ON THE MECHANISM OF DISSOLUTION OF IRON-CHROMIUM ALLOYS IN SULFURIC ACID

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ON THE MECHANISM OF DISSOLUTION OF IRON-CHROMIUM ALLOYS IN SULFURIC ACID

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The dissolution of metals in electrolyte solutions may occur either as a result of the direct interaction, in a single act, of surface metal atoms with the components of the aggressive medium (the so-called chemical mechanism), or as a result of the independent occurrence of two coupled electrode reactions, one of which (metal oxidation) is associated with the release of electrons, and the other (reduction of the depolarizer) with the acquisition of electrons from the metal (the electrochemical mechanism). The possibility is also not excluded that the process may proceed simultaneously by chemical and electrochemical mechanisms. In the latter case, dissolution may take place predominantly by one of the indicated paths.

Until recently it was believed that the chemical mechanism of dissolution, which plays an important role in the interaction of metals with gases and organic substances, is practically not realized in their interaction with aqueous electrolyte solutions. The results of investigations in recent years compel us to reconsider this point of view.

In numerous works it has been shown that the purely chemical interaction of surface metal atoms with components of the medium substantially changes the electrochemical and corrosion properties of metals. Thus, a strong influence of the chemisorption of various anions on the rate of dissolution of metals was discovered, although in these cases no deviations from the laws of electrochemical kinetics were observed. Taking into account, however, that such adsorption is the result of the establishment of a chemical bond between the adsorbing particle (molecule or ion) and an individual metal atom, such a deviation may be expected in the case where this particle itself is capable of being reduced under the given conditions. Then the oxidative and reductive stages of the process may be accomplished in a single act, i.e., by a chemical mechanism.

In agreement with this conclusion, in a recent work by Frumkin, Korshunov, and Iofa (^{1}) it was shown that the experimentally observed regularities of dissolution of alkali-metal amalgams in buffer solutions at pH > 10 are well explained on the assumption of a chemical mechanism of the process. In the work of Izydinov, Borisova, and Veselovskii (^{2}), on the kinetics of dissolution of silicon

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

in 10 *N* alkali, results were likewise obtained which are difficult to explain without resorting to the concept of a chemical mechanism of the process.

In studying the regularities of dissolution of iron alloys with chromium in acidic electrolyte solutions at elevated temperatures, we found phenomena which, for their explanation, also require the assumption that the process proceeds by a chemical mechanism.

In Fig. 1 the cathodic and anodic polarization curves obtained on an alloy of iron with 4% chromium in sulfuric acid at 90° are compared with data from the analytical determination of the dissolution rate of this alloy at various potentials, obtained under potentiostatic conditions. It is seen from the figure that the dissolution rate of the alloy, i_p, under the conditions investigated does not depend on the potential and appreciably (by more than an order of magnitude) exceeds the values calculated from electrochemical measurements. The effect of the discrepancy between the results of analytical and polarization measurements is so great that, in the region of cathodic polarizations, the values of i_p in absolute–

in magnitude turn out to be greater than the cathodic polarizing current. Analogous results were also obtained by us for many iron-chromium alloys of other quantitative compositions, as well as for pure chromium.

The independence of the rate of active dissolution from the potential can also be observed at lower temperatures, although, as is seen from Fig. 2 (curve 1), the magnitude of this rate may be lower than the cathodic polarizing current (curve 3). With increasing temperature the values of i_p increase much more substantially in comparison with the cathodic currents of hydrogen reduction,* which accounts for the more distinct manifestation of the effect under consideration at elevated temperatures.

Fig. 1. Cathodic (1) and anodic (2) polarization curves, measured on an alloy of iron with 4% chromium in 0.1 N sulfuric acid at 90°, and the corresponding curve (3) of the dependence of the alloy dissolution rate on the potential

Fig. 2. Dependence of the dissolution rate of steel 1Kh13 in 0.1 N sulfuric acid on the potential at temperatures of 20° (1) and 90° (2). 3, 4 –polarization curves, measured respectively at 20 and at 90°

At low temperatures, before a certain potential is reached, an acceleration of dissolution with potential is sometimes observed. In this case the dissolution rate proves to be equal to the density of the external anodic current. Such a phenomenon is characteristic, for example, of an Fe–Cr alloy containing 4% chromium (Fig. 3). Analogous data were also obtained for pure iron (Fig. 4).

Figure 3 and Figure 4

Figure 2: Figure 3 and Figure 4

At high temperatures we were unable to observe the effect of acceleration of the reaction with potential. It is of interest, however, that in these cases, upon reaching the passivation potential, a sharp inhibition of the process is observed (curve 2 in Fig. 2), which is consistent with data on the dissolution of silicon in alkali (^{2}).

Preliminary experiments showed that the values of i_p increase somewhat with increasing chromium content in the alloy and with increasing concentration of hydrogen ions, and do not depend on stirring of the solution.

The range of phenomena known from the literature that are associated with deviations in the behavior of dissolving metals from the laws of electrochemistry is rather limited. Acceleration of metal dissolution upon shifting the potential in the negative direction is most often associated with the transition of the metal under these conditions from the passive to the active state (^{3}). To explain the anomalous dissolution of aluminum in alkalis under cathodic polarization, the suggestion has been made of the formation of a surface alloy of aluminum with an alkali metal (^{4}). The cause of cathodic activation of a metal may also be secondary phenomena (a change in the concentration of the solution near the surface of the electrode, temperature, etc.). The data we have obtained apparently cannot be explained by any of these causes. It is most probable to assume that dissolution of the alloys we studied proceeds simultaneously by electrochemical and chemical mechanisms, and that the measured dissolution rate is the sum of the rates of the processes corresponding to these mechanisms. Depending on the conditions (magnitude of the potential, temperature, alloy composition), the total rate of metal dissolution may reflect the course of the process either by the chemical or by the electrochemical path.

