PITTING CORROSION OF ZIRCONIUM IN PERCHLORATE SOLUTIONS

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The authors of [1-3] show that in certain conditions at high anode potentials ClO_4^- ions can cause pitting corrosion of iron. In [4] we observed this aggressive effect of ClO_4^- ions while studying the electrochemical behavior of zirconium [4].

The working solutions were 0.1 and 1.0 N solutions of $NaClO_4$ and $HClO_4$. Some experiments were performed in 0.3 N $LiClO_4$. To prepare the solutions, sodium and lithium perchlorates were recrystallized twice, and perchloric acid and water distilled twice. Zirconium was 99.8% pure (0.065% Hf).

Measurements showed that in self-dissolution and anode polarization conditions, Zr in these solutions is passive below a certain critical potential φ_{cr}, at which intense pitting corrosion occurs. In this respect the anode behavior of Zr in perchlorate solutions is similar to that in chloride solutions [5], but φ_{cr} in perchlorate solutions is one volt higher than in chloride solutions. Thus, in 1N $HClO_4$ or 1N $NaClO_4$, φ_{cr} = 1.35-1.33 V (s.h.e.), and in 0.1 N $HClO_4$ or 0.1 N $NaClO_4$ φ_{cr} = 1.45-1.43 V (the corresponding values of φ_{cr} in chloride solutions are 0.40 V and 0.47 V [5]).

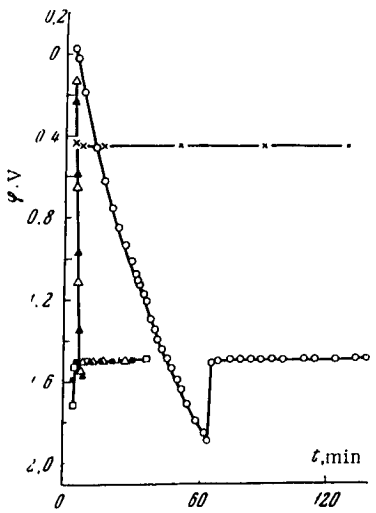

Fig. 1. Charging curves on Zr in perchlorate solutions: ○-0.1 N. $NaClO_4$, $i = 5 \cdot 10^{-6}$ A/cm²; △-0.1 N. $NaClO_4$, $i = 5 \cdot 10^{-5}$ A/cm²; □-0.1 N. $NaClO_4$, $i = 5 \cdot 10^{-4}$ A/cm²; △-0.1 N. $HClO_4$, $i = 5 \cdot 10^{-5}$ A/cm²; □-0.1 N. $HClO_4$; $i = 5 \cdot 10^{-4}$ A/cm²; ×-charging curve in 0.1 N. HCl at $i = 5 \cdot 10^{-5}$ A/cm².

The value of φ_{cr} in perchlorate solution is determined uniquely by the concentration of ClO^{-4} ions, increasing by 100 mV with a reduction in perchlorate concentration by a factor of ten; as in chloride solutions, it is independent of solution pH and anode current density. The corresponding galvanostatic curves are given in Fig.1 and Fig.2; Fig.1 gives for comparison the charging curve obtained by the present authors [5] in a chloride solution. Similar phenomena have been observed for iron in perchlorate solutions [1-3].

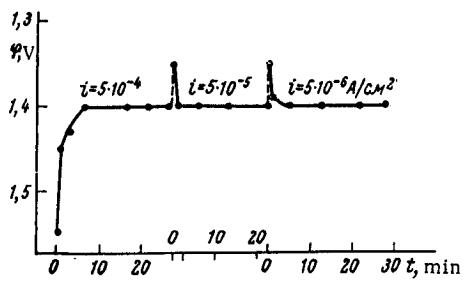

Fig. 2. Potential versus time with the successive reductions in anode current density in 0.3 M $LiClO_4$.

Halide ions are therefore not the only agents causing pitting corrosion of zirconium. ClO_4^- ions can also cause pitting, but, as in the case of iron [3, 6], their effect on zirconium is less marked than that of halide ions. In all other respects, in the case of zirconium the pitting-corrosion mechanism in perchlorate solutions is the same as that of chloride solutions [5, 7].

Since this aggressive action of ClO_4^- ions is displayed during the reaction of metals which are very different chemically (such as Fe and Zr), we can evidently infer that it is not specific for these metals, but more universal.

LITERATURE CITED

1. V. D. Kashcheev, B. N. Kabanov and D. I. Leikis, Dokl. AN SSSR, 147, 143, (1962).
2. B. N. Kabanov and V. D. Kashcheev, Dokl. AN SSSR, 151, 883, (1963).
3. L. I. Freiman and Ya. M. Kolotyrkin, Dokl. AN SSSR, 153, 886, (1963).
4. Ya. M. Kolotyrkin, Uspekhi khimii, 31, 322, (1962).
5. Ya. M. Kolotyrkin and V. A. Gil'man, Dokl. AN SSSR, 137, 642, (1961).
6. Ya. M. Kolotyrkin and L. I. Freiman, Dokl. AN SSSR, 162, 376, (1965).
7. V. A. Gil'man and Ya. M. Kolotyrkin, Dokl. AN SSSR, 143, 640, (1962).
