CHEMICAL DISSOLUTION OF IRON CHROMIUM AND IRON-CHROMIUM ALLOYS IN SULFURIC ACID

(UDC 620.193.01)

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Translated from Zashchita Metallov, Vol. 1, No. 1,
pp. 7-12, January-February, 1965
Original article submitted September 26, 1964

According to modern concepts, the corrosion of metals in electrolytes proceeds by an electrochemical mechanism. This means that in a spontaneous dissolution of the metal the electrons liberated as the result of ionization of the metal

$$\mathrm{Me} \rightarrow \mathrm{Me}^{n+} + ne, \tag{1}$$

are absorbed by some depolarizer (hydrogen ions, for example) according to the reaction

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

and the interrelated oxidation (1) and reduction (2) reactions occur not as a single act, but separately, and their rates are determined by the differences in the potentials of the metal and the solution.

According to the laws of electrochemical kinetics [1], the rate of the oxidation reaction (1), v_0, depends on the potential φ in the following way

$$v_0 = k_1 e^{\beta\varphi F/RT}. \tag{3}$$

The corresponding relationship between the rate of the reduction reaction (2), v_r, is described by the equation:*

$$v_r = k_2[\mathrm{H}^+]e^{-\alpha\varphi F/RT}. \tag{4}$$

When the dissolution is spontaneous (i.e., in the absence of external polarizing current) then $v_0 = v_r$. From Eqs. (3) and (4) it follows that this equality occurs only for a given value of the potential (usually called the steady potential, φ_{st}). When the value of the potential shifts from the value φ_{st} toward positive values as the result of the polarization of the electrode by an external anodic current i_a the value v_0 increases and the value of v_r decreases. In this case we can write the general equation

$$i_a = v_0 - v_r. \tag{5}$$

When the value of the potential shifts from the value of φ_{st} toward negative values as the result of the polarization of the electrode by the cathodic current i_c we have

$$i_c = v_r - v_0. \tag{6}$$

When the value of the potential is very different from that of φ_{st} either in the negative or positive direction and the values of v_r in (5) and v_0 in (6) can be neglected the rates of reactions (1) and (2) are practically equal to the intensity of the external polarizing current; in the case of anodic polarization

$$v_0 = i_a \tag{7}$$

and in the case of cathodic polarization

$$v_c = i_c. \tag{8}$$

* Equations (3) and (4) for the ionization of the metal and the discharge of the depolarizer are valid only when the limiting stages are the electrochemical stages of the process.

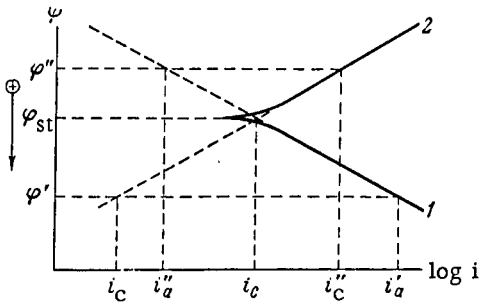

Fig. 1

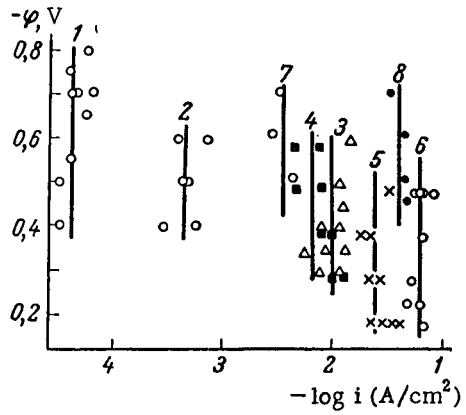

Fig. 2

Fig. 1. Schematic representation of polarization curves. 1) Anodic polarization; 2) cathodic polarization.

Fig. 2. Variation of the solution rates of iron (1-3), of an iron alloy containing 35% Cr (4-6), and of chromium (7, 8) in 0.1 N sulfuric acid with the value of the potential at the following temperatures (°C): 1) 20; 2) 70; 3) 90; 4) 40; 5) 70; 6) 90; 7) 30; 8) 90.

Under given polarization conditions Eqs. (7) and (8) make it possible to determine the rates of the oxidation and reduction reactions occurring on the metal directly from the results of polarization measurements, which are usually represented in φ—log i coordinates (Fig. 1).* Thus, when $\varphi = \varphi'$ then $v_0 = i_{a'}$ and when $\varphi = \varphi''$ then $v_r = i_{c''}$. Since the electrochemical mechanism is based on the principal of the independence of electrochemical reactions, the polarization measurements can also be used to determine v_0 and v_r at potentials at which these rates are commensurable or when one of them (the one being measured) is considerably smaller than the other. In these cases the values of v_0 and v_r can be determined by extrapolating the linear sections of the cathodic and anodic curves to potentials at which the measurements are made (dashed lines in Fig. 1). Thus, when $\varphi = \varphi''$ then $v_0 = i_{a''}$ and when $\varphi = \varphi'$ then $v_r = i_{c'}$, while when $\varphi = \varphi_{st}$ then $v_0 = v_r = i_c$.

