CHARACTERISTICS OF THE DISSOLUTION OF MANGANESE IN ACIDIC ELECTROLYTES

Ya. M. Kolotyrkin and T. R. Agladze

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In investigating the behavior of iron and a number of structural steels in 0.1 N H_2SO_4 [1-2], we hypothesized that the dissolution of the metals may proceed by chemical and electrochemical mechanisms simultaneously.

This article considers similar regularities in the anomalous dissolution of manganese in acidic solutions.

METHOD

Rectangular specimens of electrolytic manganese scale with a working surface of 0.3-0.5 cm^2 were machined on an optical grinder. Before each experiment, the specimens were also cleaned with emery paper, rinsed, and degreased.

The electrochemical behavior of manganese was investigated in sulfuric acid and in a sulfate mixture:

$$(x)\text{N.}H_2SO_4 + (1-x)\text{N.}Na_2SO_4.$$

Chemically pure sulfuric acid was additionally purified by double distillation. The sodium sulfate was twice recrystallized. The water was subjected to double distillation.

The experiments were conducted at temperatures of 25, 50, 70, and 90°.

In order to evaluate the role of diffusion difficulties, the solution was agitated with a magnetic mixer operating at 400-1200 rpm in a number of experiments. The polarization measurements were made by the potentiostatic method. Using a fixed electrode potential, balance experiments were conducted to determine the amount of metal dissolved and the amount of gas evolved, the gas being collected in a special hermetically sealed cell with a gas trap over the electrode.

In order for as large an amount of hydrogen as possible to be liberated, the electrode was polarized at a current density of $8 \cdot 10^{-2}$ A/cm^2, which could be done only when working with the stopcock between the working and auxiliary electrodes open. In order to avoid forcing the solution from one portion of the

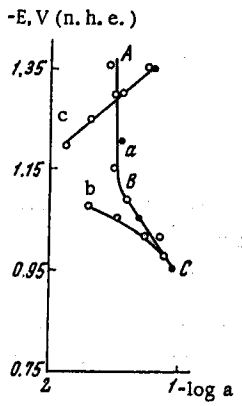

Fig. 1. Dissolution rate of electrolytic manganese as a function of potential in 0.1 N H_2SO_4, t = 50°; solution not agitated. b and c) Corresponding cathodic and anodic polarization curves.

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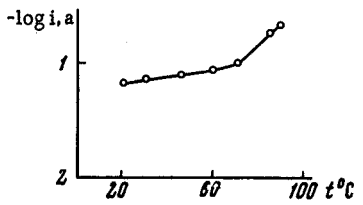

Fig. 2

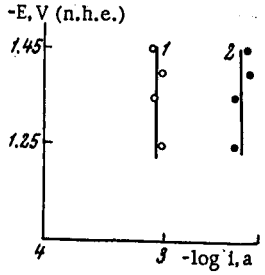

Fig. 3

Fig. 2. Influence of solution temperature on dissolution rate of manganese at E = -1.25 V in 0.1 N H_2SO_4.

Fig. 3. Dissolution rate of manganese as a function of potential. 1) In unagitated solution; 2) in agitated (1000 rpm) solution of 0.01 N H_2SO_4, t = 50°.

cell into the other, the anodic and cathodic gases were led through a surge column filled with concentrated sulfuric acid. The anodic gas was discharged into the atmosphere, while the hydrogen was collected in a measuring burette with a capacity of 500 cm^3. In calculating the amount of hydrogen liberated, corrections were made for the atmospheric pressure, the temperature, and the solubility of the hydrogen in the water. Collection of the gas lasted from 3 to 5 h at a constant potential, 250-350 cm^3 of hydrogen accumulating.

After polarization, the solution was poured from the cell and the manganese ions were oxidized with ammonium persulfate in a stabilizing phosphoric acid medium to permanganate ions, using the well-known method involving addition of silver nitrate [3]. The permanganate solution was subjected to photocolorimetric analysis.

The electrode-polarization time was governed by the time necessary to accumulate a sufficient amount of manganese ions for analysis. The dissolution rate, determined by analysis of the solution, was calculated in current-density units on the assumption that the manganese formed divalent ions. The potential was measured relative to a saturated calomel electrode and recalculated for hydrogen.

EXPERIMENTAL DATA

The analytically determined dissolution rate of the manganese (Fig. 1, curve ABC) was independent of the potential over a broad range (-1.1 to 1.35 V, segment AB). When the potential was shifted in the positive direction from -1.16 V, the dissolution rate increased (segment BC) and markedly exceeded the corresponding anodic currents (curve c).

At a constant potential E = -1.25 V, the dissolution rate increased linearly with the temperature between 25 and 70° and rose more sharply above 70° (Fig. 2). The activation energy of dissolution, which was calculated from the temperature function and was independent of the potential, was 5700 cal/mole.

