Kinetics of Pitting Corrosion on Zirconium in Mixed Chloride-Sulfate Solutions

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Pitting initiation on zirconium in chloride-containing sulfate solutions has been studied and a possible model for the reaction mechanisms has been developed. The model is based on considerations concerning the localized adsorption of the two anions. It agrees with the experimental results in showing second-order stimulation of the pitting initiation by chloride ions and first-order inhibition by sulfate ions.

Pitting corrosion on zirconium has been studied by several authors,[1-5] revealing different aspects of the corrosion behaviour of this metal in aqueous halide media. One of these aspects is the pitting induction time, which has been found to vary in a statistical manner.[6] The dependence of this induction time on the concentration of chloride ions has been less studied and is pursued in the present work. An attempt is also made to develop a reaction scheme for the initiation of pitting corrosion on zirconium in mixed chloride and sulfate solutions.

Experimental

The experiments were performed with zirconium electrodes cut from a 99.8 % zirconium sheet from Goodfellow. The electrodes were embedded in an epoxy resin, and only one end was exposed to the solution. The exposed area was about 4 mm². Usually, five electrodes were used simultaneously and controlled by the same potentiostat, through five amperemeters. Five values of the induction time could then be measured in one run. The electrodes were first stabilized in a solution of H_2SO_4 of the appropriate concentration (Figs. 1 and 2) at +0.300 V (sce) for 20 h. This gives a film thickness of about 5 nm.[7-8] HCl was then added, and galvanostatic control was applied at 5–10 μA cm^{-2}. When pitting occurred, the electrode in question was immediately disconnected. The induction time was measured with a BBC Goerz Metrawatt line recorder and a stop watch. The potentiostat was a PAR 273, the reference electrode was a saturated mercurous sulfate electrode, and the auxiliary electrode was a 1 cm² platinum foil. All chemicals were of AR grade supplied by Merck. The water used was distilled twice in quartz apparatus. The cell solution was thermostatted at 25 °C and kept in contact with air.

Results

The results of the present measurements are shown in Figs. 1 and 2. Each point is the geometric mean of at least 15

measurements, based on a log-normal distribution law. The standard deviations are generally quite large, about 0.6 decade, but additional measurements do not seem to improve this very much. This is in accordance with the statistical behaviour of pitting initiation and induction times.[6] The results agree with the following empirical equation:

$$t_p^{-1} = A \frac{[Cl^-]^2}{[HSO_4^-]} \; ; \quad A = 0.02 \ M^{-1} \ s^{-1} \tag{1}$$

where t_p is the induction time, and A is a proportionality constant of the given value. This shows a first-order inhibition effect by hydrogen sulfate ions, in addition to the
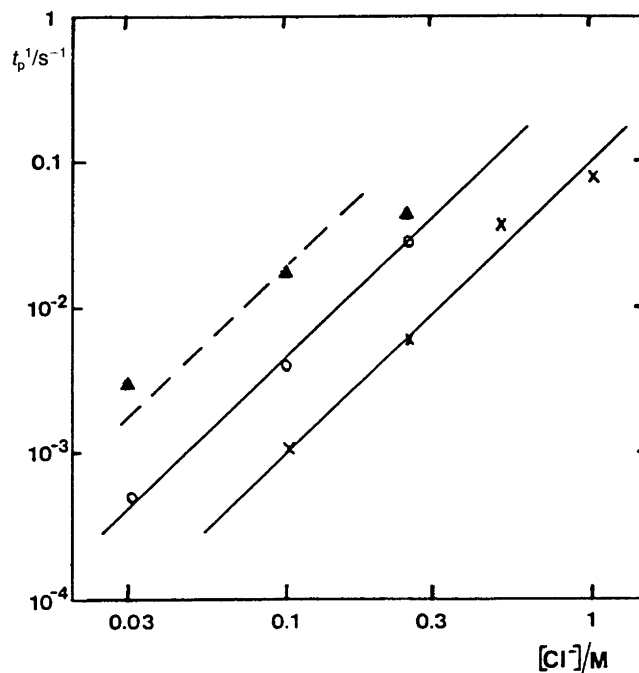

Fig. 1. Inverse pitting induction time versus concentrations of chloride ions in different aerated solutions of H_2SO_4 at 25 °C. (×): 0.20 M, (O): 0.046 M and (▲): 0.010 M H_2SO_4.
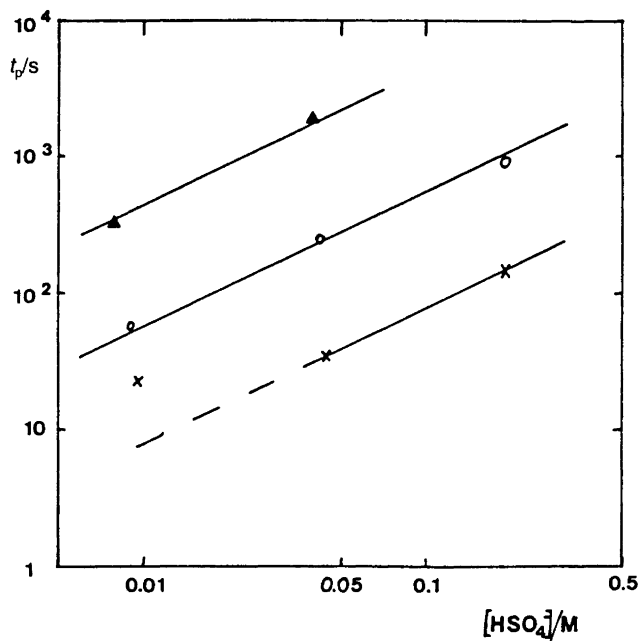
Fig. 2. Pitting induction times versus concentration of hydrogen sulfate ions at different additions of chloride ions to aerated solutions of H_2SO_4 at 25 °C. (×): 0.25 M, (O):0.10 M and (▲): 0.03 M HCl.