These assumptions, confirmed by a large number of experimental data, constitute the foundation of electrochemical methods of investigating the corrosion of metals and the protection of metals against corrosion. Our earlier experiments [2] showed, however, that the kinetics of the dissolution of some structural metals and alloys does not always obey electrochemical laws. This is shown in particular by the data in Fig. 2 representing the dependence of the solution rates of iron, chromium, and the 65% Fe—35% Cr alloy in sulfuric acid on the potential at temperatures between 20 and 90°C. The solution rate was determined from the results of photocolorimetric analysis of the solution products.†

Figure 2 shows that the solution rate of the electrodes investigated remains constant in a rather wide range of potentials. Similar data were obtained for other Fe—Cr alloys. However, this fact is not a proof that the process follows a mechanism different from the electrochemical mechanism.

In fact, it is well known that when the metals dissolve by the electrochemical mechanism the rate of the process may be independent of the potential under certain conditions. This may occur, in particular, when the reaction products are removed from the dissolving metal very slowly, under conditions where the rate of the process is limited by chemical dissolution of the oxide formed by the electrochemical mechanism, and under some other conditions. In all these cases, however, the solution rates of metals determined analytically and electrochemically (from the polarization curves in Fig. 1) must be the same.

* In Fig. 1 we represented along the x axis the logarithm of the densities of the anodic current for curve (1) and of the cathodic current for curve (2).

† The duration of the experiments (from 10 min to several hours) was determined by the amount of solution products needed for the analysis.

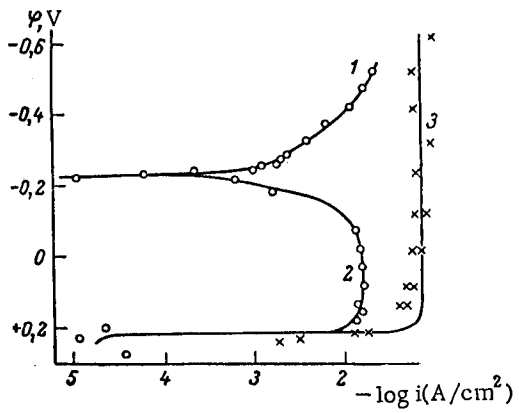

Fig. 3

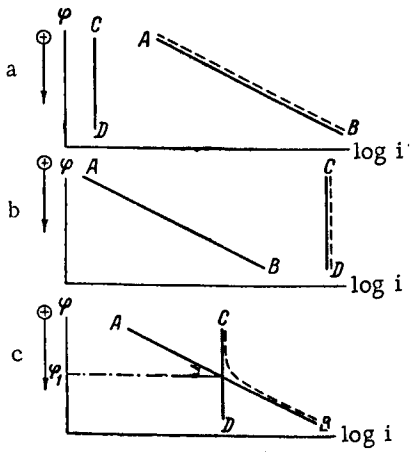

Fig. 4

Fig. 3. Cathodic (1) and anodic (2) polarization curves of 1Kh13 steel measured in a 0.1 N sulfuric acid solution at 90°C and the dependence of the solution rate of this steel determined analytically on the potential (3).

Fig. 4. Schematic representation of the variation of the solution rate of metals with the potential in the case of electrochemical (AB) and chemical (CD) reactions. The dashed lines represent the total solution rate.

Under the conditions of our investigation the solution rates determined by the two methods were different. Figure 3 shows that when the potentials are positive the solution rates of 1Kh13 steel in sulfuric acid at 90°C (expressed in current density) determined analytically are considerably higher than the value of the anodic currents. This means that Eq. (7) is not satisfied under the conditions investigated. The difference between the results of analytical and electrochemical measurements of the solution rate is even greater at potentials close to the value of φ_{st} and also in the region of cathodic polarization: according to Eq. (3), when the potential becomes more negative the value of v_0 decreases exponentially, while according to the experiments v_0 remains constant.

This difference between the results of electrochemical and analytical measurements proves that under the conditions investigated iron, chromium, and iron-chromium alloys do not dissolve according to the electrochemical mechanism. We may assume that in this case the chemical mechanism of dissolution becomes operative. According to this mechanism the ionization of metal atoms occurs directly by interaction in a single act with the particles of the solution which can be restored. Such particles can be water molecules, for example. Then the solution reaction can be written in the following way:

$$Me + nH_2O \rightarrow Me^{n+} + nOH^- + n/2\,H_2. \qquad (9)$$

The proposed explanation of the experimental data does not exclude the assumption that the dissolution of the metals investigated by the chemical mechanism may proceed at the same time by the electrochemical mechanism, whose rate, however, is much lower than the rate of chemical dissolution. A similar assumption was made in [3] to explain the behavior of amalgams in alkaline solutions.

