MECHANISM OF ZIRCONIUM PITTING CORROSION IN HALIDE SOLUTIONS

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We have already developed some ideas in [1] to the effect that the cause of zirconium pitting corrosion in chloride solutions is local depassivation of the surface of the metal by chlorine ions, which occurs only in the case, and on those parts of the surface, where the concentration of Cl^- ions reaches some critical value. Here it was also proposed that the chlorine ions are brought up to the metal surface through transference by a current. On the basis of these ideas it was natural to expect that the length of the activation induction period, i.e., the interval of time required to raise the epi-electrode concentration of chlorine ions to the critical value, would bear a functional relationship to the anode polarizing current density and would also depend on the absolute and relative chloride concentration in solution.

It seemed to be of interest to make an experimental check of the validity of these assumptions. In the experiments set up to this end, the length of the induction period was measured as a function of the time from the instant the anode polarization was applied to the beginning of activation of the surface, which was marked by the position of the minimum in the φ vs. t curve (see Fig. 1). The measurements were made both in solutions of chlorides alone and in mixtures of chlorides with sulfates and carbonates, as well as in bromide solutions. The conditions under which the experiments were made and the technique of preparing the zirconium electrodes remained the same as in the previous studies [1].

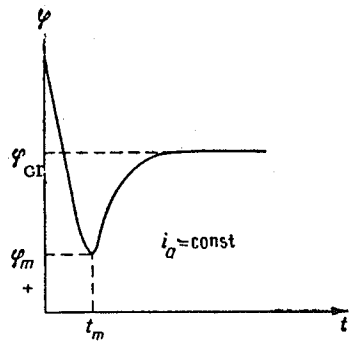

Fig. 1. General form of charging curve on zirconium in the electrolytes studied.

The results of the measurements are given in the table, where each of the values of t_m (length of induction period) is the mean of the results of 10–15 experiments. It was found during the course of the measurements that the reproducibility of the results becomes somewhat worse as the halide concentration is increased and as the anode polarizing current density is reduced. Thus, for example, in 0.01 N halide solutions at a current density of $5 \cdot 10^{-4}$ amp/cm^2, the mean deviation from the values given is 5–6%, while in 1.0 N solutions at current densities of $5 \cdot 10^{-5}$ and $5 \cdot 10^{-6}$, it reaches 18–23%.

It may be seen from the data given, above all, that at constant halide concentration a ten fold increase in the current density is accompanied by an almost ten fold reduction in the length of the induction period. This means that the quantity of electricity flowing through the solution from the moment the polarization is applied to the beginning of surface activation is constant to a first approximation, i.e., it is independent of the current density. A certain amount of deviation from this principle, observed in our experiments, apparently comes from the fact that at small current densities there is a large effect of reverse diffusion of halide ions from the metal surface into the volume of the solution, as a result of which not quite as much time is required to reach the critical concentration.

It may also be seen from the table that at constant current density the value of t_m decreases markedly as the halide salt concentration is increased. In the light of the assumptions made, this result is completely plausible,

since it is obvious that the higher the volume concentration the less need there is to bring halide ions up to the surface in order to raise the ion concentration to the critical value. It is important to note that at constant current density the time required to reach φ_m is, to a first approximation, the same in chloride and bromide solutions of the same concentration. An appreciable increase in length of the induction period is observed if another electrolyte is added to the solution containing the halide salt, the added electrolyte having no activating properties as far as

Length of Induction Period t_m (in seconds) as a Function of Current Density and Composition and Concentration of Electrolyte

i, amp per cm^2	KBr			KCl			KCl+Na_2SO_4		KCl+Na_2CO_3	
	0,01*N*	0,1*N*	1,0*N*	0,01*N*	0,1*N*	1,0*N*	0,05*N* [Cl⁻] +0,05*N* [SO_4^{2-}]	0,025*N* [Cl⁻] +0,075*N* [SO_4^{2-}]	0,05*N* [Cl⁻] +0,05*N* [CO_3^{2-}]	0,025*N* [Cl⁻] +0,075*N* [CO_3^{2-}]
$5\cdot10^{-6}$	1200	1080	—	1410	1290	—	2545	—	—	—
$5\cdot10^{-5}$	92,5	78,5	73,5	91	83,2	79,5	165	327	174	250
$5\cdot10^{-4}$	9,6	8,3	7,7	10,0	8,0	6,7	15,8	32,9	16,5	26

zirconium is concerned. The electrolytes used in this way in our experiments were sodium sulfate and sodium carbonate. It was found from special measurements that, in solutions of these salts alone, anode polarization of the zirconium causes a shift in potential to high positive values and does not produce depassivation of the surface.

Let N_0 be the halide salt concentration in a solution containing a single salt, and let t^0_m be the length of the induction period in this solution. Let N_1 and N_2 be the concentrations respectively of halide and sulfate in a mixture with $N_1 + N_2 = N_0$ (all concentrations are expressed in g-equiv/liter), and let t^1_m be the length of the induction period in the mixture. Then the relation observed in our experiments may, to a first approximation, be expressed by the following equation:

$$t'_m = \frac{N_1 + N_2}{N_1} \cdot t^\circ_m$$

with the condition that $0 \leq N_2 < 5\ N_1$ [1].

Since the difference between the mobilities of Cl^- and SO_4^{-2} (or of CO_3^{-2}) ions is small, these results seem to show that in solutions of a single salt as well as in mixed solutions the amount of electrolyte transferred by Cl^- ions during the time required to reach φ_m remains constant to a first approximation. In accordance with our assumptions this means that in both cases surface activation begins only when the epi-electrode concentration of halide ions reaches some critical value. As has been noted previously [1], the critical concentration does not have to be reached simultaneously over the whole electrode surface. On the other hand, it is entirely probable, especially in dilute solutions, that because of nonuniform current distribution it occurs mainly only on particular parts of the surface, thus giving corrosion its pock-marked character.

It should be noted that all the results given in the table were found from zirconium samples which had been subjected to previous treatment in dilute HF. Experiments, made on electrode samples oxidized in air, have shown that in this case φ_m is almost identical with φ_{cr} (the stable dissolving potential), and the time required to reach φ_m is many times (5–30) less than on electrodes subjected to HF pickling. On zirconium covered with a visible anodic oxide film, the time required to reach φ_m is even smaller than on samples oxidized in air. At the same time, the magnitude of φ_{cr} was independent of the way the samples had been previously treated and was the same in all three cases. This behavior on the part of zirconium is probably to be explained by the fact that, if there is an anodic or air oxide film on the surface, dissolving occurs in a less uniform way than on samples treated in HF, which provides the necessary conditions for reaching the critical concentration more rapidly at the small number of extremely active parts of the surface.

The measurements have also shown that the nature of the cation has no appreciable effect on the zirconium anodic dissolving reaction in chloride solutions. The measurements have shown that the time required to reach φ_m in LiCl, $ZnCl_2$, and HCl solutions was the same as in KCl solutions.

LITERATURE CITED

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