then, hydrogen atoms that form on the electrode surface as a result of the discharge of hydrogen ions and hydrogen atoms that desorb from the metals phase can differ from each other in their position with respect to the sites of iron dissolution and in the adsorption energy.

The aim of the work to study of the effect of atomic hydrogen adsorbed and absorbed by the metal on the dissolution rate of iron in acidic sulfate electrolytes in the presence of a promoter of the hydrogen entry into the metal (thiocyanate ions).

To solve this problem, we used a technique of the cyclic pulse-step alternation of the potential (which enables one to obtain the dependence of the dissolution rate of iron at a constant potential (E) on the θ value [1]) and a bipolar electrode (a membrane), which allows one to vary the concentration of hydrogen in the metal at E = const [2].

The experiments were carried out with a rotating disc electrode made of iron (0.005% C) with a surface area of 0.56 cm^2. A cycle of alternating rectangular potential pulses was set with a potentiostat PI-50. The driving time of potential accurately to 5 mv is no more than 1.5×10^{-6}s. Also the test were carried out with 100 or 150-μm think iron (0.009% C) membranes of a working surface of 4.23 or 3 cm2. The rate of hydrogen penetration through the membrane was measured in a Devanathan-Stahurski cell. The experiments were carried out in a 0.5 M Na$_2$SO$_4$ + 0.25 M H$_2$SO$_4$ solution (pH 1.3) deaerated with argon at room temperature. An admixture of 20 mM KCNS was additionally introduced.

The rate constants of individual stages of the cathodic evolution of hydrogen were defined, using IPZ model [3]. It was determined that the effect of thiocyanate ions manifests itself both in a decrease in the chemical recombination rate of hydrogen (as a result of which θ increases) and a change in the θ to C ratio toward the higher concentration of hydrogen atoms in the metal. The dependencies of the dissolution rate of iron (i_{Fe}) on the frequency of potential cycling (W) were obtained. The dissolution rate of iron noticeably decreases with an increases in W, while the degree of the electrode coverage with hydrogen increases. Obviously, the decrease in i_{Fe} is related to an increases in θ.

The dependencies of the relative dissolution rate of iron ratio on the iron surface coverage with hydrogen it shows how many times the instantaneous dissolution rate of iron increases compared to the steady-state rate at E_1. Although the electrode coverage with hydrogen in a thiocyanate-containing solution is much higher, the dissolution rates of iron in these two electrolytes are close.

The effect of absorbed hydrogen on the dissolution rate of iron was studied by changing the direction and the density of the diffusional flow of hydrogen through the metal membrane. During the polarization of the hydrogenating side of the membrane in the base solution i_{Fe} noticeably decreases, but i_{Fe} slightly increases in the presence of thiocyanate. The dependencies of the dissolution rate of iron on the concentration of hydrogen atoms in the metal were constructed.

In the base solution the anodic current decreases almost by half at a comparatively small increase in the concentration of hydrogen in the metal. With a further increase in C, the decrease in i_{Fe} is unnoticeable. C in a thiocyanate-containing solution is higher than in the base solution and the further increase in C does not slightly effects on i_{Fe}.

At relatively small C contents, hydrogen atoms, which are transferred from the bulk metal phase to the surface, block the dissolution centers of iron and decrease of the anodic current density. Starting from a certain concentration, absorbed hydrogen increases the defectness of the surface metal layer and, thus, increases the total number of the dissolution centers of the metal. However, an increase in C should result in an increase in θ, although the proportionality between C and θ is obviously violated. Consequently, the number of dissolution centers of iron inhibited with hydrogen atoms increases with an increase in C. Due to the superposition of these two effects, the ionization rate of the metal no longer depends on the concentration of hydrogen dissolved in it, but is predetermined by the relation between C and θ values. For example, at equal contents of absorbed hydrogen, θ in a thiocyanate-containing solution is much smaller than in the base electrolyte. Therefore, the ionization rate of iron in the presence of CNS$^-$ ions is higher [4].

References
1. A.I. Marshakov, A.A. Rybkina and Ya.B. Skuratnik, Elecktrokhimiya, 1999, vol. 35, no. 9, p. 1061.
2. A.I. Marshakov, A.A. Rybkina and Ya.B. Skuratnik, Elecktrokhimiya, 2000, vol. 36, no. 10, p. 1244.
3. R.N. Iyer and H.W. Pickering, J. Electrochem. Soc., 1989, vol. 136, no. 9, p. 2463.
4. A.I. Marshakov and T.A. Nenasheva, Protection of Metals, 2001, vol. 37, no. 6, p. 543.