Dissolution of the manganese was also stimulated by agitation of the solution (Fig. 3). Reducing the hydrogen-ion concentration over the pH range 0-2.5 caused a sharp drop in the dissolution rate (Fig. 4), following the equation:

$$i = K[H^+]^a, \text{ where } a = 2.$$

Analysis of the manganese ions was greatly complicated in weakly acidic and neutral solutions (pH ≥ 3) by the low dissolution rate of the metal; however, it follows from the preliminary data obtained that the dissolution rate depended little on pH.

DISCUSSION OF RESULTS

The data presented above on the dissolution of manganese do not fall within the framework of simple electrochemical rules. According to the latter, the dissolution rate of a metal drops as the

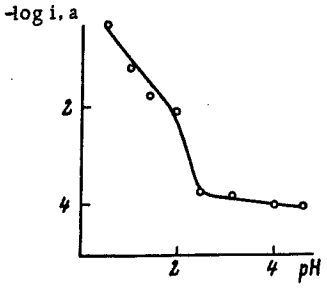

Fig. 4

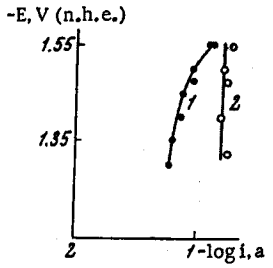

Fig. 5

Fig. 4. Dissolution rate of manganese as a function of pH at E = -1.25 V in solutions of (x) N H_2SO_4 + (1-x) N Na_2SO_4.

Fig. 5. Dissolution rate of manganese as a function of potential in 0.1 N H_2SO_4 at temperature of: 1) 20°; 2) 85°.

electrode potential shifts in the negative direction and becomes negligibly small when it reaches a sufficiently negative value. Under these conditions, the principal electrochemical process taking place at the surface of separation between the metal and the electrolyte is hydrogen-ion discharge. This phenomenon forms the basis for the well-known method of cathodic protection of metal components. However, there have been many recent reports in the literature on deviations from the aforementioned rules. In most cases, anomalously rapid dissolution of metals during cathodic polarization is due to reduction of the oxide film by cathodic hydrogen and to changes in the hydrogen-ion concentration and temperature in the perielectrode region.

In our case, there was actually a slight increase in the dissolution rate when the polarizing-current density was increased at room temperature (Fig. 5, curve 1). However, this effect completely disappeared at 80° (curve 2), although the dissolution rate remained very high and was independent of the potential. Moreover, it follows from Fig. 4 that the dissolution rate of the manganese during cathodic polarization decreased as the pH increased. The impoverishment of the perielectrode region in hydrogen ions as a result of the high discharge rate of the electrode thus obviously cannot lead to a rise in the dissolution rate of the manganese. These and other experiments enable us to conclude that the anomalous dissolution of manganese does not result from the influence of factors of this type.

The observed deviation of the dissolution of manganese from the laws of electrochemical kinetics can be explained if we acknowledge the possibility of two parallel dissolution processes: electrochemical, whose rate i_e varies with the potential in accordance with the rules of electrochemical kinetics, and nonelectrochemical, whose rate i_n is independent of the potential. This is confirmed by the fact that, at potentials more positive than point B in Fig. 1, the dissolution rate determined by analysis of the solution virtually coincided with the sum of the rates $i_e + i_n$, if we assume that i_n has the same value at these potentials as at more negative ones.

The potential-independent dissolution of manganese can be represented as the result of a chemical reaction (single-step) between the metal atoms and adsorbed water molecules. The first stage of this reaction is apparently the formation of a superficial oxide

$$Mn + H_2O \rightarrow MnO + H_2, \quad (1)$$

which then dissolves in the acid electrolyte by the reaction

$$MnO + 2H^+ \rightarrow Mn^{2+} + H_2O. \quad (2)$$

The overall reaction can thus be written in the form:

$$Mn + 2H^+ \rightarrow Mn^{2+} + H_2. \quad (3)$$

The possibility that the dissolution of metals may proceed by a chemical mechanism has been taken into account in a number of articles by other researchers in order to explain the anomalous

dissolution of an amalgam of alkali metals in buffered solutions at pH's above 10 [5] and of silicon in 10 N alkali [6]. In this case, the hypothesis in question is confirmed by comparing the amount of electricity necessary for evolution of the amount of hydrogen collected at E = -1.25 V (Q_1 = 2340 coulombs) with the amount of electricity passed through the electrode (Q_2 = 630 coulombs). The difference between these figures (Q_3 = 1710 coulombs) must obviously be assigned to the hydrogen evolved as a result of the chemical reaction between the manganese and the water.

It corresponds to a current density of $5.5 \cdot 10^{-2}$ A/cm^2, which is in satisfactory agreement with the value of $4.9 \cdot 10^{-2}$ A/cm^2 found by analysis of the solution (Fig. 1). A similar result was obtained in [1] determining the volume of hydrogen evolved during dissolution of iron, chromium, and their alloys.

