PITTING CORROSION OF ALUMINUM IN SOLUTIONS OF SODIUM PERCHLORATE AND PERCHLORIC ACID

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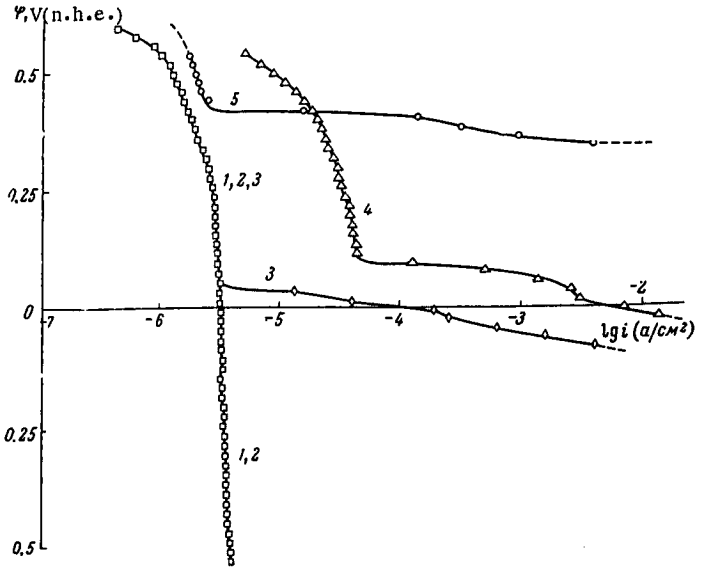
Hoar [1] has shown that ClO_4' anions may cause pitting corrosion of tin and iron. The authors of [2] observed anodic activation of passive iron by ClO_4' ions in dilute alkali (0.1N $KClO_4$+0.05N NaOH) at potential ≃-0.35 V (n.h.e.). This activation (below we refer to this as "primary"), of which the development depends very markedly on the OH-ion concentration [3] and the metal structure [4], may be suppressed in certain conditions by a positive shift of the metal's potential [3, 4]. It has also been established [3, 5] that at high anode potentials ClO_4' anions re-acquire the capacity to activate passive iron, with the development of pitting corrosion (secondary activation), if they reach a certain critical potential $\left(\varphi_{cr}^{ClO_4}\right)$; the value of the latter is virtually independent of solution acidity within a wide pH range.

The authors of [6] have shown that ClO_4' anions also cause pitting corrosion of the highly resistant metal zirconium. A comparison of data in [6] and in [3-5, 7] shows that the values of $\left(\varphi_{cr}^{ClN_4}\right)$ of iron and zirconium are very close. For example, in 1N $HClO_4$ the values of $\left(\varphi_{cr}^{ClO_4}\right)$ for these metals are in the range 1.3-1.4 V, and in 0.1N $NaClO_4$ in the range ~1.4-1.5 V. Bearing in mind that there is normally a very marked relation between φ_{cr} and the nature of the metal [8], this fact is difficult to explain. It could be attributed a priori to the existence at high potentials of an unusual type of metal activation by ClO_4' anions, not depending greatly on the nature of the metal, or to accidental coincidence. To solve this problem, it seemed of interest to study the behavior of at least one other metal in solutions containing ClO_4' ions. We chose aluminum for this purpose.

The principal measurements were performed in a borate buffer solution (pH 7.4) containing 0.1 g-equ/liter $NaClO_4$, and in 0.1 N $HClO_4$ (pH 1.3). To obtain comparative data we used a borate buffer solution with and without 0.1 g-equ/liter Na_2SO_4 and NaCl at the same pH(7.4). To prepare the solutions we used bidistillate and reagents recrystallized either two or three times (except NaCl, which was of



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Metal / $\lvert\Delta\varphi_{cr}\rvert$, b	Fe	Al	Zr
$\lvert\varphi_{cr}^{Cl'} - \varphi_{cr}^{Br'}\rvert$	0.1	0.14	0.28
$\lvert\varphi_{cr}^{Cl'} - \varphi_{cr}^{I'}\rvert$	0.2	0.26	0.55
$\lvert\varphi_{cr}^{Cl'} - \varphi_{cr}^{ClO_4'}\rvert$	(1.7)	0.33	0.95

chemically pure grade). The initial perchloric acid was redistilled three times.

Scoop-shaped specimens of size 4 × 4 mm were cut from aluminum foil (AVOOO) of thickness 0.085 mm; before an experiment they were cleaned, degreased with alcohol, and etched in 0.25 N NaOH (3 min) and 0.1 N HNO_3 (1.5 min), followed by washing in bidistillate. The experiments were performed in solutions deaerated by passing purified nitrogen through them at 20°. Before the beginning of polarization the specimens were kept in the cell for 25-35 min. To obtain the polarization curves the potential was shifted towards the positive side by means of a potentiostat at intervals of 20 mV. The residence time at each potential was 2 min.

