

ON THE PROBLEM OF THE MECHANISM OF THE SOLUTION OF IRON ALLOYS WITH CHROMIUM IN SULFURIC ACID

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The dissolution of metals in solutions of electrolytes can occur either as a result of direct interaction of the surface metal atoms with the components of the aggressive medium in one event (the so-called chemical mechanism) or as a result of the independent occurrence of two conjugated electrode reactions, one of which (oxidation of the metal) involves the emission of electrons, while the other (reduction of the depolarizer) involves the obtaining of electrons from the metal (electrochemical mechanism). Nor is the possibility excluded of the occurrence of the process simultaneously according to the chemical and electrochemical mechanisms. In the latter case, predominant solution along one of the indicated routes may occur.

Until recently, it was believed that the chemical mechanism of dissolution, playing an important role in the interaction of metals with gases and organic substances practically is not realized when they interact with aqueous solutions of electrolytes. The results of the investigations of recent years are forcing us to reexamine this viewpoint.

It has been shown in numerous works that a purely chemical interaction of the surface atoms of the metal with the components of the medium substantially changes the electrochemical and corrosion properties of metals. Thus, a strong influence of chemisorption on various anions on the rate of solution of metals has been detected, although in these cases no deviations from the principles of the electrochemical kinetics have been observed. However, considering the fact that such adsorption is a result of the establishment of a chemical bond of the adsorbing particle (molecule or ion) with the individual metal atom, such deviation might be expected in the case when this particle itself is capable of being reduced under the given conditions. Then the oxidizing and reducing steps of the process can be carried out in one event, i.e., according to a chemical mechanism.

In accord with this conclusion, it was shown in a recent work of Frumkin, Korshunov, and Iofa [1] that the experimental principles of the solution of amalgams of the alkali metals in buffer solutions at $\text{pH} > 10$ are well explained by the hypothesis of a chemical mechanism of the process. In the work of Izidinov, Borisova, and Veselovskii [2] on the investigation of the kinetics of the solution of silicon in 10 N alkali, results have also been obtained, which are difficult to explain without having recourse to the concept of the chemical mechanism of the process.

In investigating the principles of the dissolution of alloys of iron with chromium in acid solutions of electrolytes at increased temperatures, we detected phenomena, the explanation of which also requires the hypothesis of occurrence of the process according to a chemical mechanism.

Figure 1 compares the cathode and anode polarization curves, obtained on an alloy of iron with 4% chromium in sulfuric acid at 90° , with the data of an analytical determination of the rate of solution of this alloy at various potentials, obtained under potentiostatic conditions. We can see from the figure that the rate of solution of the alloy i_s under the conditions investigated is independent of the potential and appreciably (by more than an order of magnitude) exceeds the values calculated from the data of electrochemical measurements. The lack of agreement of the results of the analytical and polarization measurements is so great that in the region of cathode polarizations, the values of i_s are greater in absolute magnitude than the cathode polarizing current. We also obtained analogous results for many alloys of iron and chromium of different quantitative compositions, as well as for pure chromium.

Independence of the rate of active solution from the potential can also be observed at lower temperatures, although, as can be seen from Fig. 2 (curve 1), the value of this rate may be lower than the cathode polarizing current (curve 3). With increasing temperature, the values of i_s increase more substantially in comparison with the

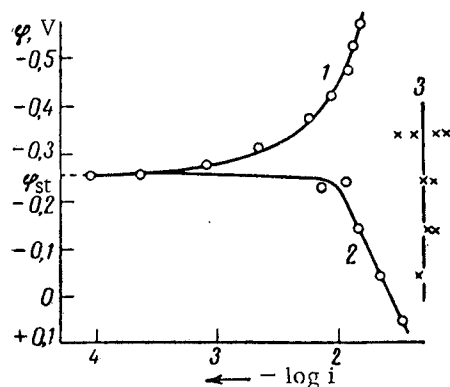


Fig. 1. Cathode (1) and anode (2) polarization curves measured on an alloy of iron with 4% chromium in 0.1 N sulfuric acid at 90° and the corresponding curve (3) of the dependence of the rate of solution of the alloy on the potential.

