ON THE QUESTION OF THE MECHANISM OF PITTING CORROSION OF ZIRCONIUM IN HALIDE SOLUTIONS

![Fig. 1. General form of the charging curve on zirconium in the electrolytes studied](image)

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Abstract

Full Text

PHYSICAL CHEMISTRY

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ON THE QUESTION OF THE MECHANISM OF PITTING CORROSION OF ZIRCONIUM IN HALIDE SOLUTIONS

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Earlier ([1]) we developed ideas according to which the cause of pitting corrosion of zirconium in chloride solutions is local depassivation of the surface of this metal by chlorine ions, which occurs only in those cases and at those areas of the surface near which the concentration of Cl^- ions reaches a certain critical value. It was also assumed that the supply of chlorine ions to the metal surface is effected through their transport by the current. On the basis of these ideas, it was natural to expect that the duration of the induction period of activation, i.e., the interval of time necessary for increasing the near-electrode concentration of chlorine ions to the critical value, would vary regularly with changes in the density of the polarizing anodic current and should also depend on the absolute and relative concentration of chloride in the solution.

Fig. 1. General form of the charging curve on zirconium in the electrolytes studied

It seemed of interest to carry out an experimental verification of the correctness of the assumptions made. In the experiments set up in this connection, the duration of the induction period was determined from the time elapsing from the moment anodic polarization was imposed until the beginning of surface activation, which was fixed by the position of the minimum of the corresponding $\varphi - t$ curve (see Fig. 1). Measurements were carried out both in individual chloride solutions and in their mixtures with sulfates and carbonates, as well as in bromide solutions. The conditions of the experiments and the procedure for treating zirconium electrodes remained the same as in the previous study ([1]).

Table 1

Dependence of the duration of the induction period t_m (in seconds) on the current density and on the composition and concentration of the electrolyte

i, a/cm^2	KBr 0.01 N	KBr 0.1 N	KBr 1.0 N	KCl 0.01 N	KCl 0.1 N	KCl 1.0 N	KCl + Na_2SO_4 0.05 N [Cl^-] + 0.05 N [SO_4^{2-}]	KCl + Na_2SO_4 0.025 N [Cl^-] + 0.075 N [SO_4^{2-}]	KCl + Na_2CO_3 0.05 N [Cl^-] + 0.05 N [CO_3^{2-}]	KCl + Na_2CO_3 0.025 N [Cl^-] + 0.075 N [CO_3^{2-}]
$5 \cdot 10^{-6}$	1200	1080	–	1410	1290	–	2545	–	–	–
$5 \cdot 10^{-5}$	92.5	78.5	73.5	91	83.2	79.5	165	327	174	250
$5 \cdot 10^{-4}$	9.6	8.3	7.7	10.0	8.0	6.7	15.8	32.9	16.5	26

The results of the measurements are given in Table 1, where each of the values of t_m (the duration of the induction period) is the average of the results of 10–15 experiments. In the course of the measurements it was established that the reproducibility of the results becomes somewhat worse with increasing concentration

halide and with a decrease in the density of the polarizing anodic current. Thus, for example, in 0.01 N halide solutions at a current density of $5 \cdot 10^{-4}$ A/cm^2, the mean deviation from the values given is 5-6%, whereas in 1.0 N solutions at current densities of $5 \cdot 10^{-5}$ and $5 \cdot 10^{-6}$ it reaches 18–23%.

From the data presented it is evident, first of all, that at a constant halide concentration, a tenfold increase in current density is accompanied by an almost tenfold decrease in the duration of the induction period. This means that the quantity of electricity flowing through the solution from the moment polarization is applied until the beginning of surface activation remains, to a first approximation, constant, i.e., does not depend on the current density. The slight deviation from this dependence observed in our experiments is apparently connected with the fact that at low current densities the reverse diffusion of halide ions from the metal surface into the bulk of the solution has a greater effect; as a result, in this case a somewhat longer time is required to establish the critical concentration.

It is also evident from Table 1 that, at a constant current density, the value t_m decreases appreciably as the concentration of the halide salt increases. In light of the assumptions made, such a result is quite natural, since it is obvious that the higher the bulk concentration, the fewer halide ions need be supplied to the surface in order to raise their concentration to the critical value. It is important to note that at constant current density the time required to reach φ_m in chloride and bromide solutions of the same concentration is, to a first approximation, the same. A marked increase in the duration of the induction period is observed when another electrolyte, one that has no activating ability with respect to zirconium, is introduced into a solution containing a halide salt. Sodium sulfate and sodium carbonate were used as such electrolytes in our experiments. Special measurements established that in individual solutions of these salts anodic polarization of zirconium causes the potential to shift to high positive values and does not lead to depassivation of the surface.

Let N_0 be the concentration of the halide salt in an individual solution, and t_m^0 the duration of the induction period in this solution; let N_1 and N_2 be the concentrations, respectively, of the halide salt and sulfate in the mixture, with $N_1 + N_2 = N_0$ (all concentrations are expressed in g-eq/l), and let t_m^1 be the duration of the induction period in the given mixture. Then the dependence observed in our experiments can be expressed, to a first approximation, by the following relation:

$$t_m^1 = \frac{N_1 + N_2}{N_1} \cdot t_m^0$$

provided that $0 \leq N_2 < 5N_1$ (^{1}).

Since the difference in the mobilities of the ions Cl^- and SO_4^{-2} (or CO_3^{-2}) is insignificant, these results apparently show that, both in individual and in mixed solutions, the quantity of electricity carried by Cl^- ions during the time required to reach φ_m remains, to a first approximation, constant. In accordance with our assumptions, this means that in both cases surface activation begins only when the near-electrode concentration of halide ions reaches a certain critical value. As was noted earlier (^{1}), the critical concentration will not necessarily be created simultaneously over the entire electrode surface. On the contrary, it is quite probable, especially in the case of dilute solutions, that owing to the nonuniform distribution of current it is created first of all only at individual areas of the surface, thereby causing the pitting character of the corrosion.

It should be noted that all the results presented in Table 1 were obtained on zirconium specimens that had undergone preliminary treatment

in dilute HF. Experiments carried out with air-oxidized electrode specimens showed that in this case φ_m almost coincides with φ_{cr} (the potential of stable dissolution), while the time required to reach φ_m is many times (5-30) shorter than on electrodes that had been etched in HF. On zirconium covered with a visible anodic oxide film, the time required to reach φ_m is still shorter than on air-oxidized specimens. At the same time, the value of φ_{cr} did not depend on the method of preliminary treatment of the specimens and was the same in all three cases. Such behavior of zirconium can probably be explained by the fact that, when an air or anodic oxide film is present on its surface, dissolution proceeds more nonuniformly than on specimens treated in HF, which creates conditions for a more rapid attainment of the critical concentration at a small number of the most active surface sites.

The measurements carried out also showed that, in the investigated process of anodic dissolution of zirconium in chloride solutions, the nature of the cation has no appreciable influence. In these measurements it was shown that the time required to reach φ_m in LiCl, $ZnCl_2$, and HCl solutions was the same as in KCl solution.

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REFERENCES

1. Ya. M. Kolotyrkin, V. A. Gil' man, DAN, 137, No. 3, 642 (1960).

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

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