The low activation energy of the process (E = 5.7 kcal/mole) and the influence of agitation on its rate indicate that the overall reaction involves a diffusion limitation on the transfer of manganese into the solution. It is obvious that this limitation can be caused either by the slowness with which the hydrogen ions reach the surface limiting reaction (2) or by the slowness of the discharge of the reaction products, i.e., Mn^{2+}, from the perielectrode layer. The observed dependence of the rate on $[H^+]$ is not in agreement with the first hypothesis, since it corresponds to a linear relationship between these quantities. We are left with the assumption that, in our case, the process is limited by the rate at which the manganese ions escape from the perielectrode layer into the bulk of the solution. Given this condition, the dissolution rate should depend on the perielectrode $[Mn^{2+}]_0$ concentration. In determining this latter quantity, it is naturally necessary to give consideration to the fact that manganese can dissolve both by a chemical mechanism, whose rate can, in accordance with Eq. (3), be expressed by the formula:

$$i_1 = K_1[H^+]^2, \tag{a}$$

and by an electrochemical mechanism

$$Mn \rightarrow Mn^{2+} + 2e,$$

for which

$$i_2 = K_2 e^{(\beta F/RT)\cdot\varphi}. \tag{b}$$

It is also necessary to take into account the fact that the Mn^{2+} ions formed cannot only diffuse into the solution at the rate

$$i_3 = K_3[Mn^{2+}]_0, \tag{c}$$

but also be redeposited on the surface of the metal by the electrochemical mechanism*

$$Mn^{2+} \rightarrow Mn - 2e \tag{d}$$

at the rate

$$i_4 = K_4[Mn^{2+}]_0 e^{(-\alpha F/RT)\cdot\varphi}. \tag{e}$$

It is obvious that, under steady-state conditions,

$$i_1 + i_2 = i_3 + i_4$$

or, taking into account (a), (b), (c), and (d),

$$K_1[H^+]^2 + K_2 e^{(\beta F/RT)\cdot\varphi} = K_3[Mn^{2+}]_0 + K_4[Mn^{2+}]_0 e^{(-\alpha F/RT)\cdot\varphi}.$$

Solving this equation for $[Mn^{2+}]$, we obtain

$$[Mn^{2+}]_0 = \frac{K_1[H^+]^2 + K_2 e^{(\beta F/RT)\cdot\varphi}}{K_3 + K_4 e^{(-\alpha F/RT)\cdot\varphi}}.$$

According to Fick's law (assuming the volumetric Mn^{2+} concentration to be 0), the rate at which the manganese passes into the bulk of the solution

$$i_{tot} = K_3 \frac{K_1[H^+]^2 + K_2 e^{(\beta F/RT)\cdot\varphi}}{K_3 + K_4 e^{(-\alpha F/RT)\cdot\varphi}}. \tag{3a}$$

* There is a real possibility of this reaction if we consider that the standard potential of an Mn/Mn^{2+} electrode is -1.18 V.

Analysis of Eq. (3a) shows that it gives a true qualitative description of the character of the dependence of the rate at which the Mn^{2+} passed into the solution on the pH and potential observed in our experiments. It is easy to demonstrate that the ratio of the rates of the partial reactions varies as a function of the electrode potential.

Thus, for example, when the potential shifts in the negative direction, the term $K_2 = e^{(\beta F/RT)\cdot\varphi}$ decreases exponentially and can be neglected for sufficiently negative potentials. The rate at which manganese ions accumulate near the electrode then depends only on the ratio of the rate of chemical dissolution to the rates of redischarge and diffusion. We cannot discount the possibility that, as a result of the increase in the overvoltage of reaction (d) (because of the possible influence of hydrogen absorption by the electrode during cathodic polarization [6]), the preexponential value of K_4 decreases and the rise in the manganese-ion discharge rate is less than exponential.

When the potential shifts in the positive direction, the discharge rate of the manganese ions decreases and the term $K_4e^{(-\alpha F/RT)\cdot\varphi}$ can be neglected, while the rate of the anodic reaction (d) rises and, at high anodic potentials, predominates over the potential-independent chemical process. At potentials close to the steady-state level, the absolute rates of the chemical and electrochemical dissolution processes are comparable and the metal dissolves under conditions similar to those obtaining for autodissolution.

It must be noted that complicating factors also affect the overall manganese-dissolution rate. Thus, in particular, we cannot exclude the possibility of partial decomposition of the electrode during cathodic polarization as a result of absorption of hydrogen atoms by the metal.

CONCLUSIONS

1. We have shown that the dissolution rate of manganese at negative potentials depends on the potential in a manner that deviates from Tafell's equation.

2. The potential-independent dissolution of manganese during cathodic polarization does not result from the influence of secondary factors (changes in solution concentration and temperature near the electrode).

3. The anomalous dissolution of manganese can be explained if we recognize the possibility of parallel electrochemical and chemical dissolution processes.

4. We have shown that the dissolution of manganese in acidic solutions is limited by the rate at which the dissolution product escapes from the perielectrode layer.

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