The measurements showed (cf. the figure) that the polarization curves (1, 2) are practically the same in pure borate buffer solution as in 0.1 N H_2SO_4. This is in accordance with [9, 10], which indicates that, as in the case of zirconium [11], SO_4^{2-} ions do not have an activating effect on passive aluminum. In 0.1 N $NaClO_4$, below potential $\simeq$ -0.05 V the polarization curve (3) coincides with curves 1 and 2, but with increase in potential to -0.03 V the current increases sharply and begins to fluctuate and increase. A typical activation sector appears on the polarization curve, its slope being due in the given case to the fact that the measurements were not carried out at equilibrium. As a result of activation the electrodes display numerous pittings, which often pass through them. Bubbles of gas are evolved at the pittings; this is evidently hydrogen, its formation being due to the negative difference effect — well known in the case of chloride solutions.

It should be noted that the above-mentioned value of $\left(\varphi_{cr}^{ClO_4'}\right)$ of aluminum in 0.1 N $NaClO_4$ is much higher than the equilibrium hydrogen electrode potential (-0.437 V) in this solution. If we assume that self-dissolution of activated aluminum has an electrochemical mechanism, the result in question is further proof that the potential within the pittings is far more negative than the measured potential of the electrode.

In 0.1 N $HClO_4$ (curve 4), as in a neutral perchlorate solution, activation of aluminum is observed, but the value of $\left(\varphi_{cr}^{ClO_4'}\right)$ is somewhat less ($\simeq$ -0.09 V). In control experiments on 0.1 N NaCl, aluminum was activated at -0.41 V (curve 5); this potential agrees within the measurement error with Kaesche's value for $\left(\varphi_{cr}^{ClO_4'}\right)$ (-0.39 V) [9], obtained in a chloride solution of the same concentration. Activation of aluminum by Cl' ions in these experimental conditions was also accompanied by formation of pits and evolution of gas on the electrodes.

Like iron and zirconium, aluminum may therefore be subjected to anodic activation in $NaClO_4$ and $HClO_4$ solutions. With regard to the similarity of the $\left(\varphi_{cr}^{ClO_4'}\right)$ values for iron and zirconium, the following remarks may be made. The difference between the critical activation potentials $\lvert\varphi_{cr}^{Cl} - \varphi_{cr}^{An}\rvert$ (An'=Br', I', ClO_4') of the given metal may serve as a criterion of the relative capacity of the anions to activate a passive metal (by comparison with chloride ions). As seen from the table, compiled from data in [3-5] and [9-11] and from the present results, the value of this difference ($\lvert\Delta\varphi_{cr}\rvert$) increases regularly in the order Fe — Al — Zr. The value of $\lvert\varphi_{cr}^{Cl'} - \varphi_{cr}^{ClO_4'}\rvert$ for iron is an exception if calculated from the value of $\varphi_{cr}^{ClO_4'}$ for secondary activation. This exception might not be present if we used the value of $\varphi_{cr}^{ClO_4'}$ corresponding to primary activation. Although there is still a lack of data, bearing in mind the results in [2-4] we may assume that the value of $\lvert\Delta\varphi_{cr}\rvert$ in question is less than 0.2-0.3 V, in contrast to the value given in the table (1.7 V).

We may therefore consider the similarity of the values of $\varphi_{cr}^{ClO_4'}$ for iron (secondary activation) and zirconium as accidental, the high value of $\varphi_{cr}^{ClO_4'}$ for zirconium being perfectly logical, but that of iron (secondary activation) anomalous. This is evidently due to certain passivation characteristics of iron.

When iron is passivated at potentials > 0.5 V in neutral or weakly acid solutions in the presence of activating ions like SO_4^{2-} and ClO_4^-, the passivating layer, in contrast to layers on Al and Zr, must have a different nature and higher activating properties than in absence of these ions in the solution [12].

LITERATURE CITED

1. T.P. Hoar, Disc. Far, Soc., No.1, 299 (1947); Trans. Far. Soc., 45, 7, 683 (1949).
2. L. Vanyukova and B. Kabanov, Dokl. AN SSSR, 59, 917 (1948).
3. V.D. Kashcheev, B.N. Kabanov and D.I. Leikis, Dokl. AN SSSR, 147, 143 (1962); B.N. Kabanov and V.D. Kashcheev, Dokl. AN SSSR, 151, 833 (1963); V.D. Kashcheev, Author's abstract of Dissertation, Inst. Electrochem. AN SSSR, (1963).
4. L.I. Freiman, Ya.L. Kolotyrkin and A.Ya. Givental', Zashchita Metallov, 1, 286 (1965).
5. L.I. Freiman and Ya.M. Kolotyrkin, Dokl. AN SSSR, 153, 886 (1963).
6. V.A. Gil'man and Ya.M. Kolotyrkin, Zashchita Metallov, 2, No.3 (1966).
7. Ya.M. Kolotyrkin and L.I. Freiman, Dokl. AN SSSR, 162, 376 (1965).
8. Ya.M. Kolotyrkin, Khim. prom., No.9, 38 (1963).
9. H. Kaesche, Z. phys. chem., N.F., 26, 138 (1960); 34, 87 (1962); Werkstoffe und Korrosion, 14, 557 (1963).
10. E.I. Storchai and A.V. Turkovskaya, Zashchita Metallov, 1, 293 (1965).
11. Ya.M. Kolotyrkin and V.A. Gil'man, Dokl. AN SSSR, 137, 642 (1961).
12. L.I. Freiman and Ya.M. Kolotyrkin, Zashchita Metallov, 1, 161 (1965); Dokl. AN SSSR, (in press), (1966).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of the first issue of this year.
