CHEMICAL SOLUTION OF MANGANESE

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From a previous report [1] on the anomalous behavior of manganese in acid solutions it follows that over a wide range to the negative side of the stationary potential the analytically determined rate of solution remains high and independent of potential. This rate is much higher than the rate of solution calculated from the results of electrochemical measurements, i.e., from the point of intersection of the extrapolated cathodic and anodic polarization curves. In addition, in the anode-polarization region, shift of potential towards positive values is accompanied by an increase in the rate of solution. However, quantitative agreement between the rates of solution obtained from the current and from analysis of the solution is observed only at potentials about 0.5 V to the positive side of the stationary value.

From these data the inference was drawn that in acid solutions manganese dissolves simultaneously by an electrochemical and a chemical mechanism; the first of these predominates in the region of anodic polarizations, and the second in the region of cathodic polarization. This hypothesis is supported by the fact that at potentials more positive than the stationary value (Fig. 1, point B) the rate of solution determined from analysis of the solution (i_c) practically coincides with the total velocities of the chemical (i_{ch}) and electrochemical (i_{el}) processes, provided that we assume that in anodic polarization i_{ch} has the same value as in cathodic polarization. In this paper this important assumption receives experimental confirmation.

An electrode of electrolytic manganese was polarized anodically, and the quantity of hydrogen evolved during polarization was measured.

From Fig. 1 we see that, within the experimental error, the rate of evolution of hydrogen, converted to electrical units (curve BD), remains constant throughout the potential range studied, which lies to the positive side of φ_{st}, and practically coincides with the analytically determined rate of solution in the cathodic-polarization region. At the same time, the value of this rate is about $1^1/_2$ orders of magnitude greater than the rate of electrochemical emission of hydrogen, determined by extrapolation of the cathodic polarization curve in the anodic-potential region.

Losev et al. [2] showed that excess evolution of hydrogen during anodic polarization may be observed also when there is a stagewise mechanism of solution of a metal, if electrochemical ions of intermediate valence are formed and are then oxidized in solution by reacting with hydrogen ions. However, in the general case the rate of this process is proportional to the H^+ concentration and the excess hydrogen should not be greater than the quantity equivalent to the anodic current. From this viewpoint we cannot explain the data referring to cathodic polarization also.

In our first communication we remarked that the rate of solution of manganese at potentials to the negative of φ_{st} is practically independent of the nature and concentration of the electrolyte anion, and at a given temperature is a function only of the hydrogen-ion concentration:

$$i = K[H^+]^2. \quad (1)$$

To explain this relation we supposed that the solution of manganese by a chemical mechanism takes place in two stages, of which the first is direct interaction between metal atoms and adsorbed H_2O molecules leading to the formation of a surface oxide:

$$Mn + H_2O \rightarrow MnO + H_2,$$

which then dissolves with the aid of H^+ ions,

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

From (1) it was shown that in weakly-acid and neutral solutions the rate of anomalous solution of manganese

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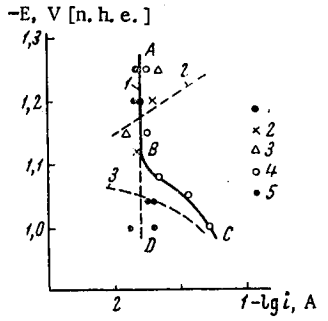

Fig. 1

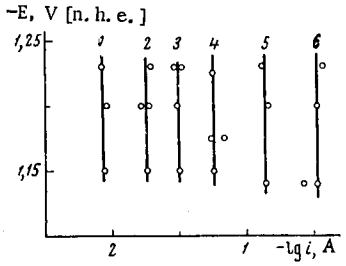

Fig. 2

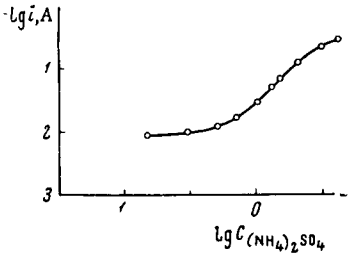

Fig. 3

Fig. 1. Rate of solution of manganese versus potential at t = 25°: 1) 0.1 N HCl, 2) 0.1 N $HClO_4$, 3) 0.1 N HBr, 4) 0.1 N H_2SO_4, 1)-4) [from analysis of solution (curve ABC)], 5) 0.1 N H_2SO_4 – from the hydrogen (curve BD) 2 and 3 (dashed): respectively cathodic and anodic polarization curves.

Fig. 2. Potential dependence of rate of solution of manganese, in xM $(NH_4)_2SO_4$ + (2.5 – x) M K_2SO_4, where x = 0.15, 0.7, 1, 1.25, 2, and 2.5 N; t = 25°; disk rotation rate, 2400 rpm.

Fig. 3. Rate of solution of manganese versus $(NH_4)_2SO_4$ concentration at $\varphi = -1.2$ V, in solutions of xM $(NH_4)_2SO_4$ + (2.5 – x) M K_2SO_4; t = 25°; disk rotation rate 2400 rpm.

is very low. However, if we start from the proposed mechanism, it can be increased by introducing to the solution some complex-forming particles, which, like the hydrogen ions, interact with the surface oxides and accelerate the limiting stage of the process. According to the literature data [3, 4], Mn^{++} ions are able to form stable complexes with ammonia. We therefore measured the rate of solution of manganese during cathodic polarization in neutral potassium sulfate solutions containing various amounts of $(NH_4)_2SO_4$. To eliminate diffusion limitation, the cathode was a rotating disk of manganese.

From Fig. 2 we see that in this case the rate of solution is also independent of potential over a fairly wide range, and rises regularly with the $(NH_4)_2SO_4$ concentration. From the curve plotting the rate of chemical solution versus the ammonium sulfate concentration at E = 1.2 V (Fig. 3), it follows that

$$i_x = K[NH_4^+]^2.$$

The deviation from linearity when $C_{(NH_4)_2SO_4} > 2$ M is apparently due to coverage of the electrode surface by an insoluble film of a manganese salt. This is supported by the variation of the rate of solution with the speed of rotation of the disk at high $(NH_4)_2SO_4$ concentrations and by the appearance of a white salt deposit on the electrode. Taking account of these data on the effect of a complex-forming agent on the value of i_{ch}, we can propose a two-stage mechanism for the chemical solution of manganese in neutral and weakly-acid solutions containing NH_4^+ ions.

The first stage, as in acid solutions, involves interaction of manganese with water molecules:

$$Mn + H_2O \rightarrow MnO + H_2.$$

In the subsequent reaction the oxide dissolves with the formation of an ammonium complex of manganese:

$$MnO + 2NH_4^+ \rightarrow [Mn(NH_3)_2]^{++} + H_2O.$$

The overall reaction can thus be summarized as

$$Mn + 2NH_4^+ \rightarrow [Mn(NH_3)_2]^{++} + H_2.$$

Thus the experimental relation $i_{ch} + i_{el} = i_c$, and also the relation between the potential-independent solution rate and the complex-forming agent concentration, support our previous hypothesis that manganese dissolves by two parallel reactions, one of which is chemical in nature.

LITERATURE CITED

1. Ya. M. Kolotyrkin and T. R. Agladze, Zashchita Metal., 4, 413 (1967).
2. A. P. Pchel'nikov and V. V. Losev, Zashchita Metal., 5, 482 (1965).
3. K. B. Yatsimirskii and V. P. Vasil'ev, Constants of Complex Compounds [in Russian], Izd-vo AN SSSR (1959).
4. R. I. Agladze, Zh. Organ. Khim., 10, 340 (1940).