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Abstract

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ON THE QUESTION OF THE MECHANISM OF DISSOLUTION OF ZIRCONIUM IN ACID FLUORIDE SOLUTIONS

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In HF solutions, in contrast to the overwhelming majority of other electrolytes, zirconium undergoes intense general corrosion even at room temperature. Smith and Hill ([1]), who investigated the kinetics of this process by a radiochemical method (using the isotope Zr^{95}), showed that the rate at which zirconium passes into solution is directly proportional to the concentration of undissociated HF and increases linearly with increasing stirring rate of the solution. At sufficiently high stirring rates the dissolution rate reaches a certain limiting value, which, in the authors' opinion, is not, however, connected with the process leaving the region of diffusion limitation. Indeed, the value of the activation energy determined under these conditions proved to be 3.34 kcal/mole. Similar results were also obtained in the work of Straumanis et al. ([2–6]), who determined corrosion rates from the volume of hydrogen evolved. In addition, in ([5]) it was shown that shifting the potential of zirconium toward positive values (by bringing it into contact with platinum) leads to a decrease in the rate of hydrogen evolution on it, although, as is evident from the data given below, the rate of dissolution of the metal remains unchanged.

On the basis of an analysis of the data obtained, Straumanis, James, and Castead ([5]) concluded that the dissolution of Zr in HF solutions proceeds by a purely chemical mechanism, i.e., is the result of direct interaction of HF molecules with Zr atoms.

This conclusion, however, is not consistent with the positive difference effect observed in this case, which was mentioned above.

Thus, despite the existence of a number of reliably established regularities, the mechanism of dissolution of zirconium in HF solutions cannot be considered finally elucidated. In order to fill this gap, in the present work we investigated not only the kinetics of the transfer of Zr into solution, but also the kinetics of hydrogen evolution. In doing so, in contrast to other investigators ([1–6]), considerable attention was given to establishing the dependence of the rate of these processes on the potential of zirconium.

Figure 1

Figure 1: Figure 1

The main experiments were carried out in solutions of $0.1\,N\,H_2SO_4 + XHF$, where X (the HF concentration) varied from $0.001\,N$ to $1.0\,N$. Separate control experiments were performed in individual HF solutions. In the case where $[HF] \leq 0.01\,N$, the measurements were carried out in a Pyrex glass cell, and in the case of more concentrated solutions—in Teflon or polyethylene cells. Special experiments established the identity of the results obtained in both cases. The preliminary preparation of zirconium electrodes was carried out according to the method described earlier ([7,8]). The solution was saturated with nitrogen thoroughly purified of traces of oxygen. In full agreement with the results of Smith and Hill, it was established, however, that the ingress of atmospheric oxygen into the cell does not exert a noticeable influence on the measurement results. This indicates that the dissolution of Zr under the conditions considered proceeds with hydrogen depolarization. The dissolution rate was determi-

was determined both from the magnitude of the anodic current and analytically —by colorimetry of the solution using xylenol orange as indicator.

For stirring the solution a standard MM-2 magnetic stirrer with a small ($l = 13$ mm) magnet was used. The design characteristics of the stirrer allowed the rotation rate of the magnet to be varied only within narrow limits (from ~ 800 to ~ 1200 rpm). Under these conditions the intensity of stirring of the solution, and consequently the rate of dissolution of the metal v, changed only slightly with changes in the number of revolutions of the stirrer.

Fig. 1. Dependence of the rate of dissolution of Zr on potential in $0.1\,N$ $H_2SO_4 + 0.01\,N$ HF:
1 —without stirring, 2 —with stirring by a small magnet

The dissolution rates found in this case differed very little from the corresponding values reported in the work of other investigators. Thus, for example, the dissolution rate obtained by us in $0.1\,N$ $H_2SO_4 + 0.01\,N$ HF at 25° had a value equal to $2.7 \cdot 10^{-3}$ A/cm^2, whereas according to the data of Straumanis and co-workers, referring to $0.01\,N$ HF, it is $2.9 \cdot 10^{-3}$ A/cm^2. At the same time, increasing the linear dimensions of the magnet led to a significant increase in the rate of dissolution of Zr. Our experiments showed that replacing the small magnet by a large one ($l = 20$ mm) led to an increase in v by more than a factor of two.

Potentiostatic measurements, combined with analysis of the solution, showed that the value of v does not depend on the potential. As is seen from Fig. 1 (curve 2), throughout the entire potential range we investigated, beginning from -0.70 V up to $+2.0$ V, the value of v remains constant. At the same time it was found that v increases linearly with increasing HF content in the solution up to a concentration of $0.2\,N$.

Fig. 2 and Fig. 3

Figure 2: Fig. 2 and Fig. 3

A similar picture is observed also in the absence of external stirring. In this case, however, the dissolution rate had a lower value, which remained constant only at potentials lying more positive than −0.50 V. The transition to more negative values invariably led to a noticeable increase in the dissolution rate. Analysis of this phenomenon led us to the conclusion that such acceleration of the process is in this case completely due to stirring of the near-electrode part of the solution by gaseous hydrogen, which is evolved intensely in this region of potentials.

The results presented above may be regarded as additional confirmation of the correctness of the conclusions made in the work of other investigators, according to which the transition of Zr into solution under the conditions considered is limited by the rate of supply to the metal surface of undissociated HF molecules. These results also do not contradict the suggestion of Straumanis and co-workers concerning a purely chemical mechanism of dissolution of Zr in HF solutions.