second-order initiation by chloride ions. The induction time was measured under galvanostatic conditions, but a few potentiostatic measurements made seem to agree quite well with the galvanostatic ones.

Measurements made on electrodes with significantly greater areas show that the pitting induction time decreases with increasing area. A decrease is also seen when the hydrogen sulfate ions are complexed in the solution, e.g. by uranyl(VI) ions.

Discussion

There are several theories on the course and initiation mechanism of pitting corrosion. This is well reviewed by Szklarska-Smialowska and others.[9–10] It may be concluded from these theories that it will be necessary for chloride ions to be present at or in the oxide/solution interface, presumably as adsorbed chloride anions. This adsorption may occur according to eqn. (2) if there is no coadsorption:

$$Cl^-_{(aq)} \rightleftharpoons Cl^-_{(ads)}. \tag{2}$$

Because of the potential difference across the oxide/solution interface ($\varphi_{(s)}-\varphi_{(sl)}$), it is necessary to have an exponential potential term in the equilibrium constant:

$$\frac{\theta}{(1-\theta)[Cl^-]} = K \exp\left[\frac{F(\varphi_{(s)}-\varphi_{(sl)})}{RT}\right] \tag{3}$$

where θ is the coverage of chloride ions adsorbed on the oxide surface. Competing with the adsorption of chloride

ions, hydrogen sulfate ions will adsorb according to a similar equation:

$$HSO_4^-_{(aq)} \rightleftharpoons HSO_4^-_{(ads)}. \tag{4}$$

As for chloride ions, this adsorption is potential-dependent:

$$\frac{\theta'}{(1-\theta')[HSO_4^-]} = K' \exp\left[\frac{F(\varphi_{(s)}-\varphi_{(sl)})}{RT}\right] \tag{5}$$

where θ' is the coverage of adsorbed hydrogen sulfate ions. It is convenient to assume hydrogen sulfate to be active, because it is the dominant sulfate species in the solution used. It is convenient to define the parameter β as follows:

$$\beta = \exp\left[\frac{F(\varphi_{(s)}-\varphi_{(sl)})}{RT}\right]. \tag{6}$$

At equilibrium with two competing anions, we have:

$$\theta = K[Cl^-](1-\theta-\theta')\beta \tag{7a}$$

$$\theta' = K'[HSO_4^-](1-\theta-\theta')\beta \tag{7b}$$

where $(1-\theta-\theta')$ is the fraction of uncovered surface sites. Solving these equations for θ and θ', one obtains:

$$\theta = \frac{K[Cl^-]\beta}{1 + K[Cl^-]\beta + K'[HSO_4^-]\beta} \tag{8a}$$

$$\theta = \frac{K'[HSO_4^-]\beta}{1 + K[Cl^-]\beta + K'[HSO_4^-]\beta}. \tag{8b}$$

Turning to the mechanism of pitting itself, it may be assumed that some of the few adsorbed chloride ions will react with an underlaying zirconium ion, presumably a less coordinated one, forming a chloride complex in the oxide surface:

$$Zr^{4+}_{(ox)} + Cl^-_{(ads)} \xrightarrow{k_1} ZrCl^{3+}_{(ox)} \tag{9}$$

where k_1 denotes the rate constant. This chloride complex may react with more adsorbed chloride ions:

$$ZrCl^{3+}_{(ox)} + xCl^-_{(ads)} \xrightarrow{k_2} ZrCl^{(3-x)+}_{(x+1,ox)} \tag{10}$$
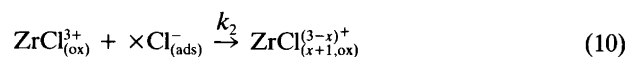
where k_2 denotes the rate constant. Clearly, the most convenient value of x will be 1. This is also the assumption made in the following. This complex may act as the stage of localized adsorption. Being less coordinated by oxide ions, this complex dissolves with hydrolysis, leaving the chloride ions for further corrosion, together with a local acidification of the freshly formed pit nucleus.

$$ZrCl^{2+}_{2(ox)} + 2H_2O \rightarrow Zr(OH)^{2+}_{2(aq)} + 2Cl^-_{(aq)} + 2H^+_{(aq)}. \tag{11}$$
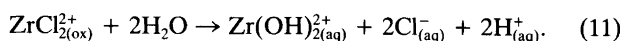
The dissolved zirconium species will form more stable solution species as the reaction proceeds. Localized acidification during pitting corrosion is a quite common phenomenon[9] and has also been observed on zirconium.[4] The freshly formed protons may then attack the less coordinated oxide ions, forming water and new zirconium ions ready to react with the chloride ions. As long as the oxide film thickness is only about 5 nm, this process cannot be repeated many times before the electric field strength becomes so high that it causes electrical breakdown in the film, and the pit formation is registered by a fall in the electrode potential.