What has been said is illustrated, for example, by the data of Fig. 3. In the region of potentials more negative than -0.3 V (on the normal hydrogen scale), the behavior of the alloy obeys the laws of chemical dissolution. At more positive potentials, the laws of electrochemical kinetics come into force. In the case of dissolution

Fig. 3. Dependence of the dissolution rate on potential (1) and cathodic (2) and anodic (3) polarization curves for an iron alloy with 4% chromium in 0.1 N sulfuric acid at 20°

Fig. 4. Dependence of the dissolution rate of iron in 0.1 N sulfuric acid at 20°

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* The values of the apparent activation energy of the dissolution process and of cathodic hydrogen evolution, calculated for a potential of -0.5 V on the normal hydrogen scale, are respectively 18,000 and 1400 cal/mol.

on potential (1). (2, 3) are the corresponding cathodic and anodic polarization curves

of 1Kh13 steel at a temperature of 90° (Fig. 2), the rate of chemical dissolution (curve 2) remains greater than the rate of electrochemical dissolution (curve 4) up to the passivation potential,* so that at all potentials corresponding to the active state of the steel, its dissolution under these conditions proceeds by the chemical mechanism.

The insufficient amount of experimental data does not yet permit an unambiguous conclusion regarding the nature of the particles interacting with metal atoms during their dissolution by the chemical path. Such particles may be, for example, water molecules. Then the process may proceed according to the equation:

$$\mathrm{Me} + n\mathrm{H_2O} \rightarrow \mathrm{Me(OH)}_n + n/2\,\mathrm{H}_2^{*} \quad \text{(slow stage)} \tag{1}$$

with subsequent dissolution of $\mathrm{Me(OH)}_n$ in acid:

$$\mathrm{Me(OH)}_n + n\mathrm{H}^+ \rightarrow \mathrm{Me}^{n+} + n\mathrm{H_2O}; \tag{2}$$

In the case of the electrochemical mechanism, the dissolution process consists of two coupled electrode reactions:

$$\mathrm{Me} \rightarrow \mathrm{Me}^{n+} + ne, \tag{3}$$

$$n\mathrm{H}^+ + ne \rightarrow n/2\,\mathrm{H}_2^{**}. \tag{4}$$

Additional experimental confirmation of the conclusions drawn may be provided by the results obtained by us in determining the amount of hydrogen evolved on the alloy under conditions of its cathodic polarization. Taking into account what was said above, the total volume of evolved hydrogen V_{H2} must be equal to:

$$V_{\mathrm{H2}} = V_{\mathrm{H2}}^{*} + V_{\mathrm{H2}}^{**}, \tag{5}$$

where V_{H2}^{*} and V_{H2}^{**} are the volumes of hydrogen evolved, respectively, according to equations (1) and (4). Under conditions of cathodic polarization, the value V_{H2}^{**} can be calculated by Faraday' s law from the magnitude of the polarizing

* This is consistent with our results, according to which the temperature increase of the anodic dissolution currents of Fe–Cr alloys in H_2SO_4 near the passivation potential occurs only up to a certain critical temperature, an increase of which is accompanied by a decrease in these currents.

cathodic current I_k (at sufficiently strong cathodic polarization, the decrease in I_k due to the occurrence of reaction (3) may be neglected). The value V^*_{H2} does not depend on I_k, but increases linearly with increasing electrode surface. Therefore, in the case of predominant dissolution by the chemical mechanism, it is possible to select conditions under which $V^*_{\text{H2}} \gg V^{**}_{\text{H2}}$. Then from equation (5) follows the inequality

$$V_{\text{H2}} \gg V^{**}_{\text{H2}}. \tag{6}$$

If, however, the process proceeds predominantly by an electrochemical mechanism, then always $V^{**}_{\text{H2}} \gg V^*_{\text{H2}}$, and equation (5) takes the form:

$$V_{\text{H2}} = V^{**}_{\text{H2}}. \tag{7}$$

Measurement of V_{H2} under cathodic polarization of 1Kh13 steel (surface 4.8 cm^2) in 0.1 N sulfuric acid at a potential of -0.35 V versus the normal hydrogen electrode, at a temperature of 90°, showed that under these conditions equation (7) is not fulfilled. In accordance with inequality (6), the experimental value of V_{H2} exceeded the value V^{**}_{H2} calculated from the cathodic current by a factor of 10.*

The results obtained show that metals of various natures may undergo dissolution by the chemical mechanism, and not only in alkaline but also in acidic electrolyte solutions. It also follows from the results obtained that, when selecting methods for protecting metals and alloys from corrosion, it is necessary to take into account the possibility that their behavior may deviate from that described by electrochemical laws. In particular, these results show the limited possibilities, in a number of cases, of cathodic and protector protection of metals.

For more definite conclusions about the detailed mechanism of the chemical reaction, it is necessary to obtain additional data and, first of all, data on the influence of pH and the anionic composition of the solution on the dissolution process. For the time being, it may be assumed that, under certain conditions, a change in the rate of chemical dissolution with potential is possible as a consequence of desorption from the metal surface or a change in the dipole moment of the particles participating in chemical dissolution. It is apparently precisely this that is connected with the inhibition of the process described above near the passivation potential.

Further development of work in this direction will make it possible not only to broaden our ideas about the kinetics of metal dissolution, but may also prove useful for elucidating the nature of the passive state.

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* These data refer to the initial period of dissolution, since we observed a decrease in the dissolution rate of 1Kh13 steel with time, which is connected with a change in the composition of the solution and, first of all, with an increase in pH due to very strong hydrogen evolution.

Note: Figure translations are in progress. See original paper for figures.

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