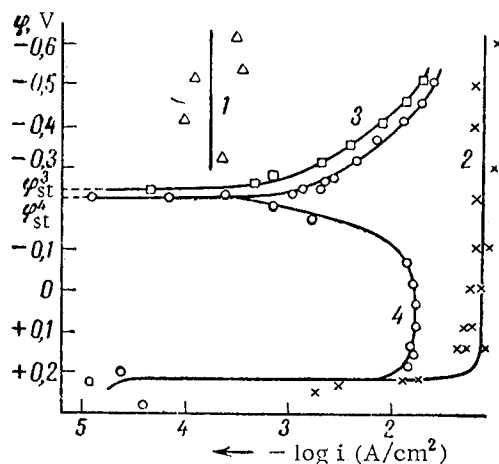


Fig. 2. Dependence of the rate of solution of steel 1Kh13 in 0.1 N sulfuric acid on the potential at temperatures of 20 (1) and 90° (2). 3,4) polarization curves measured at 20 and at 90°, respectively.

cathode currents of the reduction of hydrogen,* to which the most distinct manifestation of the effect under consideration at increased temperatures is related.

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

At high temperatures, we were unable to observe the effect of acceleration of the reaction with the potential. It is interesting, however, that in these cases when the passivation potential has been reached, a sharp inhibition of the process is observed (curve 2, Fig. 2), which agrees with the data on the solution of silicon in alkali [2].

Preliminary experiments have shown that the values of i_s increase somewhat with increasing chromium content in the alloy and with increasing hydrogen ion concentration and do not depend on mixing of the solution.

The group of phenomena related to the deviation in the behavior of dissolving metals from the laws of electrochemistry, known from the literature, is rather limited. The acceleration of solution of a metal with displacement of the potential in the negative direction is most often related to transition of the metal under these conditions from the passive to the active state [3]. The hypothesis of the formation of a surface alloy of aluminum with the alkali metal [4] has been advanced to explain the anomalous solution of aluminum in alkalis during cathode polarization. Secondary phenomena (change in the concentration of the solution close to the surface of the electrode, temperature, etc.) may also be causes of cathode activation of the metal. The data we obtained apparently cannot be explained by any one of these factors. It is most probable to assume that the solution of the alloys that we investigated proceeds simultaneously according to electrochemical and chemical mechanisms, and that the measured rate of solution is a sum of the rates of the processes corresponding to these mechanisms. Depending on the conditions (value of the potential, temperature, composition of the alloy), the summary rate of solution of the metal may reflect the occurrence of the process either along the chemical, or along the electrochemical pathways.

The above is illustrated, for example, by the data of Fig. 3. In the region of potentials more negative than -0.3V (with respect to normal hydrogen electrode), the behavior of the alloy obeys the laws of chemical solution. At more positive potentials, the laws of electrochemical kinetics are in force. In the case of solution of steel 1Kh13 at a temperature of 90° (Fig. 2), the rate of chemical solution (curve 2) remains greater than the rate of electrochemical solution (curve 4), all the way up to the passivation potential,† so that at all potentials corresponding to the active state of the steel, its solution under these conditions proceeds according to a chemical mechanism.

* The values of the apparent activation energy of the process of solution and cathode liberation of hydrogen, calculated for the potential -0.5 V with respect to the normal hydrogen electrode, comprise 18,000 and 1400 cal/mole, respectively.

† This agrees with our results, according to which the temperature increase in the anode solution currents of Fe-Cr alloys in H_2SO_4 close to the passivation potential occurs only up to some critical temperature, an increase in which is accompanied by a reduction of these currents.

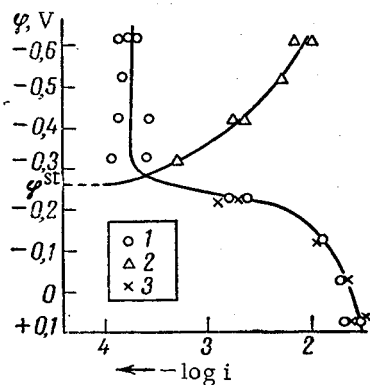


Fig. 3. Dependence of the rate of solution on the potential (1) and cathode (2) and anode (3) polarization curves for the alloy of iron with 4% chromium in 0.1 N sulfuric acid at 20°.