If this latter process takes place at a spot where the film thickness is less than the average, the process will go faster and lead to an earlier recording of the pit creation than on the average. Such spots with thin films can be assumed to be statistically distributed in the surface, leading to a statistical behaviour of the induction time. The probability of finding a spot with a low film thickness will also increase with the electrode area, which supports the observation of shorter induction times on electrodes with larger area.

There is also the possibility of interference in the reaction scheme, due to the hydrogen sulfate ions adsorbed:

$$\text{ZrCl}^{3+}_{(ox)} + \text{HSO}^-_{4(ads)} \xrightarrow{k_3} \text{ZrSO}^{2+}_{4(ox)} + \text{Cl}^-_{(aq)} + \text{H}^+_{(aq)}. \qquad (12)$$
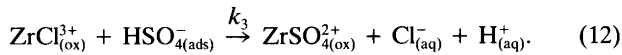
k_3 denotes the rate constant for this inhibition reaction. It has previously been seen that other anions may react in a similar way.[5]

Assuming reaction (10) to be the controlling pitting initiation reaction, the rate of this reaction will be proportional to the inverse induction time. This leads to eqn. (13):

$$t_p^{-1} = kk_2[\text{ZrCl}^{3+}_{(ox)}][\text{Cl}^-] \qquad (13)$$

where $[\text{ZrCl}^{3+}_{(ox)}]$ is the concentration of this species in the oxide surface and k is a proportionality constant.

Assuming the $\text{ZrCl}^{3+}_{(ox)}$ complex to be in a steady state during the induction period, eqns. (9), (10) and (12) yield:

$$\frac{d[\text{ZrCl}^{3+}_{(ox)}]}{dt} = k_1\sigma\theta - k_2[\text{ZrCl}^{3+}_{(ox)}]\theta - k_3[\text{ZrCl}^{3+}_{(ox)}]\theta' = 0 \quad (14)$$

provided none of the three reactions are near equilibrium. σ denotes the surface concentration of possible sites for pit nucleation. Further treatment of eqn. (14) yields:

$$[\text{ZrCl}^{3+}_{(ox)}] = \frac{k_1\sigma\theta}{k_2\theta + k_3\theta'} . \qquad (15)$$

Substitution of eqns. (7) and (8) into (15) yields:

$$[\text{ZrCl}^{3+}_{(ox)}] = \frac{k_1K\sigma[\text{Cl}^-]\beta}{k_2K[\text{Cl}^-]\beta + k_3K'[\text{HSO}_4^-]\beta} . \qquad (16)$$

Putting this into eqn. (13) will give:

$$t_p^{-1} = \frac{kk_1k_2K\sigma[\text{Cl}^-]^2}{k_2K[\text{Cl}^-] + k_3K'[\text{HSO}_4^-]} . \qquad (17)$$

As shown, the potential term β cancels out. If now $k_2K \ll k_3K'$, the first term of the nominator can be neglected, and the result is:

$$t_p^{-1} = \frac{kk_1k_2K\sigma[\text{Cl}^-]^2}{k_3K'[\text{HSO}_4^-]} \qquad (18)$$

which agrees quite well with the observed data. The assumption that $k_2K \ll k_3K'$ is strongly supported by the observation that sulfate ions may be incorporated in the oxide film during anodization of zirconium.[11-13] It has also been shown that sulfate ion adsorb specifically on zirconium dioxide, while chloride ions show no or only weak tendency to do so.[14]

Eqn. (18) has two apparent limitations, shown by the results in Fig. 1. At a relatively high ratio of hydrogen sulfate to chloride, it was found early that no pitting occurred. This may be due to the sulfate adsorption and uptake in the oxide film completely blocking the possibility of localized adsorption of two chloride ions to one zirconium site [eqn. (10)].

At low ratio of hydrogen sulfate to chloride, where the induction time should be rather short, the induction time seems to be somewhat longer than expected. This may be due to the experimental conditions, mainly the time taken to mix the solutions thoroughly.

Conclusion

It may be concluded from the present work that pitting initiation on zirconium seems to show second-order stimulation by chloride ions and first-order inhibition by hydrogen sulfate ions. This is shown to be consistent with a theoretical treatment based on adsorption of the two types of anions. The results apply within the limits

$$0.2 < \frac{[\text{Cl}^-]}{[\text{HSO}_4^-]} < 25.$$

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