If this mechanism is followed, it would be natural to expect that the evolution of hydrogen would also be limited by diffusion of HF and, consequently, likewise would not depend on the potential. Our measurements showed, however, that this does not agree with experiment. As is seen from Fig. 2, for each given solution the dependence of the rate of hydrogen evolution on zirconium on the potential is characterized by the usual Tafel straight line

This dependence is maintained not only under conditions of cathodic polarization, when this reaction is the only possible one, but also in the absence of an external cathodic current, i.e., when hydrogen evolution occurs only at the expense of oxidation of zirconium. This is evidenced by the fact that the rate of spontaneous dissolution of Zr, determined analytically and expressed in units of electric current (see points 1 and 2 in Fig. 2), coincides almost exactly in each case with the dissolution rate found from electrochemical data, i.e., from the position of the point

Fig. 2. Polarization curves on Zr in unstirred solutions:
a–0.1 N H_2SO_4 + 0.001 N HF,
b–0.1 N H_2SO_4 + 0.01 N HF.
The abscissae of points 1 and 2 correspond to the rates of self-dissolution of Zr, found analytically, in the indicated solutions.

Fig. 3. Curves ϕ–t at i_A = const in an unstirred solution of 0.1 N H_2SO_4 + 0.01 N HF.
1–$i_A < i_3$, 2–$i_A > i_3$ ($i_3 = 3.9 \cdot 10^{-4}$ A/cm^2)

of intersection of the extrapolated continuation of the Tafel portion of the cathodic polarization curve with the line of the stationary potential. Thus, for

example, in the case of an unstirred solution of 0.1 N H_2SO_4 + 0.01 N HF, such an extrapolation gives the value $v = 3.6 \cdot 10^{-4}$ A/cm^2, whereas according to colorimetric analysis it is equal to $3.9 \cdot 10^{-4}$ A/cm^2. A similar agreement is also observed in other solutions. The imposition of external stirring, leading to an increase in the dissolution rate, is also accompanied by a shift of the stationary potential in the negative direction to such a value at which the magnitude of the new dissolution rate corresponds exactly to the same kinetic curve for hydrogen evolution. These results thus show that hydrogen evolution in the process of spontaneous dissolution of Zr in HF solutions is an independent electrode reaction, the rate of which, other conditions being equal, depends only on the potential.

It is obvious that if one of the reactions of the oxidation–reduction process proceeds in accordance with the laws of electrochemical kinetics, then the other reaction must take place by the same mechanism. From this one can apparently conclude that the transition of Zr into solution is, in the present case, a secondary reaction connected not with oxidation of the metal, but with chemical dissolution of the oxidation products.

Following these conclusions, the mechanism of dissolution of Zr in HF solutions can be represented in the form of two consecutive processes, of which the first—oxidation of zirconium—

$$\mathrm{Zr} + 2\mathrm{H_2O} = \mathrm{ZrO_2} + 2\mathrm{H_2} \tag{1}$$

proceeds by an electrochemical mechanism and, consequently, consists of two coupled electrode reactions:

$$\mathrm{Zr} + 2\mathrm{H_2O} \rightarrow \mathrm{ZrO_2} + 4\mathrm{H^+} + 4e, \tag{1a}$$

$$4\mathrm{H^+} + 4e \rightarrow 2\mathrm{H_2}. \tag{1b}$$

The second process, proceeding with a diffusion limitation that determines the rate of the entire process as a whole, may be written in the following form:

$$\mathrm{ZrO_2} + n\,\mathrm{HF} \rightarrow \mathrm{ZrF_n(OH)_{4-n}} + (n-2)\,\mathrm{H_2O}. \tag{2}$$

The proposed mechanism makes it possible to explain all the principal regularities of the corrosion and electrochemical behavior of Zr in HF solutions. This applies, in particular, to the positive difference effect, as well as to the behavior, observed in our experiments, of the electrode potential of zirconium upon polarization of this metal by a constant anodic current i_A.

If the rates of reactions (1a), (1b), and (2) are denoted by i_1, i_2, and i_3, respectively, then for stationary dissolution conditions in the absence of external polarization one may write

$$(i_1 = i_2) = i_3 = \text{const.} \tag{3}$$

The application of an external anodic current must inevitably lead to a violation of this equality, and the rate of the first process—the oxidation of zirconium—will exceed the rate of process (2), which, because of the diffusion limitation, will remain constant:

$$[i_1 = (i_2 + i_A)] > i_3. \tag{4}$$

Thus, the final result of anodic polarization will be an increase in the thickness of the oxide film and, consequently, a shift of the potential toward positive values. However, if $i_A < i_3$, and the process proceeds by an electrochemical mechanism, then the shift of the potential in the positive direction will be small ([9]). Indeed, under these conditions an increase in the potential must inevitably lead to a decrease in the rate of hydrogen evolution and, consequently, to a decrease in the left-hand side of inequality (4), which at some potential will again become equal to its right-hand side. This means that the potential of zirconium under the conditions considered cannot shift to a more positive value than that corresponding to the reversible hydrogen electrode in the same solution. As can be seen from Fig. 3, the results obtained agree with these conclusions. The condition for stationarity of the process under cathodic polarization, as follows from the same type of consideration, is: $i_2 = i_k + i_1$, where i_k is the external cathodic current, and $i_1 = i_3 = \text{const}$.

Taking into account that reaction (2) proceeds with a diffusion limitation and obeys the first-order equation $\ln \frac{C_0}{C} = kt$, where C_0 is the initial concentration and C is the final concentration of HF at time t, we attempted to establish its stoichiometry. For this purpose, special experiments were carried out with $C_0 = 0.01\,N$ HF, each lasting 1, 2, 3, and 4 hours; in these experiments, the amount of acid that had reacted was determined from the amount of Zr that had passed into solution. Comparison of the experimental data with theoretically constructed curves (see Fig. 4) showed that the number n in equation (3) is equal to 2.5.

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