SOLUTION OF ZIRCONIUM IN CONCENTRATED HCl

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The authors of [1-4] studied the corrosion and electrochemical behavior of zirconium in anode polarization conditions in dilute chloride solutions (less than 1 N), but such investigations have not been carried out for concentrated solutions. It therefore seemed of interest to extend the investigations to higher chloride concentrations.

The working solution was chemically pure 11.5 N HCl. The experimental procedure was the same as in [3, 5]. The potentials were measured with respect to a saturated calomel electrode and recalculated with respect to a normal hydrogen electrode (without taking into account the diffusion potential).

From chemical analysis of the solution, at potentials more negative than 0.17 V (below we refer to this as the "passive region") the rate of solution (based on tetravalent zirconium) is $\sim 0.2\text{-}1 \cdot 10^{-4}$ A/cm^2 and is evidently independent of the potential, including the cathodic polarization region: -0.15 to -0.35 V (Fig. 1).

However, the fairly poor reproducibility in 11.5 N HCl should be noted. The hatched region of the curve indicates the scatter of experimental data obtained in parallel experiments *.

In the case of specimens pre-etched in HF the rate of solution of Zr in the passive state corresponded to the equilibrium density of the anode current at the given potential. A rather different picture was observed in the case of specimens covered with an air-oxide film. In this case, experiments in which the solution was changed showed that the mean rate of solution of Zr in the initial periods was more than one order of magnitude greater than the anode current passing through the system, and then remained approximately constant. But the anode current increased markedly in each successive period until comparable with the rate of solution, remaining comparable up to the end of the experiment (Fig. 2).

From these data we may infer that solution of passive Zr in 11.5 N HCl takes place by a mechanism similar to that proposed in [5] for solution of Zr in HF, i.e. the process passes through a stage of electrochemical formation of oxide on the metal surface (by reaction of Zr with water), followed by chemical solution of this oxide in acid.

Since the amount of Zr going into solution is governed by the velocity at which the oxide reacts with HCl^-, and since this velocity is independent of the electrode potential, we also find no relation between the rate of solution of zirconium (the rate at which it goes into solution) and potential (with $\varphi \leq 0.17$ V). The velocity of the chemical reaction is independent of the oxide layer thickness, whereas the velocity of oxide formation rises with decreasing thickness of the layer (at the given potential). This explains the picture obtained in experiments on air-oxidized specimens:

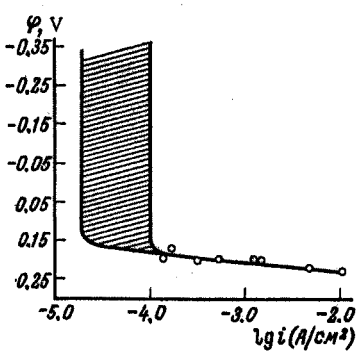

Fig. 1. Rate of solution of Zr in 11.5 N HCl, plotted versus potential.

* The scatter may be even higher. In a few, rather exceptional cases the rate of solution was at least ten times greater than the value given. We do not fully understand why such anomalies occur. They might be due to structural distortions in the upper layers of metal attacked by the acid. In any case, it should be pointed out that similar anomalies have been observed by other investigators [6] (V. M. Novakovskii — oral communication), who studied the solution of Zr in H_2SO_4 and HCl solutions.

L. Ya. Karpov Physicochemical Research Institute. Translated from Zashchita Metallov, Vol. 2, No. 4, pp. 490-492, July-August, 1966. Original article submitted April 3, 1966.

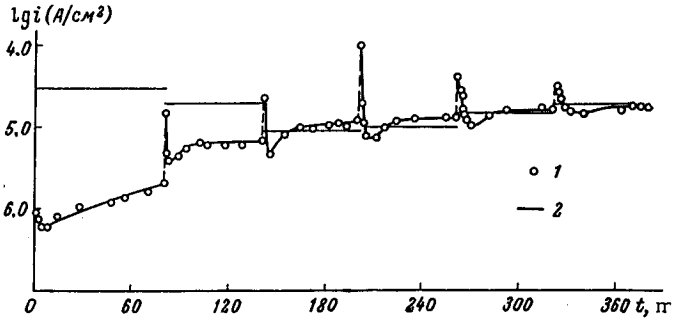

Fig. 2. Change in the anode current (1) and the mean rate of solution (2), measured from a solution of air-oxidized Zr in 11.5 N HCl; $\varphi = 0.05$ V. (Negative values of log i plotted on the axis of ordinates.)

the rate at which zirconium passed into solution remained constant throughout an experiment, whereas the rate of renewal of the oxide layer increased continuously until comparable with its rate of solution (Fig. 2).

The value obtained for the rate of solution of passive Zr in 11.5 N HCl is approximately two orders of magnitude greater than the rate of self-solution of Zr in dilute HCl [3]. In our opinion this difference is due to the presence in concentrated HCl of undissociated molecules of this acid, responsible for solution of the oxide.

In contrast to solution of Zr in HF, its rate of solution in 11.5 N HCl is independent of mixing (within the scatter of the data). This evidently means that the limiting stage of the solution process is the reaction of the oxide with HCl, and not diffusion of the acid molecules, as in [5].

At potentials more positive than 0.17 V the rate of solution, and therefore the anode current, increase markedly (Fig. 1). During this process the electrodes become very brittle (crumbling to pieces), the surface is covered with a network of fine cracks and has a dark-gray color; pits are sometimes observed. Similar disintegration of zirconium was observed by the authors of [7] during corrosion tests in concentrated HCl at 60-100°; they classified it as intercrystalline corrosion. It is of interest that only Zr obtained by induction melting undergoes this type of disintegration; it is not displayed in these conditions by arc-melted zirconium, containing ten times less carbon (0.02%) than the former. These authors therefore concluded that the difference in corrosion behavior is due to the different carbon contents in the metal. The zirconium used in our experiments had a very similar chemical composition to that of arc-melted zirconium; nevertheless, it displayed (at $\varphi > 0.17$ V) this type of brittle disintegration — moreover, at room temperature. It follows, therefore, that tests in potentiostatic conditions are more severe than corrosion tests at elevated temperatures (up to 100° C).

Finally, it may be noted that the value obtained for the critical potential $\varphi_{cr} = 0.19 \pm 0.02$ V agrees with the relation established in [3] between φ_{cr} and the chloride ion concentration if we use the activities of the corresponding electrolytes in place of the concentrations.

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