The dependence of the solution rate of metals on the potential in the case of simultaneous electrochemical and chemical reactions is represented schematically in Fig. 4a, b, c. In this figure. the AB curve characterizes the electrochemical process, whose rate is described by Eq. (3). The CD curve represents the chemical process, whose rate is independent of the potential. Figure 4 shows three possible cases of the relationship between the rates of the reactions occurring by the two mechanism. In the first case (Fig. 4a) electrochemical dissolution predominates. For practical purposes the total solution rate is described by the AB curve. The metal dissolves according to the laws of electrochemical kinetics. In the second case (Fig. 4b) the rate of chemical dissolution is higher than the rate of the electrochemical reaction in the whole range of potentials investigated. The total solution rate is represented by the CD curve. The experimental data can be explained by assuming that the metal dissolves by the chemical mechanism. Finally, in the third case (Fig. c) the rates of chemical and electrochemical reactions are commensurable. Since the rate of the electrochemical process increases while the rate of the chemical reaction remains constant after

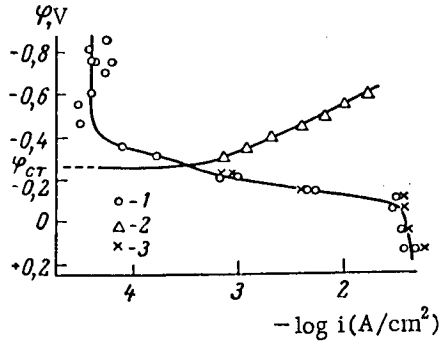

Fig. 5. Variation of the solution rate of iron in 0.1 N sulfuric acid with the potential (1) at 20°C. Curves 2 and 3 represent the cathodic and anodic polarization curves under the same conditions.

a given potential is reached (φ_1 in Fig. 4c), when the potential shifts in the positive direction the mechanism of the dominant process changes: the metal dissolves predominantly by the chemical mechanism at potentials more negative than φ_1 and by the electrochemical mechanism at more positive potentials.

The explanation given here is in good agreement with the experimental results. In fact, we may assume that the numerous published data on the solution of metals by the electrochemical mechanism correspond to the cases shown in Fig. 4a. The data in Fig. 2 can be explained by analogy with the diagram shown in Fig. 4b. Our data on the solution of iron in 0.1 N sulfuric acid at room temperature (Fig. 5) are in agreement with the case indicated in Fig. 4c. We obtained results similar to those shown in Fig. 5 for some Fe–Cr alloys at room temperature.

Our measurements of the volume of hydrogen evolved during the solution of iron, chromium, and iron-chromium alloys in sulfuric acid are additional proof of the correctness of the explanation given. We have shown that the amount of hydrogen (as well as the amount of metal dissolved) considerably exceeds what one would expect from the calculations based on the results of polarization measurements. A similar result was obtained in [4], where the authors studied the solution rate of silicon in an alkaline solution. Our study of the solution rate of 1Kh13 steel in sulfuric acid at 90°C showed also that the rate of evolution of hydrogen is high at a potential about 15 mV more positive than zero hydrogen potential. Thus, our data show that under certain conditions Eqs. (4) and (8) are not satisfied. At the same time, these data agree with the assumption that hydrogen may evolve according to reaction (9).

In view of the conclusions that dissolution proceeds by chemical reaction, the slowing down of this reaction at potentials more positive than the passivation potential (see Fig. 3) is very interesting. The explanation of this phenomenon requires additional assumptions, since according to our general concepts the rate of the chemical reaction is independent of the potential.

The assumption that chemical solution is slowed down at the passivation potential because the passivating particles adsorbed on the surface prevent direct chemical interaction of metal atoms with the aggressive components of the solution seems quite probable. It is also possible that the same particles (water molecules, for example) play the role of such aggressive components and passivators. When the potential is sufficiently negative the oxygen of the water molecule orients itself toward the metal and thus ensures the transfer of electrons from the metal to the hydrogen of the water. At some more positive potential at which the bond between the metal and oxygen reaches a certain strength (at the passivation potential) the O–H bond in the water molecule is weakened and, as the result, direct transfer of electrons from the metal to the hydrogen of the water molecule becomes impossible and chemical dissolution is slowed down.

A more detailed description of the mechanism of chemical dissolution based on experimental data on the dependence of the effect investigated on the composition of the solution (first of all on the pH of the solution) will be given in the next article. Here we must emphasize that in the light of the description given it is of practical interest to determine conditions which favor the predominance of one of the mechanisms studied here. The analysis of the results obtained already allows us to conclude that the factors favoring the predominantly chemical solution of metals are the displacement of the potential in the negative direction and the increase in temperature. This effect of potentials follows from our discussion (see Fig. 4). The effect of the temperature is apparently due to the fact that the rate of chemical solution increases with temperature much more than the rate of electrochemical dissolution. This explains the fact that with increasing temperature the reaction represented in Fig. 4a is transformed into the reaction represented in Fig. 4b.

The results obtained here indicate that in a number of cases the laws of electrochemical kinetics cannot be used to explain the increase in the corrosion resistance of metals in electrolytes. This refers first of all to cathodic protection of metals against corrosion.

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