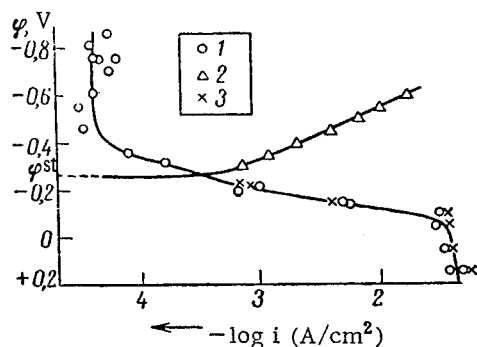
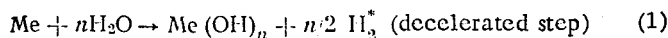
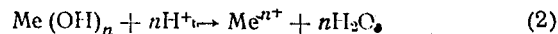


Fig. 4. Dependence of the rate of solution of iron in 0.1 N sulfuric acid at 20° on the potential (1). (2, 3) Corresponding cathode and anode polarization curves.

The insufficient number of the experimental data as yet does not permit us to draw any unambiguous conclusion with respect to the nature of the particles interacting with the metal atoms during their solution along the chemical pathway. Such particles, for example, may be water molecules. Then the process can occur according to the equation



followed by solution of $\text{Me}(\text{OH})_n$ in the acid:



In the case of the electrochemical mechanism, the process of solution consists of two conjugated electrode reactions:



A supplementary experimental confirmation of our conclusions can be found in the results that we obtained in a determination of the amount of hydrogen liberated on the alloy under conditions of its cathode polarization. Considering the above, the summary volume of hydrogen liberated, V_{H_2} , should be equal to:

$$V_{\text{H}_2} = V_{\text{H}_2^*} + V_{\text{H}_2^{**}}, \quad (5)$$

where $V_{\text{H}_2^*}$ and $V_{\text{H}_2^{**}}$ are the volumes of hydrogen liberated according to equations (1) and (4), respectively. The value of $V_{\text{H}_2^{**}}$ under conditions of cathode polarization can be calculated according to the Faraday law from the value of the polarizing cathode current I_c (in the presence of sufficient cathode polarization, the decrease in I_c on account of the occurrence of reaction (3) can be neglected). The value of $V_{\text{H}_2^*}$ does not depend on I_c but increases linearly with increasing electrode surface. Hence, in the case of predominant solution according to the chemical mechanism, conditions can be selected such that $V_{\text{H}_2^*} \gg V_{\text{H}_2^{**}}$. Then the following inequality follows from Eq. (5):

$$V_{\text{H}_2} \gg V_{\text{H}_2^{**}}. \quad (6)$$

If the process occurs primarily according to the electrochemical mechanism, then always $V_{\text{H}_2^{**}} \gg V_{\text{H}_2^*}$ and Eq. (5) takes the form

$$V_{\text{H}_2} = V_{\text{H}_2^{**}}. \quad (7)$$

Measurement of V_{H_2} during cathode polarization of steel 1Kh13 (x surface 4.8 cm²) in 0.1 N sulfuric acid at a potential of -0.35 V with respect to the normal hydrogen electrode, at a temperature of 90°, showed that under these conditions Eq. (7) is not fulfilled. In accord with the inequality (6), the experimental value of V_{H_2} exceeded the value of $V_{\text{H}_2^{**}}$, calculated according to cathode current, by ten-fold.*

* These data pertain to the initial period of solution, since we detected a decrease in the rate of solution of steel 1Kh13 with time, related to the change in the composition of the solution, primarily to the increase in the pH on account of the very strong evolution of hydrogen.

The results obtained show that metals of various characters can undergo solution according to the chemical mechanism; moreover, not only in alkaline, but also in acid electrolyte solutions. It also follows from the results obtained that in selecting the methods of protecting metals and alloys from corrosion, the possibility of deviation of their behavior from that described by electrochemical laws must be taken into consideration. In particular, these results show limited (in a number of cases) possibilities of cathode and protector protection of the metals.

For more definite conclusions on the detailed mechanism of the chemical reaction, we must obtain supplementary data, primarily data on the influence of the pH and anion composition of the solution on the process of dissolution. At present the hypothesis can be advanced that under definite conditions a change in the rate of chemical solution with the potential is possible as a result of desorption from the surface of the metal or a change in the dipole moment of the particles participating in chemical solution. The inhibition of the process close to the passivation potential, described above, is related precisely to this factor.

The further development of work along this line will make it possible not only to expand our concepts of the kinetics of the solution of metals, but may also prove useful for elucidating the nature of the passive state.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.
